

COUPLING OF ELECTROCALORIC AND  
ELECTROMECHANICAL RESPONSES IN  
RELAXOR FERROELECTRICS FOR  
DIELECTRIC COOLING

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**Doctoral Dissertation**  
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**Doctoral Dissertation**

SKLOPITEV ELEKTROKALORIČNEGA IN ELEKTROMECHANKEGA ODZIVA V RELAKSORSKIH FERROELEKTRIČNIH ZA DIELEKTRIČNO HLAJENJE

**Doktorska disertacija**

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*Anything that happens, happens.*

*Anything that, in happening, causes something else to happen, causes  
something else to happen.*

*Anything that, in happening, causes itself to happen again, happens  
again.*

*It doesn't necessarily do it in chronological order, though.*

*— Douglas Adams, Mostly Harmless*



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# Abstract

Artificial refrigeration has influenced the growth patterns of settlements and altered demographics across the world. The technology behind artificial refrigeration is vapour compression, which has been serving now for two hundred years. The time has come to search for alternatives, due to the several drawbacks of conventional refrigeration combined with new requirements.

In this PhD study we made such an attempt by following the idea by Mischenko et al. in 2007, who showed a great refrigeration potential by using the so-called electrocaloric (EC) effect, i.e., the temperature change of dielectric materials induced by application of an electric field. After the initial euphoria in the search for EC materials and ten years of intense activity in this field, we still have no commercially available devices. The main reason behind this is the low EC effect, i.e., low temperature change (up to 4.5 K), and high electric fields needed to stimulate the dielectric refrigeration. We present an EC device based on multifunctional cantilevers, which were designed in a cascade arrangement and when an external electric field is applied to them they simultaneously change temperature and bend. We have numerically modelled the behaviour of such a device and confirmed its feasibility. Relative to the temperature change of a single cantilever, such an arrangement of multifunctional elements can in principle increase the temperature change across the device several fold. On the other hand, limitations popped-up, for example, the importance of ensuring a good thermal contact between the elements.

Next, we have chosen the material system for our cantilevers, i.e.,  $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}x\text{PbTiO}_3$  (PMN-100xPT) solid solution, which was shown to exhibit a giant EC and electromechanical (EM) response. Six PMN-100xPT compositions were fabricated and characterized. Compositions ranged from the archetypal relaxors (low  $x$ ) to ferroelectric samples (high  $x$ ). This was reflected in their electrical, thermal, EM and EC properties. Based on the measured properties, we selected an optimal composition by designing Figures Of Merit. The results of the selection indicated that PMN is optimal for integration in the multifunctional EC device. PMN ceramic was then investigated in terms of its EC response under the same electric-field cycling conditions as expected in an EC cooling device. With cycling, Joule heating emerges, which degrades the EC cooling ability of PMN. By carefully examining the underlying mechanism and different cycling conditions, we propose ways to avoid the degrading effects of fatigue with the help of the electric-field-temperature ( $E$ - $T$ ) phase diagram of PMN.

In the last step we fabricated the PMN-based multifunctional cantilevers and tested the performance of the multifunctional proof-of-concept device. We showed that the heat transfer indeed occurs between the cantilevers and that the number of cantilevers increases the temperature span in the device, which is consistent with the predictions of the numerical model. However, the temperature span was not greater than the EC effect of the material due to the poor thermal contacts. This observation is discussed and proposals for an improvement to the thermal contacts are provided.





# Povzetek

V času industrijske revolucije so opazili, da fluidi ob uparitvi hladijo okolico, kar je bil prvi korak k razvoju umetnega hlajenja. Nazoren prikaz pomembnosti umetnega hlajenja so študije, ki kažejo vpliv na demografsko politiko in rast novih naselbin sveta. Kot omejeno, parno-kompresijsko hlajenje je v uporabi že več kot dvesto let, kar pomeni, da so se potrebe v svetu v tem času drastično spremenile; nove tehnologije zahtevajo specialne načine hlajenja.

V sklopu doktorskega dela smo poskušali slediti ideji, ki so jo leta 2007 predstavili Mischenko in sodelavci. Pokazali so, da določene dielektrične trdnine izkazujejo velik potencial za učinkovito hlajenje. Določeni dielektriki ob pritisnjenem električnem polju namreč izkazujejo spremembo temperature, kar imenujemo elektrokalični (EK) pojav. Kljub precejšnji evforiji pri iskanju novih materialov z visokim EK odzivom po desetih letih aktivnega dela na področju še vedno ni komercialnih EK hladilnikov.

V delu bomo predstavili EK napravo, ki temelji na večfunkcijskih ročicah (ang. cantilevers). Večfunkcijske ročice so zložene v kaskado in ob pritisnjenem električnem polju istočasno spremenijo temperaturo in se upognejo. Z numeričnim modeliranjem smo analizirali napravo in pokazali njeno smiselnost. Rezultati so pokazali, da bi naprava lahko ojačala temperaturne spremembe za večkrat v primerjavi s temperaturno spremembo merjeno v eni sami ročici. Z modeliranjem smo raziskovali tudi omejitve naprave, najbolj kritični so zagotovo termični stiki med posameznimi elementi v napravi. Sestave v sistemu  $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$  (PMN-100xPT) v literaturi povezujejo z visokimi EK in elektromehanskimi odzivi. V omenjenem sistemu smo zato izbrali šest sestav ( $x = 0, 0,1, 0,2, 0,3, 0,35, 0,4$ ), keramiko sintetizirali in jo nato podrobneje analizirali. Narava posameznih keramičnih sestav je mejila od čistega relaksorja (PMN;  $x=0$ ) do feroelektričnih sestav ( $x > 0,35$ ), kar se je odražalo v njihovih električnih, termičnih, elektromehanskih in EK lastnostih. Glede na izmerjene lastnosti smo s funkcijo cenilko izbrali optimalno sestavo. Izkazalo se je, da je relaksor PMN najbolj primeren material za integracijo v EK hladilnik. PMN kot optimalen material za dielektrično hlajenje smo nadalje testirali pod pogoji pričakovanimi v hladilni napravi. PMN smo vzbujali ciklično in spremljali njegov temperaturni odziv, ki je kazal izrazito utrujanje materiala. Utrujanje se je izkazovalo kot pretvorba v superkritično feroelektrično stanje, ki je bilo obenem gonilna sila za migracijo točkastih defektov na meje zrn. Kopičenje defektov na mejah zrn je povečalo električno prevodnost materiala. Na podlagi meritev EK odzivnosti materiala smo konstruirali diagram električno polje - temperatura ( $E$ - $T$  diagram), iz katerega so razvidne fazne transformacije materiala. S pomočjo diagrama lahko določimo pogoje, kjer se izognemo nastanku feroelektrične faze med ciklanjem in posledično utrujanju.

Nazadnje smo PMN izdelali v obliki ročic in jih sestavili v konceptualno hladilno napravo. Pokazali smo, da je prenos toplote med posameznimi elementi mogoč in da temperaturna razlika v napravi narašča s številom elementov, vendar ne v zadostni meri za učinkovito hlajenje. V bodoče bo za učinkovito delovanje predlagane naprave potrebno izboljšati termične kontakte med elementi.



# Contents

|                                                                                                                         |              |
|-------------------------------------------------------------------------------------------------------------------------|--------------|
| <b>List of Figures</b>                                                                                                  | <b>xv</b>    |
| <b>List of Tables</b>                                                                                                   | <b>xxi</b>   |
| <b>Symbols</b>                                                                                                          | <b>xxiii</b> |
| <b>1 Introduction</b>                                                                                                   | <b>1</b>     |
| 1.1 Ferroelectric and Relaxor Materials . . . . .                                                                       | 1            |
| 1.1.1 Basic definitions . . . . .                                                                                       | 1            |
| 1.1.2 Electromechanical response . . . . .                                                                              | 3            |
| 1.1.2.1 Application of EM effect . . . . .                                                                              | 5            |
| 1.1.3 Electrocaloric response . . . . .                                                                                 | 6            |
| 1.1.4 (1-x)Pb(Mg <sub>1/3</sub> Nb <sub>2/3</sub> )O <sub>3</sub> - (x)PbTiO <sub>3</sub> material system . . . . .     | 9            |
| 1.2 Integration of Electrocaloric Cooling . . . . .                                                                     | 11           |
| 1.2.1 A brief summary of the work done on electrocaloric refrigerators . .                                              | 11           |
| 1.2.2 Cooling efficiency . . . . .                                                                                      | 13           |
| 1.2.3 Electrocaloric fatigue . . . . .                                                                                  | 15           |
| <b>2 Design and Concept of the Multifunctional Device for Dielectric Cooling</b>                                        | <b>17</b>    |
| <b>3 Aims and Hypothesis</b>                                                                                            | <b>19</b>    |
| <b>4 Materials and Methods</b>                                                                                          | <b>21</b>    |
| 4.1 Building the Numerical Model of the EC Device . . . . .                                                             | 21           |
| 4.2 PMN-100xPT Ceramics . . . . .                                                                                       | 22           |
| 4.2.1 Fabrication, structural and microstructural characterization . . . . .                                            | 22           |
| 4.2.2 Electrical and electromechanical characterization . . . . .                                                       | 23           |
| 4.2.3 Characterization of thermal properties . . . . .                                                                  | 25           |
| 4.2.4 Characterization of EC properties . . . . .                                                                       | 25           |
| 4.2.5 Local electric-current mapping and domain switching characteriza-<br>tion using atomic-force microscopy . . . . . | 27           |
| 4.3 PMN Cantilevers . . . . .                                                                                           | 28           |
| 4.3.1 Fabrication, structural and microstructural characterization . . . . .                                            | 28           |
| 4.3.2 Electrical characterization . . . . .                                                                             | 30           |
| 4.3.3 Electromechanical characterization . . . . .                                                                      | 30           |
| 4.3.4 Electrocaloric characterization . . . . .                                                                         | 30           |
| 4.3.5 3D printing of the device packaging . . . . .                                                                     | 31           |
| 4.3.6 Fabrication and excitation of a proof-of-concept device . . . . .                                                 | 31           |
| <b>5 Results and Discussion</b>                                                                                         | <b>33</b>    |
| 5.1 Feasibility and Performance Evaluation of Proof-of-Concept Device by Mod-<br>elling . . . . .                       | 33           |

|                     |                                                                         |            |
|---------------------|-------------------------------------------------------------------------|------------|
| 5.1.1               | An idealistic model of the device . . . . .                             | 33         |
| 5.1.2               | Towards a more realistic model . . . . .                                | 34         |
| 5.2                 | Electrical, Thermal, EC and EM Properties of PMN-100xPT Ceramics . . .  | 38         |
| 5.2.1               | Electrical properties . . . . .                                         | 38         |
| 5.2.2               | Electromechanical response . . . . .                                    | 46         |
| 5.2.3               | Thermal properties . . . . .                                            | 52         |
| 5.2.4               | Electrocaloric response . . . . .                                       | 53         |
| 5.3                 | Material Selection for Proof-of-Concept Device . . . . .                | 56         |
| 5.4                 | PMN Ceramics Under Device-Like-Field-Cycling Conditions . . . . .       | 58         |
| 5.4.1               | Emergence of excessive heating . . . . .                                | 58         |
| 5.4.1.1             | Origin of increased electrical conductivity . . . . .                   | 61         |
| 5.4.1.2             | Rejuvenation of the fatigued state . . . . .                            | 63         |
| 5.4.1.3             | EC cycling at 50°C . . . . .                                            | 65         |
| 5.4.1.4             | Electric-field-induced ferroelectric phase . . . . .                    | 65         |
| 5.4.2               | Mechanisms responsible for the EC fatigue in PMN . . . . .              | 69         |
| 5.4.3               | Contribution of ferroelectric phase and conductivity to self-heating .  | 72         |
| 5.5                 | Multifunctional Properties of PMN Cantilevers . . . . .                 | 79         |
| 5.5.1               | Microstructural properties . . . . .                                    | 79         |
| 5.5.2               | Electrical properties . . . . .                                         | 80         |
| 5.5.3               | Electromechanical properties . . . . .                                  | 81         |
| 5.5.4               | Electrocaloric properties . . . . .                                     | 82         |
| 5.6                 | Cooling Performance of Proof-of Concept Device . . . . .                | 84         |
| <b>6</b>            | <b>Conclusions</b>                                                      | <b>91</b>  |
| <b>Appendix A</b>   | <b>Appendix</b>                                                         | <b>93</b>  |
| A.1                 | Structural and Microstructural Properties of PMN-xPT Ceramics . . . . . | 93         |
| A.2                 | Correction Factors Determined with Finite-Element Modelling . . . . .   | 94         |
| A.3                 | EC and EM effect of the cantilevers . . . . .                           | 96         |
| <b>References</b>   |                                                                         | <b>97</b>  |
| <b>Bibliography</b> |                                                                         | <b>109</b> |
| <b>Biography</b>    |                                                                         | <b>111</b> |

# List of Figures

|              |                                                                                                                                                                                                                                                                                                                                                                                                     |    |
|--------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 1.1:  | a) dielectric response of a $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})_{0.98}\text{Nb}_{0.02}\text{O}_3$ ferroelectric material and b) Typical ferroelectric polarization ( $P$ ) versus electric field ( $E$ ) hysteresis loop. The insets schematically show the perovskite crystal in the (100) projection (panel a) and domain structure corresponding to the $P(E)$ state (panel b). . . . . | 2  |
| Figure 1.2:  | Dielectric response as a function of temperature and frequency for a archetypical relaxor $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ . . . . .                                                                                                                                                                                                                                           | 2  |
| Figure 1.3:  | The states of relaxor across a broad temperature range. Identical schematic frame colours represent the state in the material and corresponding $P(E)$ response (see text for details). The temperatures on the $P(E)$ response are for illustration purposes only. Figure edited after Ref. [6] . . . . .                                                                                          | 3  |
| Figure 1.4:  | Contributions to the electromechanical response: a) electrostrictive and b) piezoelectric response. Parts of the image taken from [2], [9]. . . . .                                                                                                                                                                                                                                                 | 4  |
| Figure 1.5:  | Morphotropic phase boundary in $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ . a) The phase diagram showing different phases as a function of temperature and composition, b) room-temperature piezoelectric response as a function of composition. Edited after [1], [7] . . . . .                                                                                                                      | 6  |
| Figure 1.6:  | Bending of unimorph cantilever under electric field. . . . .                                                                                                                                                                                                                                                                                                                                        | 6  |
| Figure 1.7:  | a) The electrocaloric cycle with four stages, and b) the measured temperature response ( $\Delta T$ ) in the four stages (see corresponding numbers) with respect to the applied electric field ( $E$ ). . . . .                                                                                                                                                                                    | 7  |
| Figure 1.8:  | Variation of polarization with temperature in materials with a first- (a) and second-order phase (b) transition. . . . .                                                                                                                                                                                                                                                                            | 9  |
| Figure 1.9:  | Phase diagram of the binary solid solution PMN-100xPT. Courtesy of Mojca Otoničar, redrawn after [66]. . . . .                                                                                                                                                                                                                                                                                      | 10 |
| Figure 1.10: | Temperature dependence of a) dielectric permittivity and b) EC temperature change of PMN-100xPT ceramic compositions; taken from Refs. [67], [68]. . . . .                                                                                                                                                                                                                                          | 10 |
| Figure 1.11: | Direct piezoelectric response of the PMN-xPT compositions [67]. Courtesy of Gregor Trefalt. . . . .                                                                                                                                                                                                                                                                                                 | 11 |
| Figure 1.12: | Three generations of EC devices, a) fluid based [72], b) solid state with external mechanical motion [75] and c) solid state with a multifunctional material [76]. . . . .                                                                                                                                                                                                                          | 12 |

|              |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |    |
|--------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 1.13: | Thermodynamic Brayton cycle of the EC material for a) ideal and b) realistic case. In the panel the step 1→2 the material is subjected to an electric field in adiabatic conditions, to which it responds by a EC temperature change ( $\Delta T_{EC}^P$ ). After, in step 2→3, the generated heat must be removed. In step 3→4 the electric field is removed and the material cools below the initial temperature. Heat absorption takes place during step 4→1 [84]. . . . .                                                                                     | 14 |
| Figure 1.14: | Typical P(E) response of a ferroelectric. The blue area denotes the recoverable energy, while the area in pink enclosed by the loop is the energy loss. . . . .                                                                                                                                                                                                                                                                                                                                                                                                   | 14 |
| Figure 1.15: | Fatigue of Ba(Zr <sub>0.2</sub> Ti <sub>0.8</sub> )O <sub>3</sub> ceramics under EC field cycling [94]. a) The EC response normalized to the value measured during the first EC cycle ( $\Delta T/\Delta T(1)$ ). The inset shows the EC response of the fatigued (10 <sup>6</sup> cycles) sample where the Joule heating is the dominating response (compare to typical pristine EC response in Fig.1.7). b) The $\Delta T/\Delta T(1)$ was unchanged up to 10 <sup>6</sup> cycles after the electric field was alternated every 10 <sup>5</sup> cycles. . . . . | 15 |
| Figure 2.1:  | Working principle of the device that couples the electrocaloric and electromechanical effects for dielectric cooling. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                     | 17 |
| Figure 2.2:  | Conceptual device appearance with the considerations noted at the device parts. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | 18 |
| Figure 4.1:  | The geometry used in the model illustrated for the device with three cantilevers. The thicker gray squares represent the active material and the thinner brown squares represent Pt electrodes. The red dots show the position of the temperature probes. . . . .                                                                                                                                                                                                                                                                                                 | 21 |
| Figure 4.2:  | a) Schematic illustration of the electrical circuit for measuring the polarization - electric field hysteresis loop using the virtual ground method. b) schematic illustration of the voltage ( $U$ ) waveform applied for polarization measurements. . . . .                                                                                                                                                                                                                                                                                                     | 24 |
| Figure 4.3:  | Setup for simultaneous characterization of $s_3$ and $s_1$ . . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | 24 |
| Figure 4.4:  | Schematic illustration of the measuring setup and sample preparation for EC measurements. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | 25 |
| Figure 4.5:  | Waveform applied for analysis of the EC fatigue. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | 26 |
| Figure 4.6:  | Schematic illustration of the working principle behind the conductive atomic force microscope. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                            | 27 |
| Figure 4.7:  | Making of cantilevers: a) preparation of slurry for b) tape casting. The tape is then screen-printed with Pt as shown on c). Lamination of tapes follow as depicted in d). . . . .                                                                                                                                                                                                                                                                                                                                                                                | 28 |
| Figure 4.8:  | Temperature program for fabrication of cantilevers. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | 29 |
| Figure 4.9:  | PMN/Pt/PMN shapes used for analysis and device fabrication. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | 29 |
| Figure 4.10: | Setup for measuring electric field-induced deflections of cantilevers. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | 30 |
| Figure 4.11: | The schematics for the device packaging. The schematics provided an input for the 3D printer. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                             | 31 |
| Figure 4.12: | Driving set-up for the proof-of-concept device. The device consisting from two cantilever elements was connected to a relay switch. The relay switch was controlled via a Arduino Uno microcontroller programmed by a Labview-made application. . . . .                                                                                                                                                                                                                                                                                                           | 32 |

|              |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |    |
|--------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 5.1:  | Time-dependant operation of the device with three EC elements. The green shows the temperature of the first element, while red and black show the temperature of the 2 <sup>nd</sup> and 3 <sup>rd</sup> element, respectively. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                        | 34 |
| Figure 5.2:  | Temperature difference between cold and hot side of the device (i.e., between the first and last element in the cascade; see inset) for devices with different number of elements. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | 35 |
| Figure 5.3:  | Temperature gradient between the cold and hot side as a function of number of elements modelled in ideal and realistic conditions. The insets show the simulated finial temperature distribution in the device for these two heat-transfer conditions. The dark-blue colour represents the lowest temperature and the dark-red the highest. . . . .                                                                                                                                                                                                                                                                                                                            | 35 |
| Figure 5.4:  | Ratio of the temperature span between the first and the last element in the array for a finite contact resistance ( $\Delta T$ ) and that for the ideal contact with no resistance ( $\Delta T_{ic}$ ) as a function of the contact resistance ( $R_{contact}$ ) between the cantilevers. On the secondary horizontal axis the corresponding change of $t_c$ with the $R_{contact}$ is shown. The dependence of the regeneration factor on the contact resistance ( $R_{contact}$ ) is shown on the secondary (right) vertical axis. The dashed line is drawn as a guide to the eye. The schematic shows Pt and PMN-35PT in contact with the indicated $R_{contact}$ . . . . . | 36 |
| Figure 5.5:  | Dielectric permittivity at 1 kHz for all PMN-100xPT samples. The arrow indicates the room-emperature values. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | 38 |
| Figure 5.6:  | Polarization ( $P$ ) versus electric field ( $E$ ) for PMN-100xPT compositions up to to 60 kV/cm. The loops were measured with three unipolar electric field cycles at frequency of 20 Hz (waveform shown in Materials and Methods, Fig. 4.4b). Measured $P(E)$ loops are plotted one above the other for clarity. Edges of the coloured square give polarization and electric field scales. . . . .                                                                                                                                                                                                                                                                           | 40 |
| Figure 5.7:  | Response of a virgin PMN-20PT excited with three unipolar $E$ -field cycles of magnitude of 10 kV/cm. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | 42 |
| Figure 5.8:  | Energy storage capacity ( $W_S$ ) of PMN-100xPT samples calculated for different electric field amplitudes. The lines between the points serve as a guide to the eye. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | 43 |
| Figure 5.9:  | Energy loss ( $W_L$ ) of PMN-100xPT samples calculated for different electric field amplitudes. The lines between the points serve as a guide to the eye. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | 44 |
| Figure 5.10: | Material efficiency of PMN-100xPT samples calculated for different electric field amplitudes as a ratio between energy loss density and energy storage density. The lines between the points serve as a guide to the eye. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                              | 45 |
| Figure 5.11: | Longitudinal strain ( $s_3$ ) versus electric field hysteresis loops for PMN-100xPT compositions. The loops were measured with three unipolar electric field cycles at frequency of 20 Hz (waveform shown in Materials and Methods, Fig. 4.4b). Measured $P(E)$ loops are plotted one above the other for clarity. Edges of the coloured square give polarization and electric field scales. . . . .                                                                                                                                                                                                                                                                           | 47 |
| Figure 5.12: | Maximum longitudinal strains $s_3^{max}$ and $s_3^{max}/E_0$ for PMN-100xPT compositions as a function of electric field. The lines between the points serve as a guide to the eye. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | 49 |

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |    |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 5.13: Maximum transverse strains $s_1^{max}$ and $s_1^{max}/E_0$ for PMN-xPT compositions as a function of electric field. The lines between the points serve as a guide to the eye. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | 50 |
| Figure 5.14: Electromechanical response ( $s_1^{max}/E_0$ ) of the analysed PMN-100xPT compositions for different field magnitudes. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | 51 |
| Figure 5.15: Electrocaloric effect of PMN at 30 kV/cm (black curve). Electric field used to induce EC effect is schematically depicted with blue curves. The circles denote the temperature changes during adiabatic polarization and depolarization. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | 53 |
| Figure 5.16: a) Magnitudes of EC effect as a function of electric field, b) the asymmetry between $\Delta T_{EC}^P$ and $\Delta T_{EC}^D$ at 50 kV/cm. The asymmetry is shown by calculating the ratio between $\Delta T_{EC}^P/\Delta T_{EC}^D$ . . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | 55 |
| Figure 5.17: The FOM (Eq. 5.4) calculated with the data obtained in Section 5.2 and plotted versus electric field and composition $x$ . The red colour indicates high FOM values, while blue represents low values. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | 57 |
| Figure 5.18: Emergence of excessive heating during the EC cycling of PMN at room temperature. EC temperature response during the first test cycle (black) and after applying $7 \cdot 10^4$ EC cycles (red). Here, $\Delta T_{EC}^P$ denotes the temperature change upon adiabatic polarization, $\Delta T_{EC}^D$ denotes the temperature change upon adiabatic depolarization of the sample and $\Delta T_H$ indicates the excessive heating emerging with EC field cycling. The effective cooling ( $\Delta T_{C(N)}$ ) is defined as the difference between $\Delta T_{EC}^D$ and $\Delta T_H$ at cycle number N. . . . .                                                                                                                         | 58 |
| Figure 5.19: Degradation of EC response of PMN as a function of EC cycle number (N). $\Delta T_{EC(N)}^P/\Delta T_{EC(1)}^P$ , $\Delta T_{EC(N)}^D/\Delta T_{EC(1)}^D$ and $\Delta T_C(N)/\Delta T_C(1)$ are the excessive heating, adiabatic polarization, adiabatic depolarization and effective cooling normalized on the first EC cycle (N=1). $\Delta T_H$ is the absolute value of excessive heating. . . . .                                                                                                                                                                                                                                                                                                                                   | 59 |
| Figure 5.20: Temperature variations as a function of the number of EC cycles; the black curve shows the temperature variations during initial cycling, i.e., between the first and EC cycle number 1000, while the red curve shows the temperature variations between EC cycle number $6.9 \cdot 10^4$ and $7 \cdot 10^4$ . An average temperature rise ( $\Delta T_R$ ) during the two EC cycling periods (denoted in $\Delta T_R$ in brackets) was determined as shown by the green horizontal lines. . . . .                                                                                                                                                                                                                                       | 60 |
| Figure 5.21: Excessive heating as a function of number of EC cycles. The red curve shows the $\Delta T_H$ values measured during test cycle and the green the temperature rise ( $\Delta T_R$ ) during 2-Hz cycling. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | 61 |
| Figure 5.22: Correlation between electrical current and Joule heating observed during test cycles. The current values were measured at electric field ( $E_{ON}$ ) of 70 kV/cm at room temperature. a) Electrical current versus time measured during the first test cycle (black) and after $2.8 \cdot 10^4$ EC cycles (red), b) average electrical current ( $I_L$ ) versus number of EC cycles ( $I_L$ was determined from current points in the last 10 s before switching off the field; see arrows in panel (a)) and c) temperature change due to excessive heating ( $\Delta T_H$ ) plotted versus number of cycles; dots correspond to measured data, while the solid line corresponds to the calculated data (see text for details). . . . . | 62 |
| Figure 5.23: Conductivity mapping with the cAFM. a) the virgin sample b) sample with notable Joule heat cycled to $3 \cdot 10^4$ cycles. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | 63 |



|                                                                                                                                                                                                                                                                                                                                                                                                                                                   |    |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 5.24: Rejuvenation experiments. A sample was cycled, fatigued and rejuvenated several times. The plot shows the effective cooling normalized ( $\Delta T_{C(N)}$ ) on the initial value of effective cooling( $\Delta T_{C(1)}$ ). Red $\times$ symbol shows where the cycling was paused and flame symbol represents the moment the samples was rejuvenated. Arrows indicate the degradation and the rejuvenation of the samples. . . . . | 64 |
| Figure 5.25: EC properties of PMN cycled at 50 °C. The normalized effective cooling ( $\Delta T_{C(N)}/\Delta T_{C(1)}$ ) stays unchanged upto $5 \cdot 10^5$ cycles. The insets shows the initial EC response in time domain and EC response after $5 \cdot 10^5$ cycles. . . . .                                                                                                                                                                | 65 |
| Figure 5.26: <i>In-situ</i> XRD pattern recorded during EC cycling at a) room temperature and b) 50° C. The insets schematically show crystal structure as inferred from the XRD patterns. The numbers in panel b represent the cycle interval in which the XRD pattern was recorded. . . . .                                                                                                                                                     | 66 |
| Figure 5.27: Room-temperature XRD patterns recorded one minute and 30 minutes after cycling. . . . .                                                                                                                                                                                                                                                                                                                                              | 67 |
| Figure 5.28: PFM response of the virgin and cycled PMN sample. a) PFM out-of-plane amplitude image of the virgin (black-left) and cycled sample (red-right). b) PFM phase hysteresis loop obtained on a virgin (black) and cycled (red) PMN sample at the location depicted with a cross in the two samples in panel a. . . . .                                                                                                                   | 68 |
| Figure 5.29: $P(E)$ and $x(E)$ loops measured before (black) and after fatigue (red, $10^4$ cycles) in PMN. . . . .                                                                                                                                                                                                                                                                                                                               | 69 |
| Figure 5.30: Electric field vs. temperature ( $E$ - $T$ ) diagram for PMN. The vertical arrows show the trajectories of the field excitation for the fatigue tests performed at room temperature and 50 °C. The dotted line delineate the ergodic relaxor and supercritical ferroelectric state. The color scale indicates the magnitude of the responsivity. . . . .                                                                             | 71 |
| Figure 5.31: Comparison of the EC response in three different EC materials, relaxor PMN, donor-doped ferroelectric PZT and undoped ferroelectric PZT. . . . .                                                                                                                                                                                                                                                                                     | 73 |
| Figure 5.32: a) Current ( $I$ ) vs. time ( $t$ ) plots for hard PZT at different temperatures. The marker indicates the range for calculation of an average values used in the b) Arrhenious plot, logarithm of resistivity is plotted as a function of the inverse temperature. With the plot we estimated that the activation energy ( $E_a$ ) of resistivity is 1.05 eV. . . . .                                                               | 74 |
| Figure 5.33: Temperature evolution during electric-field cycling of PMN, PZT75/25-Nb and PZT75/25 using 4 Hz of unipolar square waveform. The temperature rise, i.e., the difference between the initial (prior to cycling) and final (steady-state) temperature of the sample (denoted as $\Delta T_R$ ) is 40 mK, 245 mK and 434 mK for PMN, PZT75/25-Nb and PZT75/25, respectively. . . . .                                                    | 75 |
| Figure 5.34: a) Temperature rise ( $\Delta T_R$ ) and b) corresponding calculated energy loss density ( $u$ ) as a function of electric-field cycling frequency for PZT75/25-Nb determined at different ambient temperatures. . . . .                                                                                                                                                                                                             | 76 |
| Figure 5.35: a) Temperature rise ( $\Delta T_R$ ) and b) corresponding calculated energy loss density ( $u$ ) as a function of electric-field cycling frequency for PZT75/25 determined at different ambient temperatures. . . . .                                                                                                                                                                                                                | 77 |
| Figure 5.36: $P(E)$ loops of a) PZT75/25-Nb and b) PZT75/25 measured at 0.6 Hz (full curves) and 10 Hz (dashed curves) and at temperatures of 24, 55 and 65 °C . . . . .                                                                                                                                                                                                                                                                          | 78 |

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |    |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 5.37: Microstructure cross-section of the PMN/Pt/PMN plates sintered at different temperatures, from left to right: 1000 °C, 1100 °C and 1200 °C. The thickness of the PMN layer is given next to the microstructure.                                                                                                                                                                                                                                                                                                                                                                                                                       | 79 |
| Figure 5.38: XRD of the tape sintered at 1200 °C for 2h. XRD pattern shows a pure perovskite crystal structure without any secondary phases. Miller indices are given above the diffraction peaks. The inset shows the enlarged area in which pyrochlore peaks usually appear.                                                                                                                                                                                                                                                                                                                                                                     | 80 |
| Figure 5.39: Polarization ( $P$ ) vs. electric field ( $E$ ) loops measured on the sintered tapes. The square's edge represents the scale for polarization and electric field.                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | 81 |
| Figure 5.40: Electromechanical response of the cantilevers. a) The deflections ( $\delta$ ) of the cantilever versus electric field, b) the calculated values of transverse electromechanical coefficient by using Equation 1.4 in Section 1.4.                                                                                                                                                                                                                                                                                                                                                                                                    | 82 |
| Figure 5.41: EC temperature change of the cantilever during adiabatic polarization ( $\Delta T_{EC}^P$ ) and depolarization ( $\Delta T_{EC}^D$ ). Left y-axis shows the directly measured values, while the right y-axis shows the corrected temperature changes. The correction factor was calculated using the procedure described in the Materials and Methods, Section 4.15.                                                                                                                                                                                                                                                                  | 83 |
| Figure 5.42: Driving set-up for the proof-of-concept device. The device was electrically wired to ground and high voltage. The high voltage was switched between cantilever 1 and 2 by a relay switch controlled by an Arduino Uno microcontroller. The microcontroller was programmed with Labview.                                                                                                                                                                                                                                                                                                                                               | 84 |
| Figure 5.43: Determination of the optimum operation frequency of the driving field with one active cantilever. One cycle with one active cantilever element at 43 kV/cm. The active cantilever is in contact with the upper element for half of the cycle period ( $0-2/f$ ) and the second half of the period ( $0-1/f$ ) in contact with the heat source where the temperature is measured.                                                                                                                                                                                                                                                      | 85 |
| Figure 5.44: Frequency ( $f$ ) dependence of normalized cooling of the first cantilever in the proof-of-concept device. The measured temperatures ( $\Delta T_{HS}$ ) are normalized with respect to the uncorrected EC effect ( $\Delta T_{EC}^D$ ) of the cantilever at an identical electric field.                                                                                                                                                                                                                                                                                                                                             | 86 |
| Figure 5.45: Determination of cooling capacity with two active cantilevers. One cycle with two active cantilever elements at 43 kV/cm is shown. The active cantilever is in contact with the upper element for a quarter of the cycle period ( $0 - \frac{4}{f}$ ) and the second quarter of the period ( $\frac{4}{f} - \frac{2}{f}$ ) in contact with the heat source where the temperature is measured. During $\frac{2}{f} - \frac{3}{4f}$ the electric field is applied to the cantilever element 2, which is then in contact with the heat sink. The electric field is then reduced to zero during the period $\frac{3}{4f} - \frac{1}{f}$ . | 87 |
| Figure 5.46: Temperature of the heat source as a function of time when one element is active (purple line) and when both elements are active (pink).                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | 88 |
| Figure A.1: XRD patterns of PMN-xPT ceramics.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | 94 |
| Figure A.2: Simulated temperature distribution in the sample after 0.5 s.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | 95 |
| Figure A.3: Simulated volume-averaged temperature evolution on the thermistor as a function of time.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | 96 |
| Figure A.4: Cantilever B deflections plotted versus the EC temperature change during adiabatic depolarization.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | 96 |

# List of Tables

|            |                                                                                                                                                                                                                                                                                                                               |    |
|------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Table 1.1: | Longitudinal piezoelectric coefficient ( $d_{33}$ ) of bulk ceramic materials [16] at room temperature. . . . .                                                                                                                                                                                                               | 5  |
| Table 1.2: | Electrocaloric temperature change of bulk ceramic materials. The electric field applied and temperature corresponding to the temperature change measured are added in the table. . . . .                                                                                                                                      | 7  |
| Table 1.3: | A summary of electrocaloric refrigerators. . . . .                                                                                                                                                                                                                                                                            | 13 |
| Table 5.1: | The dielectric properties of PMN-100xPT samples at 1 kHz. The maximum dielectric permittivity ( $\epsilon'_{rmax}$ ) and temperature of the maximum are shown in the first column. The dielectric permittivity and dielectric loss ( $D$ ) values at room temperature are summarized in the second and third columns. . . . . | 39 |
| Table 5.2: | The thermal conductivity ( $\lambda$ ) and specific heat ( $c_p$ ) for PMN-xPT ceramics and thermal transport coefficient ( $\frac{c_p \rho}{\lambda} \cdot 10^6$ ). . . . .                                                                                                                                                  | 52 |
| Table 5.3: | Correction factors of the analysed PMN-100xPT samples. . . . .                                                                                                                                                                                                                                                                | 54 |
| Table 5.4: | Dielectric permittivity and loss of sintered tapes measured at room temperature and 1 kHz. . . . .                                                                                                                                                                                                                            | 80 |
| Table A.1: | Density of the ceramics under investigation. . . . .                                                                                                                                                                                                                                                                          | 93 |
| Table A.2: | Grain size of the ceramics under investigation. . . . .                                                                                                                                                                                                                                                                       | 93 |



# Symbols

|                   |     |                                                                                                      |
|-------------------|-----|------------------------------------------------------------------------------------------------------|
| $A$               | ... | ratio between the Young's modulus of electrode and the Young's modulus of piezoelectric material [/] |
| $\alpha$          | ... | thermal diffusivity [ $\text{m}^2/\text{s}$ ] or heat transfer coefficient [ $\text{W}/\text{m}^2$ ] |
| $B$               | ... | ratio between the thickness of the electrode and the piezoelectric layer in the cantilever [/]       |
| $b$               | ... | thickness [m]                                                                                        |
| $D$               | ... | charge density [ $\text{C}/\text{m}^2$ ]                                                             |
| $\rho$            | ... | density [ $\text{kg}/\text{m}^3$ ]                                                                   |
| $i$               | ... | element number from bottom to top [/]                                                                |
| $E_a$             | ... | activation energy [eV]                                                                               |
| $E_0$             | ... | amplitude of electric field [ $\text{V}/\text{m}$ ]                                                  |
| $E_{subs}$        | ... | Young's modulus of the passive part of the cantilever [ $\text{N}/\text{m}^2$ ]                      |
| $E_{piezo}$       | ... | Young's modulus of the piezoelectric material in the cantilever [ $\text{N}/\text{m}^2$ ]            |
| $F$               | ... | mechanical force [F]                                                                                 |
| $f$               | ... | frequency [ $\text{s}^{-1}$ or Hz]                                                                   |
| $d_{ij}$          | ... | piezoelectric effect [ $\text{pm}/\text{V}$ ]                                                        |
| $L$               | ... | length [m]                                                                                           |
| $U$               | ... | voltage [V]                                                                                          |
| $\delta$          | ... | deflection [m]                                                                                       |
| $c_p$             | ... | specific heat [ $\text{J}/\text{kgK}$ ]                                                              |
| $\lambda$         | ... | heat conductivity [ $\text{W}/\text{mK}$ ]                                                           |
| $P$               | ... | polarization [ $\text{C}/\text{m}^2$ ]                                                               |
| $P_s$             | ... | spontaneous polarization [ $\text{C}/\text{m}^2$ ]                                                   |
| $P_r$             | ... | remanent polarization [ $\text{C}/\text{m}^2$ ]                                                      |
| $R$               | ... | thermal resistivity [ $\text{K}/\text{W}$ ]                                                          |
| $Q_{ij}$          | ... | electrostrictive coefficient [ $\text{m}^4/\text{C}^2$ ]                                             |
| $Q_{eci}$         | ... | electrocaloric heat [J]                                                                              |
| $\varrho$         | ... | internal heat source [ $\text{W}/\text{m}^3$ ]                                                       |
| $T$               | ... | temperature [K]                                                                                      |
| $T_C$             | ... | Curie temperature [K]                                                                                |
| $T_m$             | ... | temperature of dielectric peak maximum [K]                                                           |
| $\Delta T$        | ... | temperature change [K]                                                                               |
| $\Delta T_{EC}^P$ | ... | electrocaloric temperature change during adiabatic polarization [K]                                  |
| $\Delta T_{EC}^D$ | ... | electrocaloric temperature change during adiabatic depolarization [K]                                |
| $\Delta T_{(J)H}$ | ... | excessive (Joule) heating [K]                                                                        |
| $\Delta T_R$      | ... | temperature rise due to losses during EC cycling [K]                                                 |
| $t_c$             | ... | heat exchange time [s]                                                                               |
| $t$               | ... | time [s]                                                                                             |
| $N$               | ... | cycle number [/]                                                                                     |
| $M$               | ... | electrostrictive coefficient [ $\text{m}^2/\text{V}^2$ ]                                             |
| $\tau$            | ... | thermal time constant [s]                                                                            |

|                   |     |                                                                          |
|-------------------|-----|--------------------------------------------------------------------------|
| $s_i$             | ... | mechanical strain, longitudinal i=3, transverse i=1 [/] or entropy [J/k] |
| $\varepsilon_r$   | ... | relative dielectric constant [/]                                         |
| $\varepsilon_r'$  | ... | real part of relative dielectric constant [/]                            |
| $\varepsilon_r''$ | ... | imaginary part of relative dielectric constant [/]                       |
| $W_s$             | ... | stored electrical energy density [J/m <sup>3</sup> ]                     |
| $W_L$             | ... | electrical loss density [J/m <sup>3</sup> ]                              |
| $u$               | ... | energy loss calculated from $\Delta T_R$ [J/m <sup>3</sup> ]             |
| $\zeta$           | ... | electrical efficiency [%]                                                |

# Chapter 1

## Introduction

*In this chapter the background to the PhD topic is given. The aim of the following chapters is to introduce the material compositions based on the  $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$  (PMN-100xPT) investigated during the thesis and their multifunctional properties, which makes them interesting for electrocaloric refrigeration. In the final part, a brief summary is given on the potential use of these materials in actual refrigeration devices, with particular emphasis on the cooling efficiency and electric-field cycling stability as the primary parameters relevant for the integration of the EC material into cooling devices.*

### 1.1 Ferroelectric and Relaxor Materials

#### 1.1.1 Basic definitions

A special subgroup of dielectric materials are ferroelectrics, which possess a spontaneous polarization ( $P_s$ ), associated with a permanent separation of positive and negative charges inside the material, which can be switched in at least two different directions by the application of an external electric field [1]. Ferroelectric materials with a perovskite crystal structure characterized by the general chemical formula  $\text{ABO}_3$  (schematically shown in the (100) projection in Fig. 1.1a) are the most investigated because of their good electrocaloric, electromechanical and dielectric properties [2].

Ferroelectric materials typically exhibit a polymorphic phase transition from a high-temperature non-polar or paraelectric (e.g., cubic phase) to a lower-temperature polar or ferroelectric phase (e.g., tetragonal). This transition is reflected in a sharp peak of the dielectric permittivity, as shown in Fig. 1.1a. The temperature at which the transition occurs is called the Curie temperature ( $T_c$ ) and this is the temperature at which the spontaneous polarization ( $P_s$ ), which is zero in the paraelectric phase, attains a finite value in the ferroelectric phase on cooling.

After the transformation from the paraelectric to the ferroelectric phase during cooling, the  $P_s$  in the material becomes randomly oriented because of the complex electric and mechanical boundary conditions within the material during the transition. The appearance of polarization in the material when it emerges from zero at  $T_c$  leads to surface charges and consequently a depolarizing electric field inside the material. To reduce the thermal stresses and energy of the depolarizing electric field, ferroelectric domains form.

Ferroelectric domains are regions in the material with equally oriented  $P_s$ . Domains are separated by domain walls. Domain walls that separate oppositely oriented domains are called  $180^\circ$  walls. Other types of domain walls exists, such as non- $180^\circ$  domains. As stated previously, a characteristic property of ferroelectric materials is the polarization reversal with an applied electric field. A consequence of the domain switching process in

ferroelectrics is the polarization-electric field ( $P(E)$ ) hysteresis loops (see Fig. 1.1b).

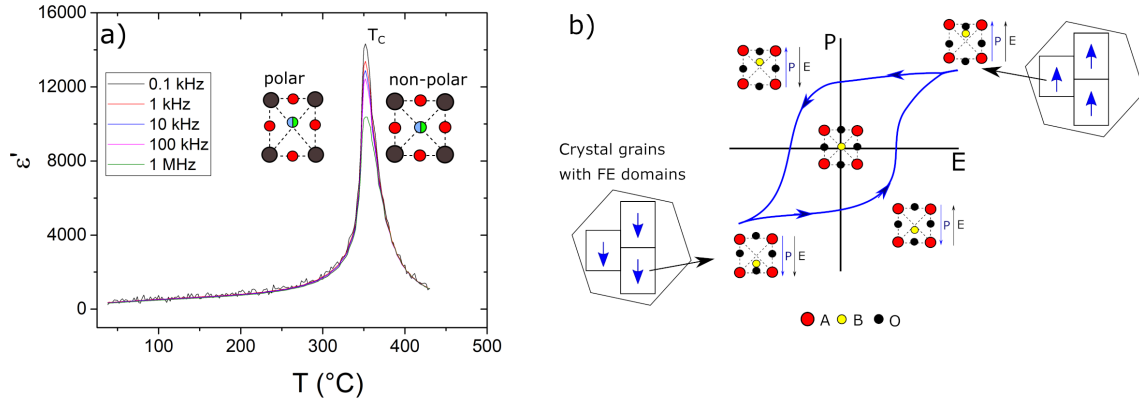


Figure 1.1: a) dielectric response of a  $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})_{0.98}\text{Nb}_{0.02}\text{O}_3$  ferroelectric material and b) Typical ferroelectric polarization ( $P$ ) versus electric field ( $E$ ) hysteresis loop. The insets schematically show the perovskite crystal in the (100) projection (panel a) and domain structure corresponding to the  $P(E)$  state (panel b).

Relaxors are similar to ferroelectrics; however, in relaxors no long-range polar order develops and the average symmetry is cubic to low temperatures [3], [4]. The main source of their polarization are nano-sized regions (so-called polar nanoregions, PNRs) in the non-polar cubic matrix.

The characteristic property of the relaxor materials is the frequency-dependent temperature of the dielectric permittivity maximum ( $T_m$ ), as shown in Fig. 1.2b. In contrast to ferroelectrics, the dielectric maximum ( $T_m$ ) does not correspond to a phase transition but is rather related to relaxation phenomena [5].

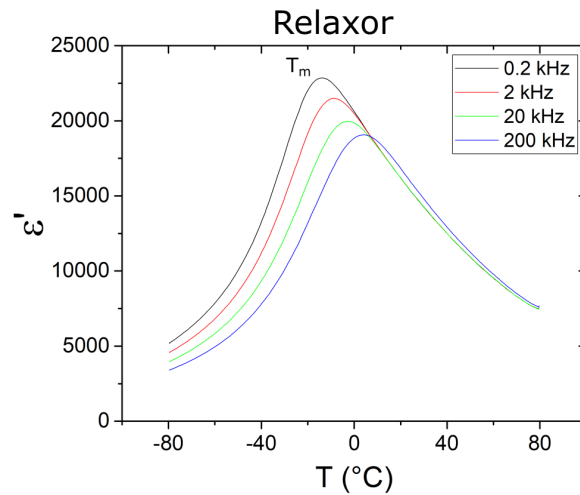


Figure 1.2: Dielectric response as a function of temperature and frequency for a archetypical relaxor  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ .

The temperature evolution of the polarization-field response and internal polarity in relaxors is depicted in Fig. 1.3. At high temperatures, relaxors are in a paraelectric state, thus showing a linear  $P(E)$  relationship and a non-polar matrix, as shown in Figure 1.3 (see



green panels). PNRs begin to form at the so-called Burns temperature (or depolarization temperature,  $T_d$ ) as shown in blue panels. In the ergodic relaxor state the number of PNRs is believed to grow with decreasing temperature and combine to larger clusters. In this region, the maximum dielectric response is measured at  $T_m$  and strongly depends on the electric-field frequency (see also Fig. 1.2). The  $P(E)$  becomes non-linear and hysteretic. By further reducing the temperature the material can either transform to a non-ergodic relaxor (below freezing temperature -  $T_f$ ) or to ferroelectric (below  $T_c$ ). The non-ergodic relaxor state can be transformed to ferroelectric state with wide  $P(E)$  hysteresis through the induced ferroelectric transition by the application of a sufficiently large electric field (see pink panels).

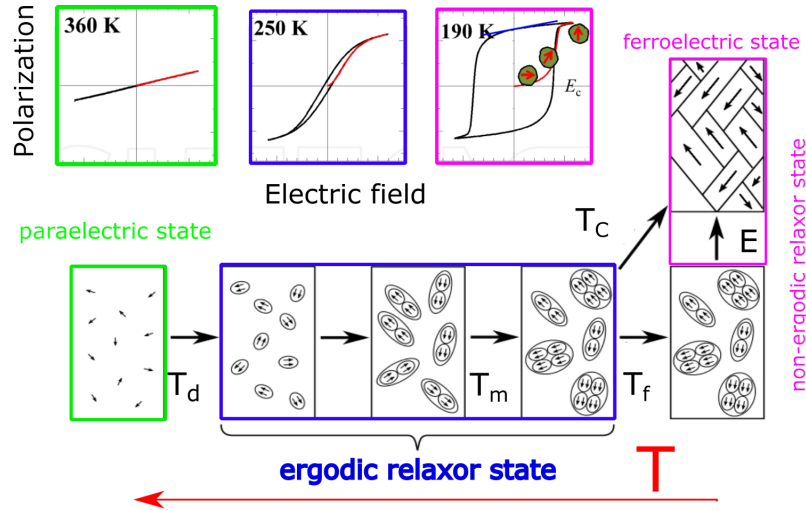


Figure 1.3: The states of relaxor across a broad temperature range. Identical schematic frame colours represent the state in the material and corresponding  $P(E)$  response (see text for details). The temperatures on the  $P(E)$  response are for illustration purposes only. Figure edited after Ref. [6]

In the literature, relaxor ferroelectrics are often linked to outstanding functional properties, such as electromechanical and electrocaloric responses. Typically, these materials are a solid solution of a relaxor and a ferroelectric, for example, PMN-100xPT and  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$  [3]. Upon cooling they undergo a transformation directly from the ergodic to ferroelectric state.

### 1.1.2 Electromechanical response

Ferroelectrics and relaxors are also electromechanically active materials. The electromechanical (EM) response is defined as the change of dimensions of the material upon the application of an electric field. In general and on a purely descriptive basis, we divide the contributions to the EM response to the intrinsic i) and ii) extrinsic contribution. The first usually refers to the lattice effect, while the second to non-lattice contributions, such as domain-wall displacements and switching in ferroelectric materials [7]. Additionally, it is important to note that the mechanisms contributing to the EM response strongly depend on the electric field magnitude; usually we divide the response into subcoercive, where the fields applied to the material are lower than the coercive field ( $E_C$ ) of the material, and the supercoercive regime, where the applied fields are larger [7].

The intrinsic EM response can be further separated on electrostrictive and piezoelectric [2]. In its most simplified view, the electrostrictive response is caused by the anharmonic

nature of chemical bonds in ionic solids - the bonds are easier to extend than to contract. When an electric field ( $E$ ) is applied to a dielectric, oppositely charged ions move, respectively, toward the cathode and the anode, whereas one bond is extended (tensed) while the other shortens (compressed). Because compression is less favourable, meaning the energy of compression is higher than tension, a slight difference in the ionic shifts is created, which is observed as strain ( $s$ ) [8] (see Fig. 1.4a). This atomistic detail leads to lattice expansion, which is independent of the field polarity (material expands for both positive and negative fields).

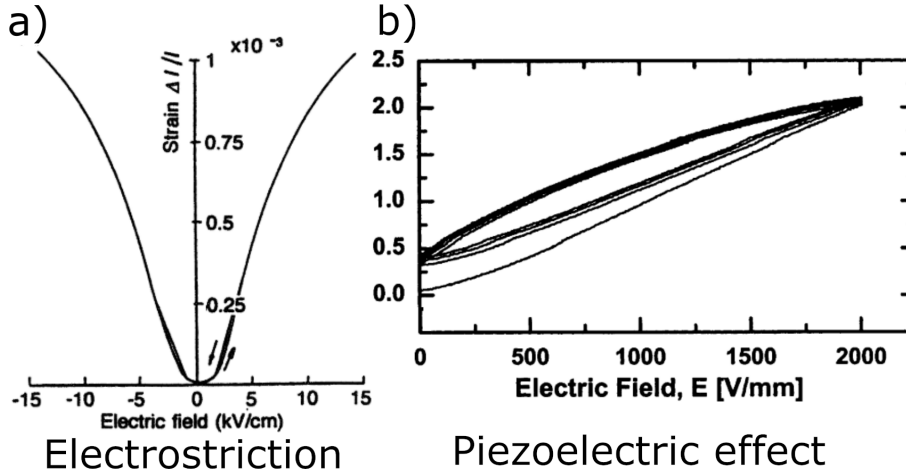


Figure 1.4: Contributions to the electromechanical response: a) electrostrictive and b) piezoelectric response. Parts of the image taken from [2], [9].

The electrostrictive strain ( $s$ ) in the solid under electric field ( $E$ ) can be described with even powers of the electric field:

$$s = m_1 E^2 + m_2 E^4 + m_3 E^6 \dots \quad (1.1)$$

At low electric fields the prevailing term is the quadratic one, thus we simplify the relation between the strain and electric field to:

$$s = M E^2 = Q P^2, \quad (1.2)$$

where  $M$  and  $Q$  are the electrostrictive coefficients and  $E$  is the externally applied electric field,  $P$  is the polarization of the material. The electrostriction coefficients depend on the crystallographic orientation and are usually described in tensor notation.

The piezoelectric effect is closely related to electrostriction. It is crystallographically conditioned (anisotropic) and exhibited in crystals that do not possess the center of symmetry [10]. A particular group of such materials are perovskite materials (see Fig. 1.1a), where the central cation is shifted from the center of the perovskite lattice. The piezoelectric effect can be separated into direct and indirect, where the charge and or strain are induced by mechanical or electric fields, respectively. The piezoelectric coefficient ( $d$ ) can be derived from Equation 1.2 as [11]:

$$d = \frac{ds}{dE} = 2QP \frac{dP}{dE} = 2QP\epsilon \quad (1.3)$$

where  $Q$  is the electrostrictive charge coefficient and  $d$  is the piezoelectric coefficient, which is also a tensor quantity. The relation between strain and electric field follows a linear relationship; such a response is, for example, observed in poled ferroelectric materials. As

shown in Fig. 1.4b the piezoelectric response in ferroelectrics is very often hysteretic. This is often due to the presence of ferroelectric domains and domain walls, which may strongly contribute to the EM response. In total they can add up to 50 % of the total EM response [12]. This extrinsic contribution originates from the motion and vibration of non-180° domain walls. The correlation between the macroscopic strain and the 90° domain wall movement was analysed using in-situ X-ray diffraction analysis for modified tetragonal PZT by Pramanic et al. [13]. They showed a coupling between the volume fraction of the switched 90° domain walls and macroscopic strain thus confirming the early idea of a significant contribution of domain-wall displacements to the electromechanical response [14], [15]. Some typical values of the longitudinal piezoelectric coefficient  $d_{33}$  (the first and second subscript denoting the direction of the measured piezoelectric strain and applied field, respectively) in ceramic is shown in Table 1.1.

Table 1.1: Longitudinal piezoelectric coefficient ( $d_{33}$ ) of bulk ceramic materials [16] at room temperature.

| Material                                                                                                                             | $d_{33}$ (pC/N) | Ref.       |
|--------------------------------------------------------------------------------------------------------------------------------------|-----------------|------------|
| Ba(Zr <sub>0.2</sub> Ti <sub>0.2</sub> )O <sub>3</sub> -based                                                                        | 54              | [17]       |
| PbZr <sub>0.52</sub> Ti <sub>0.48</sub> O <sub>3</sub>                                                                               | 223             | [1]        |
| Pb <sub>0.92</sub> La <sub>0.08</sub> Zr <sub>0.65</sub> Ti <sub>0.35</sub> O <sub>3</sub>                                           | 682             | [18]       |
| PMN                                                                                                                                  | 0               | [19]       |
| PMN-10PT                                                                                                                             | 10              | [20], [21] |
| PMN-20PT                                                                                                                             | 230             | [22]       |
| PMN-35PT                                                                                                                             | 650             | [23]       |
| Bi <sub>1/2</sub> Na <sub>1/2</sub> TiO <sub>3</sub> -0.1SrTiO <sub>3</sub> -0.1Bi <sub>1/2</sub> Li <sub>1/2</sub> TiO <sub>3</sub> | 115             | [24]       |

When excitation is increased above the so-called coercive field  $E_C$ , we observe an EM response due to switching. This phenomenon is complex and can lead to large strain. However, it is less commonly used in actual applications due to the detrimental effects of polarization switching on the properties and long term stability of the response [2].

A giant piezoelectric effect was observed in materials where two crystal structures coexist and have similar internal energies (referred to as Morphotropic Phase Boundary - MPB, see Fig. 1.5a). Such an enhanced response has been observed in PbZr<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub>, as shown in Fig. 1.5. Fig. 1.5a shows the phase diagram for PZT as a function of Zr/Ti ratio and temperature. At appropriately  $x=0.52$  in PbZr<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub> [25]–[27] the ceramics exhibit high piezoelectric properties. The mechanism behind the phenomenon is the so-called polarization rotation [28] where the polarization direction upon field application undergoes several intermediate crystal states to minimize the energy cost of the path and thus ensure a effective electric-to-mechanical (or *vica-versa*) energy conversion.

### 1.1.2.1 Application of EM effect

In general, EM effects are employed in a broad spectrum of applications from sensors to high-precision positioning systems [2], [29]. Interesting structures for achieving high displacements (up to few mm) are cantilevers. Cantilevers consisting of a combination EM active (piezoelectricly or electrostrictively) and passive layers. Depending on their particular design, the cantilevers can be unimorph, bimorph and multimorph cantilevers; unimorph actuators consists of an active and passive layer, bimorph possess two active and one passive layer, while multiple interchanging active and passive layers are present in multimorphs.

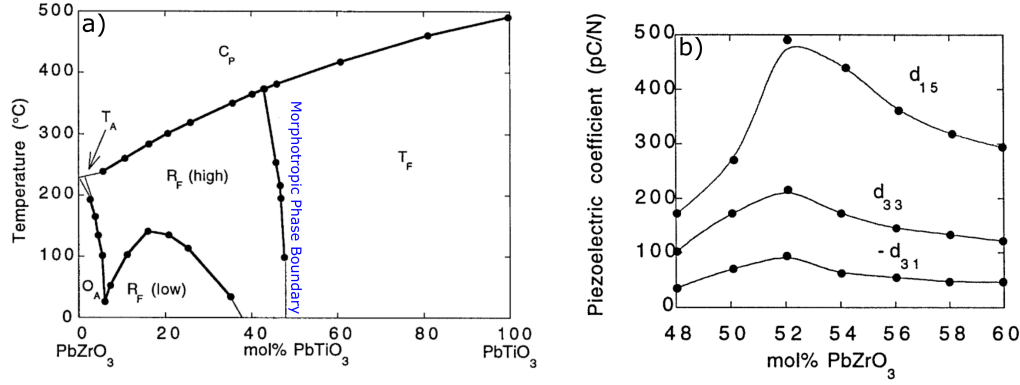


Figure 1.5: Morphotropic phase boundary in  $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ . a) The phase diagram showing different phases as a function of temperature and composition, b) room-temperature piezoelectric response as a function of composition. Edited after [1], [7]

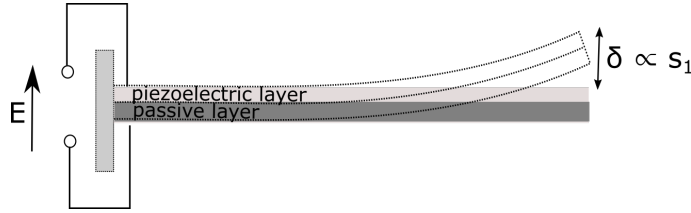


Figure 1.6: Bending of unimorph cantilever under electric field.

When subjected to an electric field the piezoelectric layer deforms and causes bending of the structure, as shown in Fig. 1.6. Usually, the transverse EM coefficients define the bending magnitude. The equation developed by Wang et al. [30] is used to estimate the deflections ( $\delta$ ) of the cantilever:

$$\delta = \frac{3L^2}{2b_p} \cdot \frac{2AB(1+B)}{(A^2B^4) + 2A(2B + 3B^2 + 2B^3) + 1} s_1, \quad (1.4)$$

where  $\delta$  is the deflection of the cantilevers tip,  $L$  is length of the cantilever,  $b_p$  is thickness of the active (e.g., piezoelectric) layer,  $b_m$  is thickness of the passive (e.g., electrode) layer,  $A$  is ratio of  $E_{subs}/E_{piezo}$  where  $E_{subs}$  and  $E_{piezo}$  are the Young's modulus of the passive and active parts, respectively,  $B$  is the ratio  $b_m/b_p$  and  $s_1$  is the strain in the active layer.

### 1.1.3 Electrocaloric response

Ferroelectrics and relaxors have been extensively researched due to their high electrocaloric (EC) effect, a special type of dielectric cooling [31]. The EC effect is defined as an adiabatic and reversible temperature change induced by the application of an electric field. The EC effect was reported several years ago by Kobeko et al.[32], but due to the small measured effect (0.0036 K), it was only academically researched at that time. After the publication by Mischenko et al. [33], who reported on a large EC effect ( $\Delta T_{EC} = 12$  K) in ferroelectric  $\text{Pb}(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3$  thin films, the effect gained wider interest (EC effect of some bulk ceramic materials shown in Table 1.2). The EC effect shows great potential for future energy-efficient and environmentally friendly cooling devices; however, the main problem is still a too small temperature change ( $\Delta T_{EC}$  up to 4.5 K) induced in the bulk materials

[34]. In addition, these maximal values are often measured close to the electric breakdown of the materials.

Table 1.2: Electrocaloric temperature change of bulk ceramic materials. The electric field applied and temperature corresponding to the temperature change measured are added in the table.

| Material                                                                                   | $\Delta T_{EC}$ (K) | E (kV/cm) | T (°C) | Ref. |
|--------------------------------------------------------------------------------------------|---------------------|-----------|--------|------|
| Ba(Zr <sub>0.2</sub> Ti <sub>0.2</sub> )O <sub>3</sub> -based                              | 4.5                 | 87        | 35     | [34] |
| PbZr <sub>0.53</sub> Ti <sub>0.47</sub> O <sub>3</sub>                                     | 0.1                 | 30        | 22     | [35] |
| Pb <sub>0.92</sub> La <sub>0.08</sub> Zr <sub>0.65</sub> Ti <sub>0.35</sub> O <sub>3</sub> | 2.25                | 88        | 107    | [22] |
| PMN-10PT                                                                                   | 3.45                | 140       | 110    | [36] |
| PMN-30PT                                                                                   | 3                   | 90        | 157    | [22] |
| PMN                                                                                        | 2.5                 | 90        | 65     | [22] |
| Bi <sub>1/2</sub> Na <sub>1/2</sub> TiO <sub>3</sub> -0.25SrTiO <sub>3</sub>               | 2.5                 | 40        | 102    | [37] |

The Brayton EC refrigeration cycle can be divided in four stages. In Figure 1.7 the four stages are presented schematically and can be described as follows: 1) the adiabatic polarization of the EC material, during which the material heats up ( $T_{initial} + \Delta T_{EC}^P$ ) when an electric field is applied, 2) the isoelectric heat removal, where the generated heat dissipates in the surrounding environment, 3) the adiabatic depolarization, during which the material cools down below the initial temperature ( $T_{initial} - \Delta T_{EC}^D$ ) when the electric field is removed, and 4) the isoelectric heat absorption where the material heats back to the environmental temperature by absorbing heat from the surroundings [38].

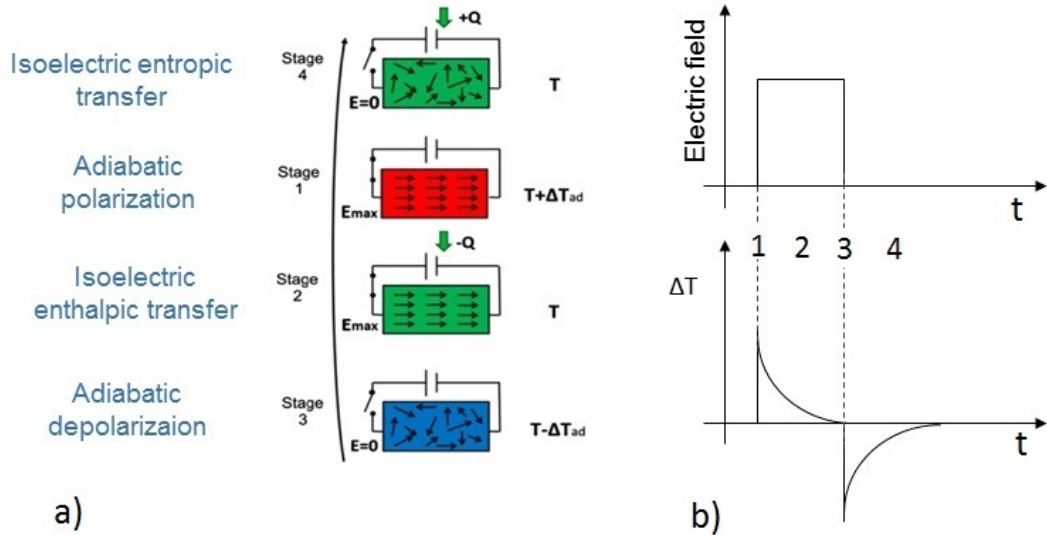


Figure 1.7: a) The electrocaloric cycle with four stages, and b) the measured temperature response ( $\Delta T$ ) in the four stages (see corresponding numbers) with respect to the applied electric field ( $E$ ).

In the literature the EC effect is evaluated by several methods. The most important and reliable methods are direct, meaning the temperature or heat is measured directly with an

appropriate temperature. Direct characterization of the EC temperature change is made by mounting a temperature sensor to a sample and measuring the temperature during electric field excitation [38]. Various types of temperature sensors have been used in the literature, most commonly thermocouples and resistance temperature detectors (RTDs). Differential scanning calorimetry can also be used for measuring the heat flux [39] during the EC stages.

Alternatively, thermal imaging is a novel method of EC characterization [40]. The main benefit of the thermal cameras is the ability to monitor the temperature distribution spatially across the sample.

Indirect methods are more commonly found in the literature. The idea is to measure the variation of  $P$  under an applied electric field in the temperature range of interest. By using the Maxwell equation the EC effect can be evaluated [41]:

$$\Delta T = \int_{E_1}^{E_2} \frac{1}{\rho c_P} \left( \frac{\Delta P}{\Delta T} \right) dE, \quad (1.5)$$

where  $\rho$  denotes the density of the material,  $c_P$  the specific heat,  $E_1$  and  $E_2$  the electric field applied to the material, and  $\frac{\Delta P}{\Delta T}$  change of polarization with temperature.

Besides the Maxwell relation there are other theoretical approaches that can be used to evaluate the EC effect indirectly [42]. Indirect methods are a fast and accessible way for evaluating the EC effect since the  $P(E, T)$  values are widely available in the literature; however, the relation between the polarization and EC temperature change is non-trivial and can lead to large discrepancies [43]. Especially problematic for an indirect evaluation of the EC effect can be materials with discontinuous changes in  $P$  (as observed in first order phase transition), materials with Joule heating and materials with large extrinsic effects [44].

As nicely shown in the review paper by Moya et al. [45], the EC effect is strongly enhanced near the structural phase transitions. When a polar material is heated under an electric field the  $P$  reduces continuously with increasing temperature. This is because of the interplay between the thermal agitation and the long-range polar order in the ferroelectrics (and relaxors). When the temperature  $T_C$  (or  $T_d$ ) is reached the material goes through a polar to non-polar phase transition. During the first-order transition  $\frac{\Delta P}{\Delta T}$  changes abruptly in a narrow temperature range (Fig. 1.8a, red curve). By observing Equation 1.5, we can see that a larger  $\frac{\Delta P}{\Delta T}$  leads to a higher EC effect. If the phase transition is of second order the  $\frac{\Delta P}{\Delta T}$  is altered continuously (Fig. 1.8, green curve), leading to a smaller EC response, but less temperature dependent, due to the broad nature of the temperature transition.

The simplified explanation of the enlarged EC effect in the vicinity of the phase transition is as follows [46], [47]. It is known that in the vicinity of  $T_C$  the dipoles can be oriented easily [48]. When an electric field is applied, a drastic ordering of dipoles occurs, which leads to a decrease of the entropy of the dipolar system. The excess energy of the ordered dipoles is converted into the entropy of the lattice, causing increased lattice vibrations, reflected as an increase in temperature  $\Delta T_{EC}^P$ .

Not only is the EC effect enhanced in the proximity of the polymorphic phase transition, an electric field or pressure-induced phase transition also contribute to the EC effect. A significant enhancement of the electrocaloric responsivity ( $\frac{\Delta T_{EC}^D}{\Delta E}$ ) in the vicinity of a field-induced phase transformation was observed in PLZT ceramics [22],  $0.75\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ - $0.3\text{SrTiO}_3$  (BNT-25ST) and PMN ceramics [37], [49].

Uniaxial stress in several ferroelectric and relaxors provokes an elastocaloric response, which combined with an electrocaloric response leads to a giant temperature effect [50]. In addition, uniaxial and isostatic pressure shift the temperature of phase transitions [51].

A similar shift of the phase transformation closer to the room temperature can also

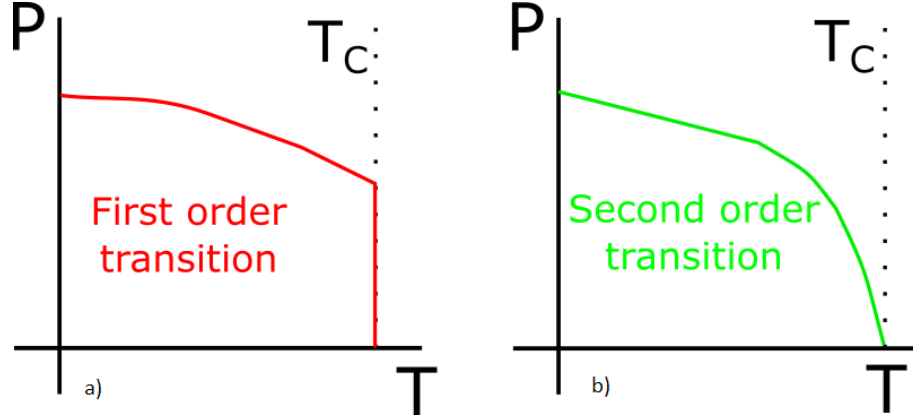


Figure 1.8: Variation of polarization with temperature in materials with a first- (a) and second-order phase (b) transition.

be achieved by chemical modification of the material, as shown by numerous studies, for example, in Refs. [52], [53]. The compensating point defects, such as oxygen vacancies, in combination with an appropriate application of the electric field, have been suggested to enhance the EC effect [54], [55]. However, oxygen vacancies and other mobile defects which contribute to the electric conductivity of the material, can significantly impact the EC effect [56], [57]. In fact, a large conductivity leads to Joule heating effects, which lower the cooling capability of electrocalorics [58], [59].

In addition, several studies have been conducted to investigate the influence of planar defects, including grain boundaries and domain walls, on the EC effect. Vrubelj et al. [36] showed that in the PMN-10PT with an optimal grain size of 6  $\mu\text{m}$  shows the largest EC responsivity ( $\frac{\Delta T_{EC}^D}{\Delta E}$ ). However, they also show that ceramics with a finer grain-size can sustain larger electric fields, which leads to larger induced electrocaloric temperature changes. It was also shown theoretically that certain domain configurations in combination with appropriate mechanical and electric fields enhance the EC effect in  $\text{BaTiO}_3$  [60]. This was later experimentally confirmed by studies on PZT thin films [61]. On the other hand, it is well known that domain-wall displacements and switching under a field, strongly contribute to the electric losses of ferroelectrics [62], [63]. This aspect was not discussed in the mentioned papers.

#### 1.1.4 $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - (x)\text{PbTiO}_3$ material system

$\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PMN)-based materials are widely used in commercial piezoelectric applications and exhibit superior EM and EC properties (see Tables 1.2 and 1.1). PMN by itself is the archetypal relaxor material, with a broad maximum in the dielectric permittivity [4], [64]. The addition of  $\text{PbTiO}_3$  (PT) to PMN marked the first generation of PMN-100xPT relaxor-ferroelectrics, which will be analysed in detail in this work. Also, the second and the third generation exist, where the PMN-100xPT is modified with the addition of  $\text{PbIn}_{0.5}\text{Nb}_{0.5}\text{O}_3$  to increase the coercive field and  $T_C$ , and in third generation, doped with, e.g., Mn to reduce the losses [65].

Fig. 1.9 shows the phase diagram of the binary PMN-100xPT solid solution. With increasing content of PT the room-temperature pseudo-cubic crystal structure of PMN changes to rhombohedral. Further increasing the content of PT the rhombohedral phase is replaced by a monoclinic one (at  $x=0.28$ ). In the range from  $x=0.28$  to  $x=0.37$  multiple monoclinic phases coexist and result in peculiar properties that resemble PZT's at MPB

(see Fig. 1.5). After  $x=0.38$  the crystal structure is tetragonal.

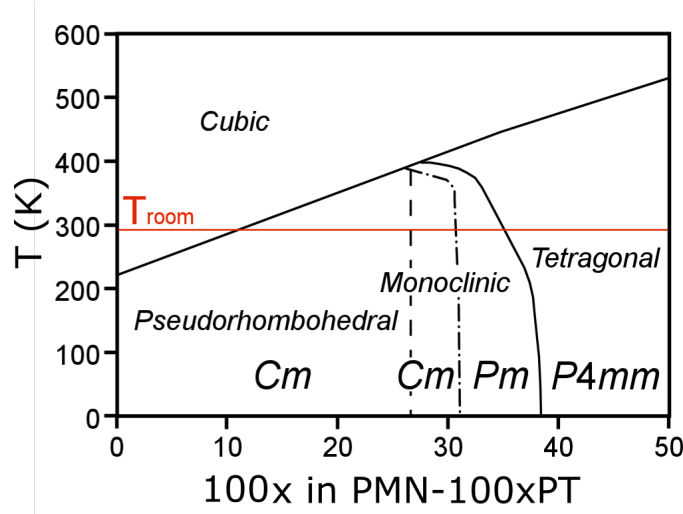


Figure 1.9: Phase diagram of the binary solid solution PMN-100xPT. Courtesy of Mojca Otoničar, redrawn after [66].

The electric and electromechanical properties of various PMN-100xPT ceramic compositions were analysed by Kelly et al. [67]. The dielectric and electrocaloric properties are shown in Fig. 1.10a. We can see that with increasing content of  $x$ , the temperature of the dielectric maximum increases, with PMN-30PT exhibiting the highest values of 40000 at 140 °C. Perhaps one of the most systematic EC studies of the PMN-100xPT ( $x=0, 0.05, 0.1, 0.15, 0.2, 0.25$  and  $0.3$ ) was made by Perăntie et al. [68]. In the study the authors measured the EC effect in a wide temperature and electric field range. In Fig. 1.10b we can see that the peak in the EC response is also shifting to higher temperatures, increasing the PT content ( $x$ ). The highest EC response at 5 kV/cm among the analysed compositions was observed in PMN-20PT. It is worth mentioning that the largest EC response in lead-based materials was later measured in PMN-10PT [36]. The temperature change of 3.5 K was measured at 130 °C and 160 kV/cm.

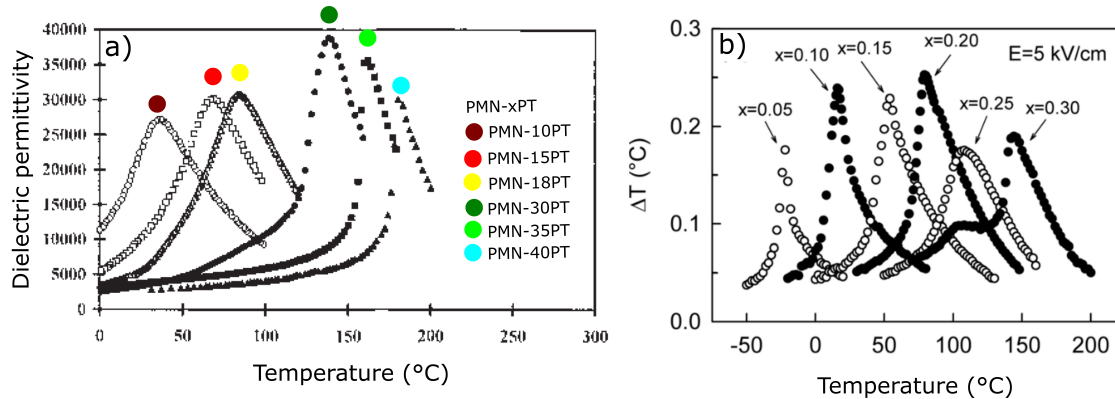


Figure 1.10: Temperature dependence of a) dielectric permittivity and b) EC temperature change of PMN-100xPT ceramic compositions; taken from Refs. [67], [68].

With the addition of PT the nature of the EM response changes drastically. Composi-



tions  $x=0$  and  $x=10$  have a relaxor-like response, meaning electrostrictive, while contents with higher  $x$  are ferroelectric and thus show a piezoelectric response. Fig. 1.11 shows the direct piezoelectric response of the PMN-100xPT compositions in the compositional range from  $x=0.27$  to  $x=0.4$ . The peak in the piezoelectric coefficient (730 pC/N) is observed close to  $x=0.35$ , i.e., in the MPB region where the monoclinic Pm and tetragonal P4mm symmetries are close in their free energy.

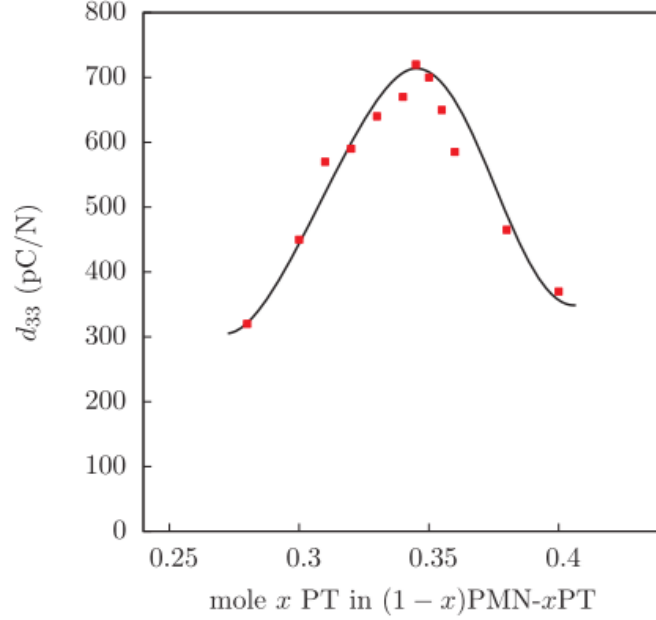


Figure 1.11: Direct piezoelectric response of the PMN- $x$ PT compositions [67]. Courtesy of Gregor Trefalt.

Recently, Fei Li et al. [69] showed that the piezoelectric response of PMN-100xPT can be greatly improved with small additions of Sm. For example, in a typical soft PZT the  $d_{33} = 550$  pm/V, while the PMN-31PT doped with 2.5 % percent of Sm exhibits  $d_{33}$  of 1500 pm/V. The enhanced response is attributed to Sm, which introduces local heterogeneities in the material, altering the energy potential of the crystal phases and thus enabling easier switching [70].

In the few mentioned examples of the latest work on the PMN-100xPT material system, it is evident that this material system possesses high EC and EM effects, making it interesting for a large number of applications. In the scope of this PhD we will show that a combination of EC and EM properties have the potential for use in small-scale refrigeration.

## 1.2 Integration of Electrocaloric Cooling

### 1.2.1 A brief summary of the work done on electrocaloric refrigerators

The first reported attempts to implement EC devices were made during the second world war by the Japanese navy; however, no public reports are available in English (Kenji Uchino, personal communication). The first reported paper on EC devices was by Sinyanski et al. [71], where  $\text{PbSc}_{0.5}\text{Ta}_{0.5}\text{O}_3$  ceramics were used and where the achieved temperature change in the device was 5 K. In recent years numerous attempts were made to integrate

EC cooling, from conceptual ideas to proof-of-concept devices. The largest obstacle in the integration of EC materials is the small EC temperature change. And this is also the main problem that the device concept should solve. Commonly, heat regeneration by smart thermal management has to be implemented.

In terms of the way the heat management is assessed, we can divide the current devices in two groups: i) fluid-based devices use a heat-transfer fluid to transfer the heat to the heat sink and the heat source. An example is given in Fig. 1.12a. The device consists of EC elements (elongated white squares) which are sunk into silicon oil (denoted with a blue color) to achieve active electrocaloric regeneration (AER). This AER is achieved with oscillatory pumping of silicon oil across the EC elements according to the EC cycle and leads to temperature changes that are several times larger than the EC temperature change of an individual EC element [71]–[74]. The drawback of such a design is poor scalability and the use of external mechanical components, which lower the efficiency of the refrigeration.

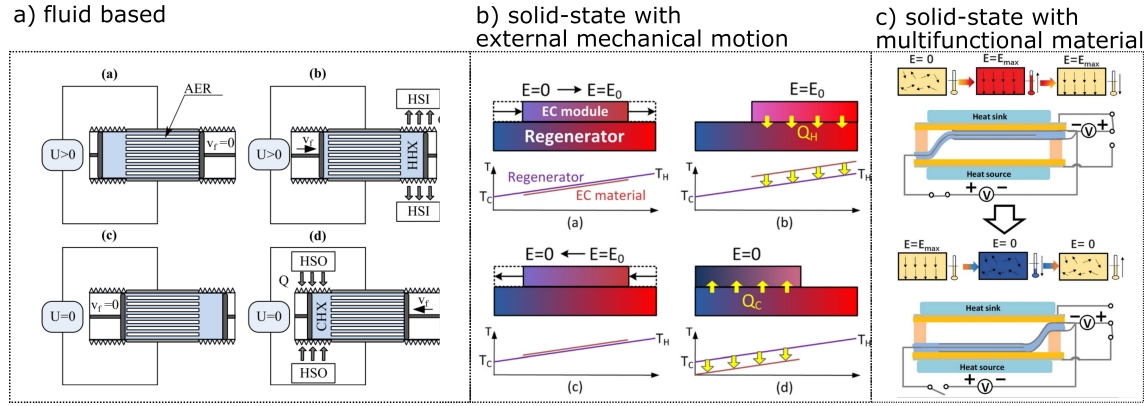


Figure 1.12: Three generations of EC devices, a) fluid based [72], b) solid state with external mechanical motion [75] and c) solid state with a multifunctional material [76].

The group of solid-state cooling devices is based purely, or to a large extent, on solid-state cooling; an example is shown in Fig.1.12b. In this case the EC element is sliding on a surface according to the EC cycle. The surface works as an AER and the temperature spans several times larger than the EC temperature change of the elements can, in principle, be achieved. Solid state cooling has a potential for use in microelectronics and small-scale devices due to the good scalability. However, here the heat transfer is solid-to-solid, which is problematic due to the large thermal resistivity of thermal contacts [75], [77]–[81]. In addition, the described devices need an external mechanical component that manages the heat and creates a temperature gradient in the device.

A step further in the solid-state cooling is the proposed coupling of the EC and electromechanical effects for solid-state cooling without external components [80]. One such device was recently proposed by Ma et al. [76], where they used PVDF-TrFE thick films; a schematic of the device is shown in Fig. 1.12c. Here, the device exploits the EC effect and the electrostatic effect of a multifunctional material at the same time. In the case shown, in Fig. 1.12c, the polymer element upon application of an electric field bends and makes contact with the heat sink where the heat is removed. Upon switching off the electric field the element returns to its initial position and absorbs the heat from the heat source. Table 1.3 shows a summary of the EC devices reported until now.

Table 1.3: A summary of electrocaloric refrigerators.

| Author           | M/E* | $\Delta T$ (K) | EC Material                                                                 | CP* |
|------------------|------|----------------|-----------------------------------------------------------------------------|-----|
| Sinyavski [71]   | E    | 5 K            | PbSc <sub>0.5</sub> Ta <sub>0.5</sub> O <sub>3</sub>                        | f   |
| Karamenenko [77] | M    | 20 K           | Ba <sub>0.4</sub> Sr <sub>0.6</sub> TiO <sub>3</sub>                        | ss  |
| Malloy [82]      | M    | /              | PZr <sub>0.9</sub> Ti <sub>0.1</sub> O <sub>3</sub>                         | f   |
| Jia [78]         | E    | 1 K            | BaTiO <sub>3</sub>                                                          | ss  |
| Gu [75]          | E    | 6.6 K          | PVDF-TrFE                                                                   | ss  |
| Wang [79]        | E    | 0.3 K          | BaTiO <sub>3</sub>                                                          | ss  |
| Plaznik [72]     | E    | 3.5 K          | Pb(Mg <sub>1/3</sub> Nb <sub>2/3</sub> )O <sub>3</sub> -PbTiO <sub>3</sub>  | f   |
| Sette [74]       | M    | 0.13 K         | Zr-BaTiO <sub>3</sub>                                                       | f   |
| Blumenthal [73]  | E    | 0.17 K         | Pb(Mg <sub>1/3</sub> Nb <sub>2/3</sub> )O <sub>3</sub> -PbTiO <sub>3</sub>  | f   |
| Bradeško [80]    | M    | 12 K           | Pb(Mg <sub>1/3</sub> Nb <sub>2/3</sub> )O <sub>3</sub> -xPbTiO <sub>3</sub> | ss  |
| Zhang [81]       | M    | 2 K            | Zr-BaTiO <sub>3</sub>                                                       | ss  |
| Ma [76]          | E    | 8 K            | PVDF-TrFE                                                                   | ss  |

\***M**odel or **E**xperiment; CP cooling principle, either solid-state (**ss**) or fluid (**f**).

### 1.2.2 Cooling efficiency

The EC efficiency (or Coefficient-of-performance - COP) is in principle the ratio between the input electric energy and the output thermal energy. EC efficiency was studied by Moya et al. [83], Plaznik et al. [84], Defay et al. [85].

Several thermodynamic cycles are suggested to be used in EC devices; however, Brayton cycles are the most common [86]. From the aspect of EC integration, the EC material, when subjected to an electric field, undergoes an adiabatic polarization as shown Fig. 1.13a in stage 1→2. During stage 2→3 the material is cooled by  $\Delta T_{EC}^P$  under an electric field. Work is done in this stage due to the temperature variation of  $P$  when cooling under a field. When the electric field is released (stage 3→4) the entropy is adiabatically increased, causing the temperature to drop. Finally, step 4→5 is the steady increase of temperature and entropy in the material.

The work done ( $W_n$ ) during the described cycle can be expressed as:

$$W_n = w_{1 \rightarrow 2} + w_{2 \rightarrow 3} + w_{3 \rightarrow 4} + w_{4 \rightarrow 1}, \quad (1.6)$$

where the symbols  $w_{1 \rightarrow 2}, w_{2 \rightarrow 3}, w_{3 \rightarrow 4}, w_{4 \rightarrow 1}$  represent the work done during steps 1→2, 2→3, 3→4, 4→1, respectively. In the realistic Brayton EC cycle shown in Fig. 1.13b, we have to additionally consider the energy-loss mechanisms. Stage 1→2 is accompanied by some losses, e.g., due to irreversible switching of the domains in ferroelectric materials [35]. Step 2→3 could cause additional dissipation of energy due to the significant electric conductivity of the materials and Joule heating. The Joule heating also lowers the temperature span of the device (discussed in Section 5.4). Step 3→4 is usually smaller due to the irreversible switching induced during step 1→2. Note that large portions of  $W_n$  can be regenerated with an appropriate electrical circuit [84]. The idea is described in Ref. [85]. The possibility of regenerating electrical energy is the main benefit of EC cooling [87].

In the literature energy losses have been assessed in relaxor and ferroelectric materials [2], [88]. It was shown by Zheng et al. [89] and Uchino et al. [63] that the energy loss in ferroelectric materials is dominated by the electrical losses. Electrical losses are typically estimated by inspecting the  $P(E)$  hysteresis response of the material [90]. The surface area of the hysteresis is proportional to the electrical-energy-loss density ( $W_L$ ) (as depicted in Fig. 1.14) [63], [89]. The surface area (shown in Fig. 1.14) can be calculated using the

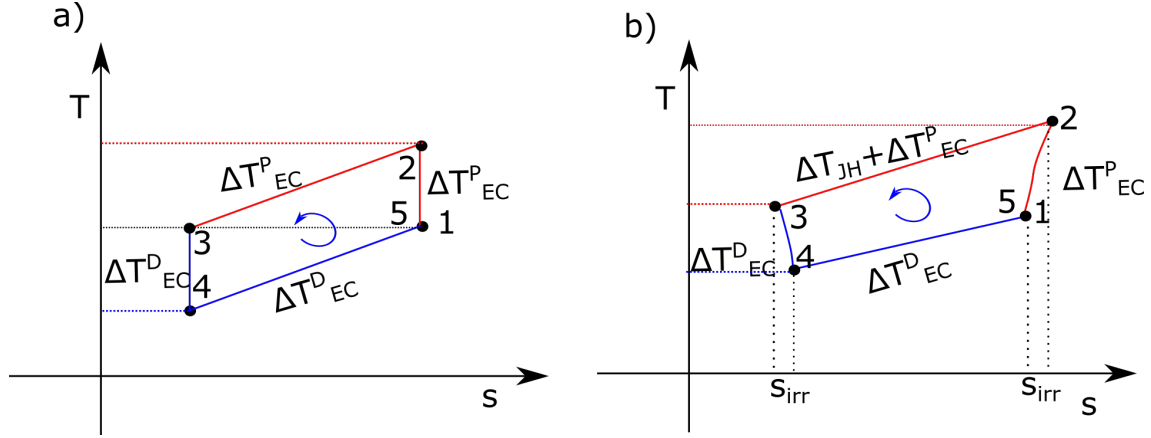


Figure 1.13: Thermodynamic Brayton cycle of the EC material for a) ideal and b) realistic case. In the panel the step 1→2 the material is subjected to an electric field in adiabatic conditions, to which it responds by a EC temperature change ( $\Delta T^P_{EC}$ ). After, in step 2→3, the generated heat must be removed. In step 3→4 the electric field is removed and the material cools below the initial temperature. Heat absorption takes place during step 4→1 [84].

contour integral:

$$W_L = \oint E dP = W_n. \quad (1.7)$$

The lower branch of the loop in Fig. 1.14 is equivalent to the step 1→2 in Fig. 1.13b, while the upper branch is equivalent to the step 3→4 in Fig. 1.13b. The gap between the zero-field values (first and last point) and the hysteresis shows irreversibility is present in the materials. Irreversibility affects the adiabatic polarization and depolarization, as noted in Fig. 1.13, where the entropy change between the step 1→2 is larger than during step 3→4.

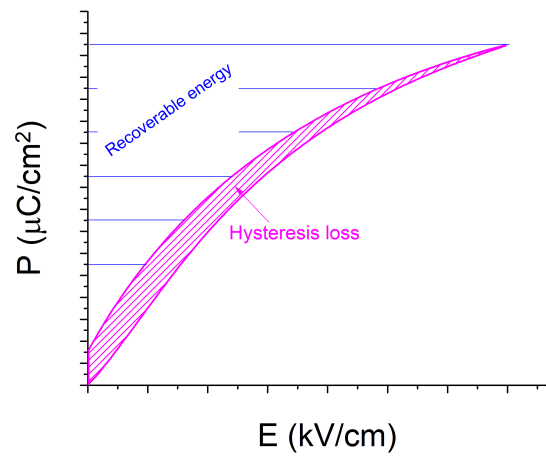


Figure 1.14: Typical  $P(E)$  response of a ferroelectric. The blue area denotes the recoverable energy, while the area in pink enclosed by the loop is the energy loss.

### 1.2.3 Electrocaloric fatigue

An issue which is often overlooked in the field of EC materials, is the fatigue of EC materials [91]. Since a significant EC temperature change (0.5 K) requires electric fields which are, in bulk ceramics, above 30 kV/cm, degradation of such materials should be addressed [31]. Until now, only four studies exist on the fatigue of EC materials. Bai et al. [92] observed a minor degradation in BaTiO<sub>3</sub> thin films after five cycles. Fulanović et al. [93] showed that PMN multilayers exhibit fatigue-free behaviour to about 10<sup>6</sup> cycles. Weyland et al. [94] showed that with cycling Joule heating emerges in Ba(Zr<sub>0.2</sub>Ti<sub>0.8</sub>)O<sub>3</sub> ceramics, which is reflected as an offset in temperature during an applied electric field (see Fig. 1.15a).

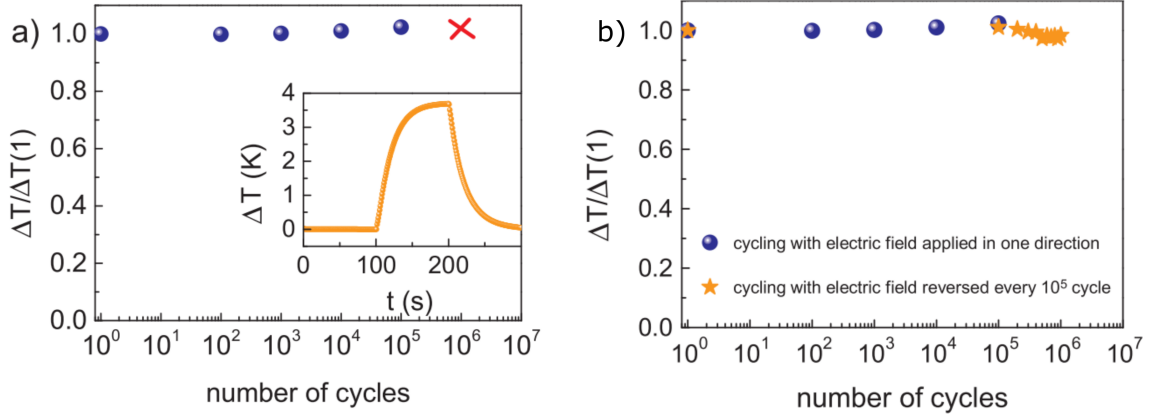


Figure 1.15: Fatigue of Ba(Zr<sub>0.2</sub>Ti<sub>0.8</sub>)O<sub>3</sub> ceramics under EC field cycling [94]. a) The EC response normalized to the value measured during the first EC cycle ( $\Delta T / \Delta T(1)$ ). The inset shows the EC response of the fatigued (10<sup>6</sup> cycles) sample where the Joule heating is the dominating response (compare to typical pristine EC response in Fig.1.7). b) The  $\Delta T / \Delta T(1)$  was unchanged up to 10<sup>6</sup> cycles after the electric field was alternated every 10<sup>5</sup> cycles.

Only when the electric field applied to the material is alternated every 10<sup>5</sup> cycles, does the material exhibit fatigue-free behaviour up to 10<sup>6</sup> cycles, as shown in Fig. 1.15b. They attributed the Joule heating effect and this fatigue to field-cycling-induced ordering of oxygen vacancies into conductive paths, which led to an increased electrical conductivity of the sample. Reversing the field causes redistribution of the vacancies in the opposite direction and prevents the formation of paths. A similar effect was achieved by thermally annealing the fatigued samples.



## Chapter 2

# Design and Concept of the Multifunctional Device for Dielectric Cooling

In the scope of my PhD study I analysed a device that couples the electromechanical and electrocaloric properties of multifunctional dielectric materials. The idea of the device was to exploit the multifunctional nature of the materials under consideration (see Fig. 2.1).

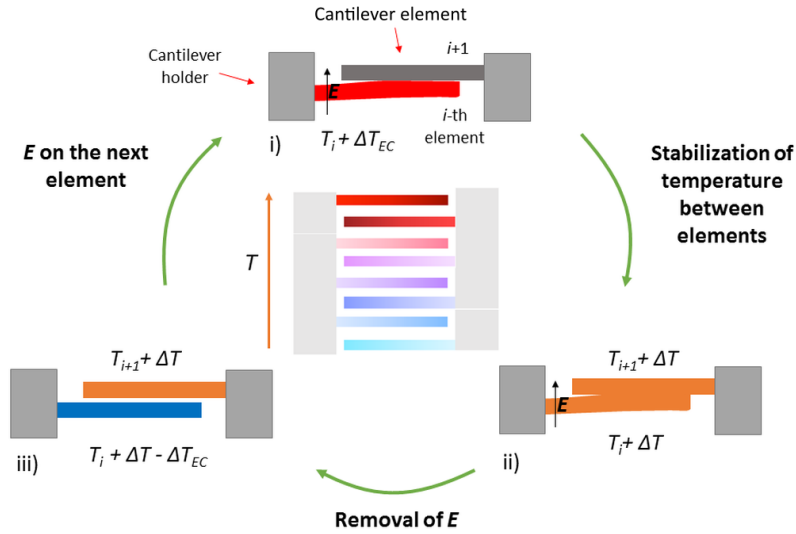


Figure 2.1: Working principle of the device that couples the electrocaloric and electromechanical effects for dielectric cooling.

The device consists of an array of cantilever elements that are periodically excited. The electric field has a dual role: i) it triggers the EC effect in the elements and ii) it creates a bending strain due to the EM effect of the elements, which is used to create thermal contacts between the neighbouring elements. Therefore, when an electric field is applied to an element it simultaneously bends to contact with its neighbour and it heats up due to the adiabatic polarization. When the heat exchange with the adjacent element is completed, the electric field is switched off and the element undergoes adiabatic depolarization, meaning that it cools below its initial temperature, while, at the same, it displaces to terminate the contact with the neighbouring element. This procedure continues

throughout the whole array of elements (one by one), repeatedly from first to last element. Such an excitation procedure should lead to a temperature span within the device (see schematics in the center of Fig.2.1). The device should be scalable and thus suitable for use in microelectronics, for example, for cooling of infrared sensors.

Prior to the device's fabrication and validation, several problems need to be clarified and resolved. First, an appropriate material composition within the PMN-100xPT material system needs to be selected for the cantilever's fabrication. The cantilever-fabrication procedure needs to be optimized to achieve the highest possible properties and to maintain their flatness. The cantilevers need to be electrically, electrocalorically and electromechanically characterized. An appropriate packaging for the cantilevers needs to be designed and fabricated in order to stack them in a cascade arrangement (as shown in Fig. 2.2). We have to ensure the electrical wiring and appropriate distance between the cantilever elements. Electronics for driving the cantilevers periodically needs to be designed and developed.

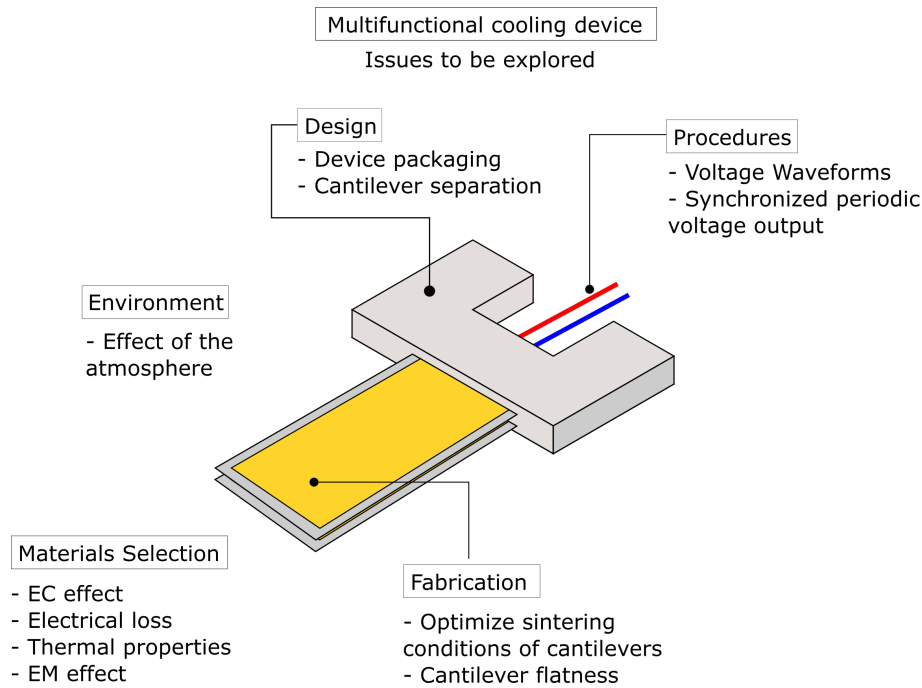


Figure 2.2: Conceptual device appearance with the considerations noted at the device parts.



## Chapter 3

# Aims and Hypothesis

Within this PhD study we tackle the issue of the integration of multifunctional materials into EC cooling devices. The aim was to

- Design and validate an EC device that couples electromechanical and electrocaloric effects.
- Numerically investigate the feasibility of such an electrocaloric device.
- Study the EC temperature response, EM response and relations between the two over a wide compositional range in the PMN-100xPT ceramic system.
- Determine an optimal ceramic composition for the designed electrocaloric device.
- Clarify the effect of electrical losses on the EC temperature response, including the possible degradation of the EC effect by field cycling (fatigue).
- Fabricate the cantilever elements for the device.
- Characterize the electrocaloric and electromechanical properties of a single cantilever elements for the device.
- Fabricate the device and characterize its performance with multiple cantilevers.
- Characterize the performance of the device.
- Provide an outlook for the development of multifunctional materials.

The hypotheses are as follows:

- The search for the most suitable material in the PMN-100xPT system will show the importance of electrical losses.
- Little information is available on the EC fatigue. We expect this will be an important issue due to the high electric fields needed to induce a significant EC effect.
- Issues will arise during the fabrication of the cantilever elements. Most difficult and important will be maintaining the flatness of the cantilevers, which is expected to impact the thermal contact resistance between neighbor cantilevers.
- Device operation will probably be limited by the heat transfer between the cantilevers.



## Chapter 4

# Materials and Methods

### 4.1 Building the Numerical Model of the EC Device

In the first step the time-dependent behaviour of the device was investigated, with finite-element modelling using the commercial software COMSOL Multiphysics. The device geometry was considered to be two-dimensional as shown in Fig. 4.1, as temperature variations are only expected in two directions.

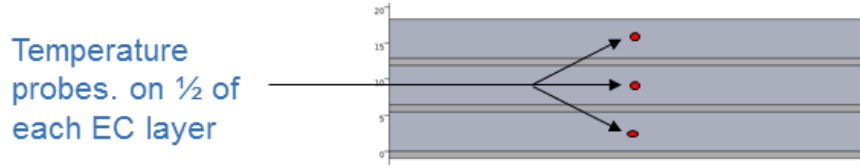


Figure 4.1: The geometry used in the model illustrated for the device with three cantilevers. The thicker gray squares represent the active material and the thinner brown squares represent Pt electrodes. The red dots show the position of the temperature probes.

The cantilever elements, clamped on one side onto Al holders, were 20 mm long and consisted of a 50- $\mu\text{m}$ -thick EC layer, i.e., PMN-35PT, and a 10- $\mu\text{m}$ -thick bottom Pt electrode [95]. The upper electrode of the cantilever was sputtered Au and was thus neglected in the model due to its small thickness (up to 100 nm). To avoid a multi-field description of the device, we modelled only its thermal aspects. The contacts between the cantilevers were described as thin resistive layers that work as thermal switches. This means that in the time frame of the mechanical contact between the cantilevers, a thermal contact ( $R$ ) was assumed to have a finite thermal resistance ( $R_{\text{contact}}$ ), while in the absence of a mechanical contact the thermal contact resistivity was set to be infinitely high. Thus, the thermal resistivity of the contacts between the cantilevers along the structure was mathematically described using the following expressions:

$$R = \begin{cases} (\text{incontact})R_{\text{contact}}, & \text{if } (it_c < t < (i+1)t_c). \\ (\text{notincontact})R_{\text{infinite}}, & \text{else,} \end{cases} \quad (4.1)$$

where  $i$  is the cantilever number, counted from the bottom to the top of the array and  $t_c$  is the time during which the two cantilevers are in contact. Depending on the position in the array (number  $i$ ), it is assumed that the cantilever can be in three different states.

If the simulation time ( $t$ ) matches the element's time interval between  $it_c$  and  $it_c+t_p$ , during which the EC cycle begins, the cantilever generates the EC heat ( $Q_{eci}$ ). This step simulates the adiabatic polarization of the material. After a certain time  $t_c$ , the adiabatic depolarization follows. In the time between  $(i+1)t_c$  and  $(i+1)t_c+t_p$  the material cools down. Before and after these two steps there is no heat generation or termination in the material. These steps of the device's operation are described with Equation 4.2:

$$Q_{eci} = \begin{cases} mc_p\Delta T, & \text{if } (it_c < t < it_c + t_p). \\ -mc_p\Delta T, & \text{if } ((i+1)t_c < t < (i+1)t_c + t_p). \\ 0, & \text{else,} \end{cases} \quad (4.2)$$

where  $m$  is the mass of the EC layer,  $t_p$  is the time duration of the heat generation or termination,  $c_p$  is the specific heat capacity and  $\Delta T_{EC}$  is the EC temperature change induced by the cantilever. The assumption was that the EC effects during adiabatic polarization and depolarization are the same, i.e.,  $\Delta T_{EC}^P = \Delta T_{EC}^D$ . Additionally, it was also assumed that  $c_p$  is field and temperature independent, which is often not the case in polar ceramics [96].

The time  $t_c$  was determined based on the thermal time constant ( $\tau$ ), which is the time necessary for two cantilevers to stabilize their temperatures. The time constant  $\tau$  was estimated using an equivalent thermal circuit of two cantilevers in contact:

$$\tau = R_{total}C_{total} \quad (4.3)$$

where  $R_{total}$  is the sum of the contacting cantilevers' thermal resistances and the contact resistance.  $C_{total}$  is the total thermal capacity.  $R_{total}$  is 0.68 K/W and  $C_{total}$  is  $1.35 \cdot 10^{-3}$  J/K [97]. At this stage we neglected the  $R_{contact}$ .

For  $t_c$  the value of  $10\tau$  was considered, which in our case is 0.01 s. This value is in agreement with previously reported values of thermalization in thin structures. For each cantilever we assumed  $\Delta T_{EC}$  of 0.2 K, which is the value measured on the PMN-30PT thick film [98] at 30 kV/cm. The values of  $c_p$  and  $\lambda$  for the materials in the device were taken from Ref [99].

## 4.2 PMN-100xPT Ceramics

### 4.2.1 Fabrication, structural and microstructural characterization

For the synthesis of the  $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}x\text{PbTiO}_3$  (PMN-100xPT) ceramic powder, PbO (99.9%, Aldrich), MgO (98%, Aldrich) and Nb<sub>2</sub>O<sub>5</sub> (99.9%, Aldrich) powders were mixed in a stoichiometric molar ratio to prepare for six compositions:

- PMN
- PMN-10PT
- PMN-20PT
- PMN-30PT
- PMN-35PT
- PMN-40PT.

The homogenized powder mixtures were high-energy milled (i.e., mechanochemically treated) in a planetary mill (Retsch, PM 400) at  $300 \text{ min}^{-1}$  for 90 h and additionally in an attritor mill (Netzsch, PE 075/PR 01) at 800 rpm for 4 h in isopropanol. Powder compacts were pressed uniaxially at 50 MPa and then isostatically at 300 MPa, and sintered in double

alumina crucibles in the presence of the PMN-100xPT packing powder (same composition as the sintered pellets) at 1200 °C for 16 h. The heating and cooling rates were 2 °C min<sup>-1</sup>. Details of mechanochemical synthesis of the samples are published elsewhere [36], [93], [100].

The Pb(Zr<sub>0.75</sub>Ti<sub>0.25</sub>)O<sub>3</sub> (PZT 75/25) and Pb(Zr<sub>0.75</sub>Ti<sub>0.25</sub>)<sub>0.98</sub>Nb<sub>0.02</sub>O<sub>3</sub> (PZT75/25-Nb) samples used in the self-heating studies were prepared by the conventional mixed-oxide route. The details regarding the preparation can be found in Ref. [101].

The density of the sintered samples was measured by Archimedes' method. The phase compositions of the as-sintered samples were analyzed using an X-ray diffractometer (XRD, X'Pert PRO MPD, PANalytical, Almeo) with Cu-K $\alpha$ 1 radiation. The XRD patterns were recorded in the 2 $\Theta$ -region from 10° to 70° using a 1D detector (X'Celerator, PANalytical, Almeo) with a capture angle of 2.122°.

*In-situ* X-ray diffraction experiments during fatigue tests were carried out using a PANalytical Empyrean X-ray diffractometer with Cu-K $\alpha$  radiation (1.5418 Å wavelength), a linear detector, and an Anton Parr XRK 900 heating chamber that was modified to include the application of an electric field to samples at elevated temperature. These measurements were made in collaboration with the group of Prof. Jacob L. Jones at North Carolina State University.

Microstructural characterization of the sintered samples was performed using a field-emission scanning electron microscope (FE-SEM) JEOL JSM 7600. The surfaces of the bulk ceramic samples were ground and polished with standard metallographic techniques. The bulk ceramics were thermally etched at 900 °C. Prior to analysis in the FE-SEM, the samples were coated with a few-nm-thick carbon layer (Balzers SCD 005, BAL-TEC GmbH), to provide electrical conductivity and avoid charging effects during FE-SEM imaging. The average grain size (GS) and GS distributions were determined by applying a stereological analysis of the micrographs. The grain size was analyzed with the Image Tool Software. The grain size values are expressed as the Feret's statistical diameter [102].

#### 4.2.2 Electrical and electromechanical characterization

Polarization–electric-field  $P(E)$  hysteresis loops of the bulk ceramic PMN-100xPT samples were measured with a commercial system Aixacct aixPES. The polarization of the samples during field application is measured using the virtual ground method. The circuit is schematically depicted in Fig. 4.4a. The core of the virtual ground method is an operational amplifier (op-amp) that acts as a current-to-voltage converter. The inverting input (-) of the operational amplifier is connected to the ground, while the input (+) is connected to the output by a feedback resistor. When the electrical current flows through the (+) input, the op-amp generates a proportional voltage drop (determined by  $R_g$ ) on the output side of the op-amp. The current values are then integrated numerically to obtain the polarization. For measurements, we applied to the samples three single sinusoidal-like field waveforms in sequence, as illustrated in Fig 4.4b.

Electrical-current-voltage ( $I(V)$ ) curves of the PMN-100xPT samples were measured using a Keithley High Voltage Source-Measure Unit 237. The dielectric permittivity ( $\epsilon'_r$ ) was measured with an LCR HP4248 in the frequency range from 100 Hz to 1 MHz by applying an AC voltage of 1 V. The specified level of measurement uncertainty is 1 % relative [103].

The longitudinal strain - ( $s_3$ ) under an applied electric field was measured in parallel with the polarization - field hysteresis using the Aixacct system, meaning that the same field waveform as shown in Fig. 4.3b was used. The strain was measured using the laser interferometry. The source emits light with a certain frequency and wavelength. Through a series of mirrors the light is directed to the sample that is in contact with a mirror.

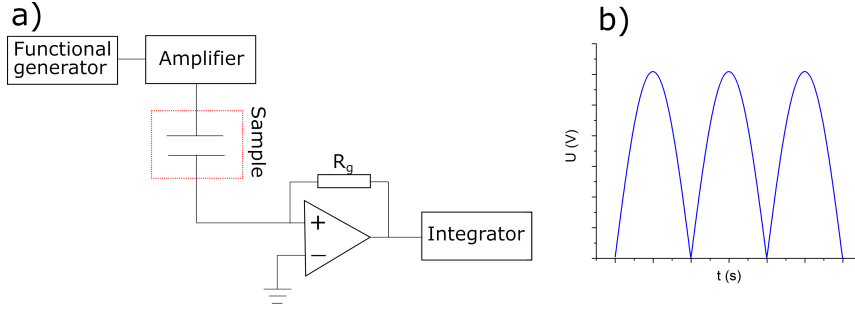


Figure 4.2: a) Schematic illustration of the electrical circuit for measuring the polarization - electric field hysteresis loop using the virtual ground method. b) schematic illustration of the voltage ( $U$ ) waveform applied for polarization measurements.

The mounted mirror is mechanically coupled with the sample. Light reflected on the mirror generates a phase angle between the incoming and outgoing light, which can then be analysed to determine the displacement of the sample. The uncertainty of displacement measurements is  $\pm 25$  nm.

Simultaneous longitudinal  $s_3$  and transverse  $s_1$  strains under an applied field were additionally measured using linear variable differential transformer (LVDT) sensors. The setup is shown in Fig 4.3. An identical waveform as for the polarization measurements was generated by a National Instruments Data Acquisition Card (DAQ) and amplified using a TREK PD05034. The frequency of the applied field was 0.1 Hz.

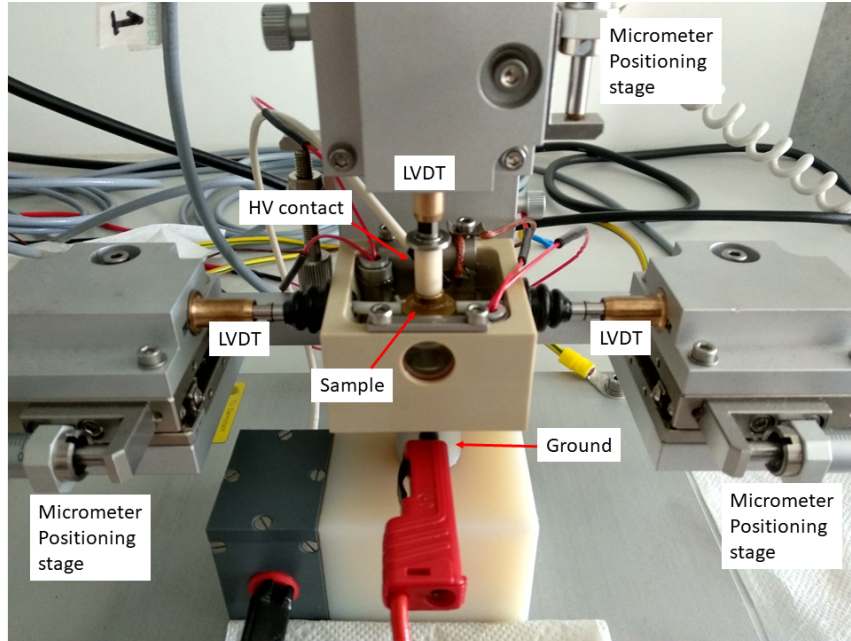


Figure 4.3: Setup for simultaneous characterization of  $s_3$  and  $s_1$ .

The direct  $d_{33}$  coefficient was measured at 100 Hz of stress frequency using a standard Berlincourt piezometer (Take Control PM10). The specified level of measurement uncertainty is 1 pC/N.

### 4.2.3 Characterization of thermal properties

For the measurements of the heat conductivity, the 8-mm-thick pellets with 18 mm in diameter were prepared. The measurements were performed by HotDisk TPS 2500S equipment. The basic principle of the system is to supply a constant power to the sample via a Hot Disk sensor. The sensor is used as the heat source and the temperature monitor. The material was heated at 100 mW for 10 s at room temperature. The length of the heating pulse was chosen to be short enough so that the sensor could be considered in contact with an infinite solid throughout the recording. The specified uncertainty is 5 % relative [104].

The specific heat capacity versus temperature  $c_p$  of the ceramic samples was determined from the differential scanning calorimetry curves measured using a differential scanning calorimeter (DSC) Netzsch 204 F1. The samples of 5 mm in diameter and a thickness of 0.5 mm and heated in a calorimeter with a heating rate of 2 °C/ min from 35 °C to 300 °C. To determine the  $c_p$  of the samples, sapphire (Netzsch, diameter of 5.2 mm, thickness of 0.5 mm) was used as the standard material. The uncertainty of the obtained values is within 5 % relative [105].

### 4.2.4 Characterization of EC properties

For the EC measurements at elevated temperatures (-20 °C - 120 °C) a modified Netzsch DSC 204 F1 was used for the temperature stabilization and the EC signal was measured with a small thermistor attached to the sample. The electrical signal was applied using a Keithley High Voltage Source-Measure Unit 237 and the thermistor resistance was monitored using a Keithley 2100 digital multimeter.

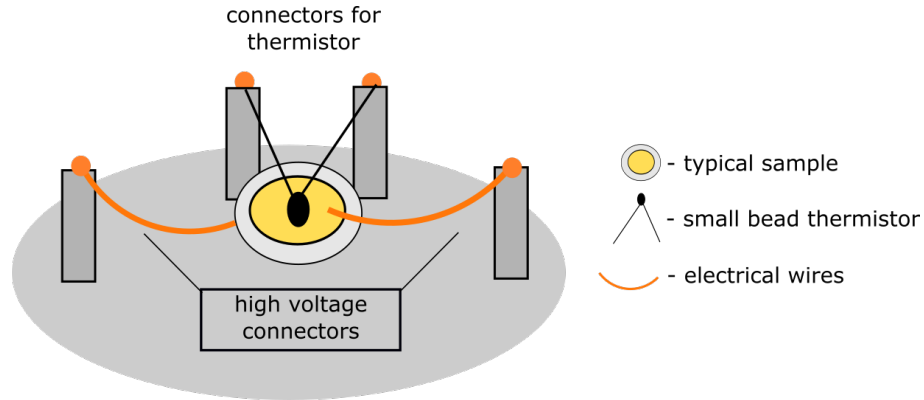


Figure 4.4: Schematic illustration of the measuring setup and sample preparation for EC measurements.

For the evaluation of the EC effect's magnitudes, we used a square waveform with a period of 200 s (=5 mHz, 100 s on-field, 100 s off-field). The samples were 150  $\mu\text{m}$  thick. To exclude the influence of EC inactive parts of the samples on the temperature response, we used a procedure proposed by Kutnjak et al.[31]. The magnitudes of the EC temperature change are multiplied by a correction factor ( $C$ ), which is calculated as:

$$C = \frac{\sum_i m_i c_{pi}}{m^a c_p^a}, \quad (4.4)$$

where the numerator is the sum of all the relevant thermal masses (thermistor, wires, glue, inactive and active parts of the sample) and in the denominator is the thermal mass of the EC active part.

Several parameters influence the uncertainty of the EC measurements; 1) due to the off-centred Au electrodes the active volume is difficult to estimate; 2) temperature gradients are present in the sample and thus the position of the thermistor on the sample influences the measured temperature changes; 3) calculation of  $C$  assumes constant specific heats; 4) the response time of the thermistor varies due to the different glue masses from sample to sample. Thus the accuracy of the measurements is difficult to determine, however, the reproducibility between different samples was experimentally determined to be on the level of 10 % relative. An interesting comparison on different methods of characterization of EC effect and their errors was done in Ref. [106].

For fatigue experiments we used an identical set-up as for the EC measurements, only the excitation procedure was altered. The electric field was applied in two steps: i) test cycle consisted of a typical 5-mHz-square signal that was used to monitor the changes during, ii) the second step was 2-Hz cycling performed with square signal, as shown in Fig. 4.5. The steps were repeated until a significant change in the EC response was observed or the sample broke.

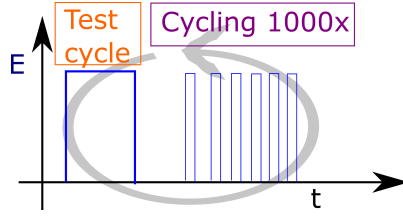


Figure 4.5: Waveform applied for analysis of the EC fatigue.



#### 4.2.5 Local electric-current mapping and domain switching characterization using atomic-force microscopy

Atomic force microscopy (AFM) (Asylum Research, Molecular Force Probe 3D) was used to determine the local electrical conduction of the samples. A Pt-coated Si tip with a radius of curvature of about 10 nm (OMCL-AC240TM-R3, Olympus) was used. Conductive-AFM (c-AFM) experiments were performed by applying a dc voltage of 80 V between the conductive tip and an Ag-painted bottom electrode. A schematic illustration of the working principle of c-AFM is shown in Figure 4.6.

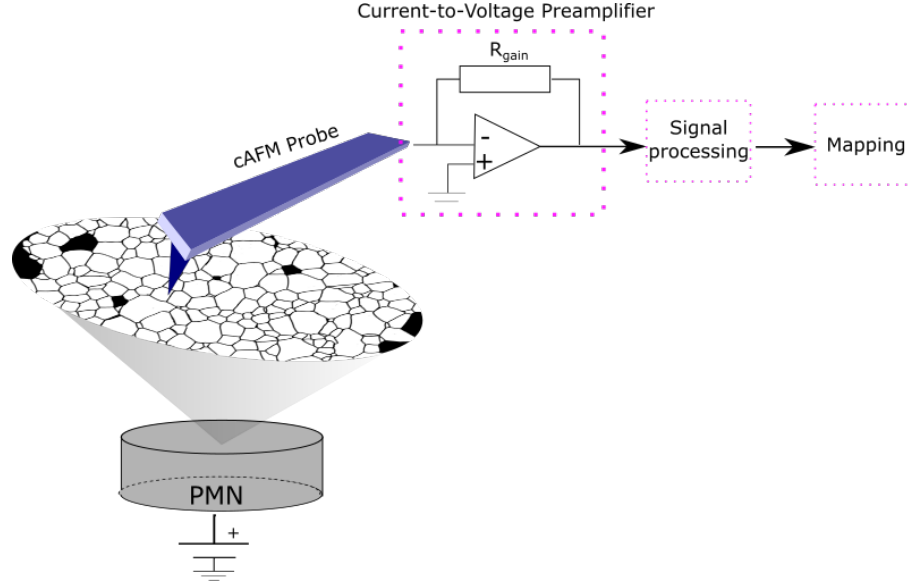


Figure 4.6: Schematic illustration of the working principle behind the conductive atomic force microscope.

Additionally, piezo-force microscope (PFM) hysteresis loops were measured in local regions of the two samples by applying a pulse DC signal. DC step pulses with a duration of 0.05 seconds were applied from zero to the maximum voltage of 40 V, and then back to zero with the same steps. To complete the whole voltage cycle, this procedure was then repeated with DC voltages of negative polarity. The time of the whole voltage cycle was 5 seconds. Three such cycles were measured in the same local region of the sample. The PFM signal was measured after each voltage pulse by first reducing the DC voltage to zero (off-field mode) to minimize the electrostatic interaction between the tip and the sample. Conditions of the PFM measurements were 13 V AC voltage amplitude and 330 kHz of frequency. Details of the measurement can be found elsewhere [107]. The out-of-plane amplitude PFM images were measured in the Dual AC Resonance Tracking (DART) mode at an AC amplitude signal of 12 V and a frequency of 300 kHz.

## 4.3 PMN Cantilevers

### 4.3.1 Fabrication, structural and microstructural characterization

The cantilevers were prepared in several steps, as shown in Figure 4.7: Slurry mixing, tape-casting, screen-printing of Pt and lamination, firing, laser-cutting and deposition of electrodes. The slurry was prepared with a three-step mixing process (step a in Fig. 4.7). First, PMN powder is mixed with a solvent and a dispersant. The solvent was a mixture of methyl ethyl ketone and ethanol in the volume ratio 6:4, and the dispersant was oleic acid. The mixture was homogenized in a planetary mill for 2 hours at  $100 \text{ min}^{-1}$ . A 250-ml YSZ vial and 10 YSZ balls of 10 mm diameter were used. In the second step the plasticizer polyethylene glycol was added and the slurry was milled for an additional 0.5 hour. In the final step the binder polyvinyl butyral was added, and the slurry was again milled for a further 22 hours with the same conditions as in the previous steps. Prior to the tape casting the slurry was filtered through a  $500 \mu\text{m}$  sieve, which also acted as a de-airing step. About 50 ml of the slurry was then used for a tape-casting experiment [93].

The temperatures of the drying segments of the tape caster were set at  $25^\circ\text{C}$  for both heating zones and the temperature of the air was  $25^\circ\text{C}$ . The tape speed was set at  $0.8 \text{ m/min}$ . The tape casting of 50-ml slurry batches resulted in an about 15.5-cm-wide green tape of 1.5 m in length, see Fig. 4.7b). Platinum paste (Ferro 6482 0002) was screen printed on sheets of PMN tapes as shown in Fig. 4.7c. On top of the tape with a screen-printed Pt another layer was placed and pressed in the isostatic press with 20 MPa (shown in Fig. Fig. 4.7d).

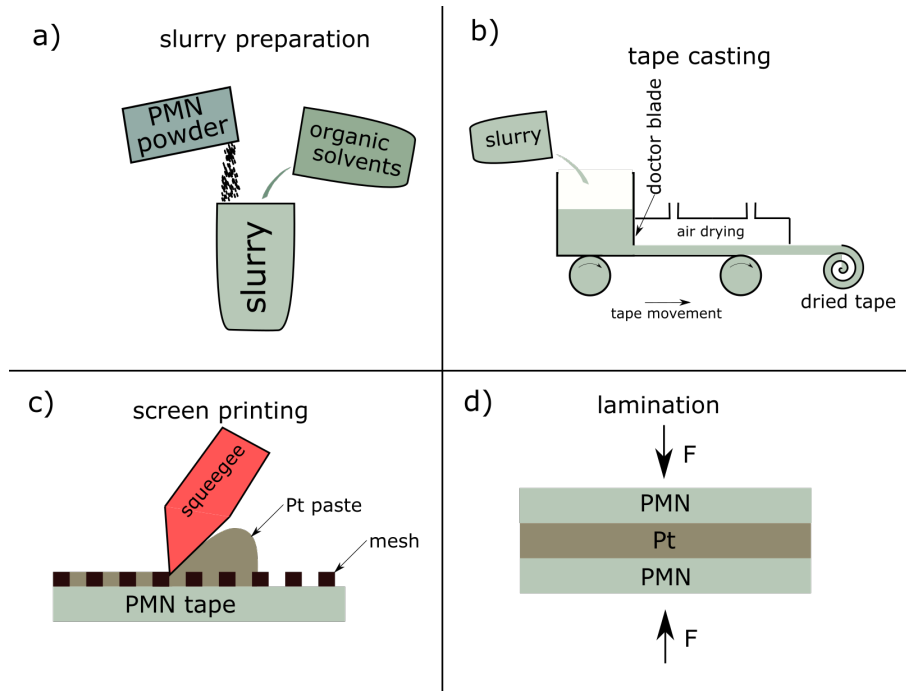


Figure 4.7: Making of cantilevers: a) preparation of slurry for b) tape casting. The tape is then screen-printed with Pt as shown on c). Lamination of tapes follow as depicted in d).

The samples were heated in two steps. In the first step the burn-out of organic components was performed. In this step, the temperature was elevated with a heating rate of  $1 \text{ K/min}$  to  $450^\circ\text{C}$ . This step was employed to perform the burn-out of organic components. In the second step, we heated the samples to the sintering temperature with a heating rate

of 5 K/min. Temperatures of 1000, 1100, 1200 °C were used to investigate the temperature of sintering on the sample properties. The temperature program is schematically depicted in Fig. 4.8.

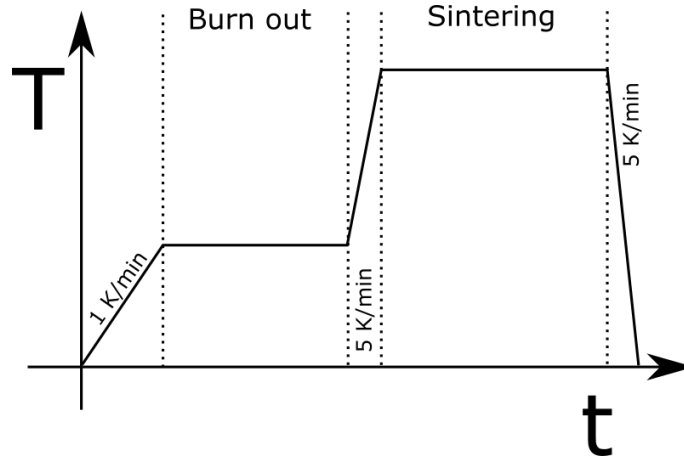


Figure 4.8: Temperature program for fabrication of cantilevers.

After sintering the samples were laser-cut (Proto Laser S, LPKF) into three different dimensions: For further analysis, the sintered PMN/Pt/PMN plates were cut into shapes as shown in Fig. 4.9. The differently shaped samples were used for different purposes:

- Disc Sample A was used for characterization of the electrical properties (dielectric response, current versus voltage characteristic) and an indirect EC effect,
- Sample B was used for the characterization of the direct EC effect and electromechanical displacements and  $P(E)$  loops,
- Sample C was used for the fabrication of the proof-of-concept device.

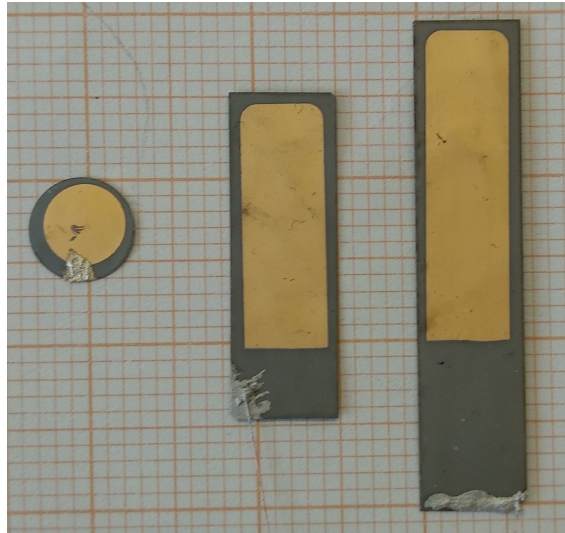


Figure 4.9: PMN/Pt/PMN shapes used for analysis and device fabrication.

The samples were electroded with 100-nm-thick Au using a radio-frequency (RF) magnetron sputtering device (5Pascal).

### 4.3.2 Electrical characterization

Electrical characterization of the cantilevers was performed with a Keithley High Voltage Source-Measure Unit 237. The dielectric permittivity was measured with a LCR HP4248 in the frequency range from 100 Hz to 1 MHz.

### 4.3.3 Electromechanical characterization

We characterized the electromechanical response of the cantilevers by recording the bending of the cantilevers using a digital camera DigiMicro Profi. The samples were mounted on a holder. The holder was wired so that the voltage could be applied to the sample (see Fig. 4.10).

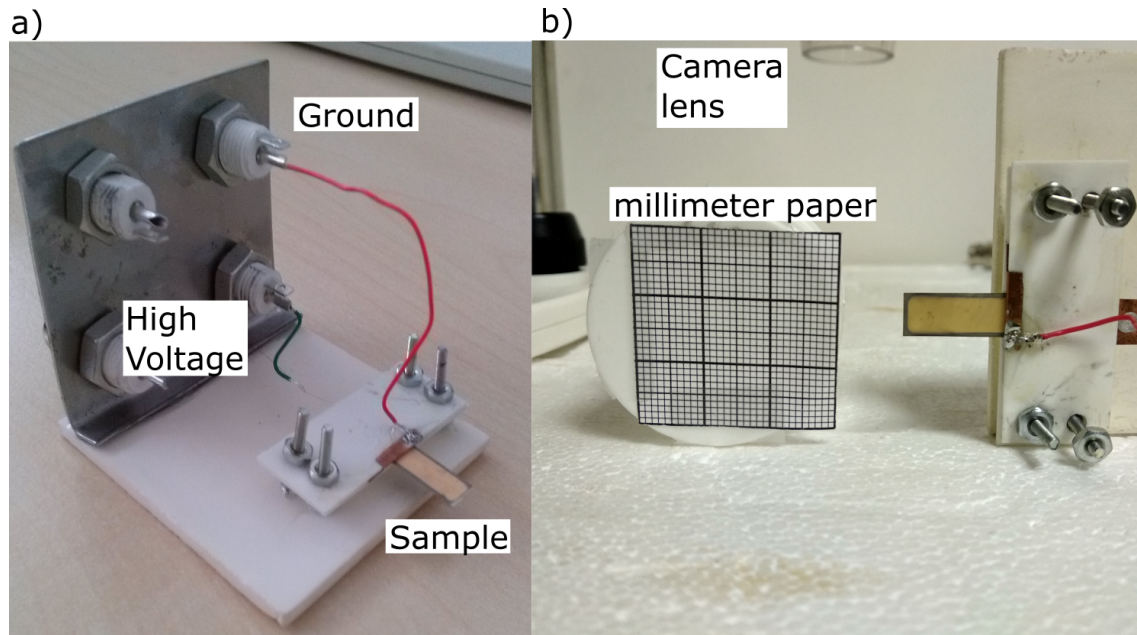


Figure 4.10: Setup for measuring electric field-induced deflections of cantilevers.

As a voltage supply, we used a Wavetek 395 function generator. The signal from the function generator was amplified by a Trek 609E voltage amplifier. The voltage on the sample was monitored with a LeCroy 100:1 voltage probe and an Algor oscilloscope. The videos were analysed with an open-source (GNU) licence program Tracker [108]. Tracker has a function of following objects on a video. We placed a millimetre paper as the background of the samples. With the millimetre paper we managed to calibrate the Tracker to measure the distances. By tracking the motion of the tip of the cantilever under electric fields, we obtained the deflections. The deflections were then plotted versus the applied electric field. The estimated error of measurements is  $\pm 20 \mu\text{m}$ .

### 4.3.4 Electrocaloric characterization

The EC effect of the cantilevers was analysed using the holder shown in Figure 4.10. In addition to the High Voltage and Ground connections, the BNC connectors were used to monitor the signal of the thermistor glued to the cantilever. The resistance of the thermistor was monitored by a Keithley 7550 digital multimeter controlled using a Labview program.

#### 4.3.5 3D printing of the device packaging

The packaging for the proof-of-concept device was designed in FreeCAD version 0.18, an open-source computer-assisted design software [109]. The schematic (shown in Fig. 4.11) was then converted to a STEP format appropriate for 3D printing. The 3D printing was carried out at the Department for automation, biocybernetics and robotics at JSI.

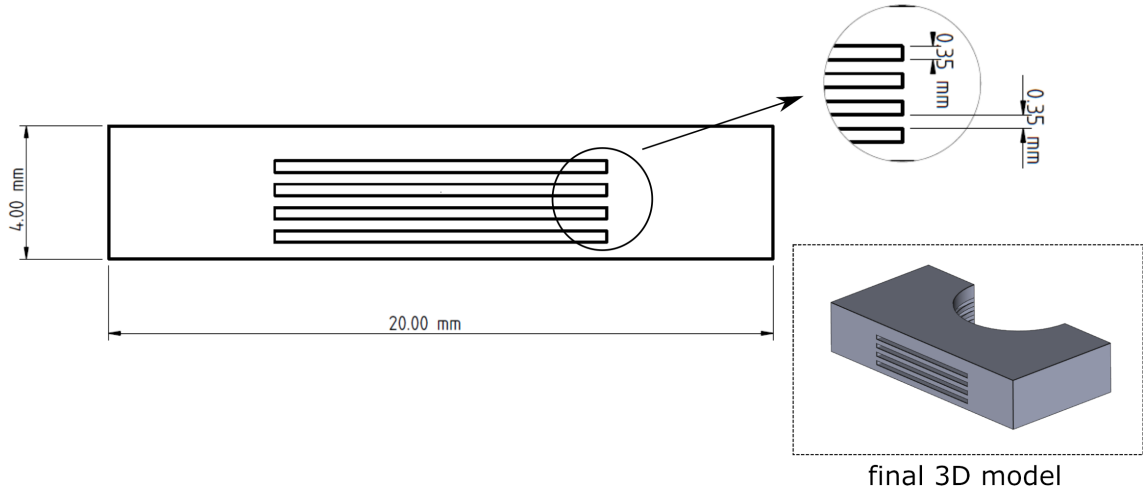


Figure 4.11: The schematics for the device packaging. The schematics provided an input for the 3D printer.

#### 4.3.6 Fabrication and excitation of a proof-of-concept device

The electronics for driving two cantilever elements is shown in Fig. 4.12. The device consists from two cantilever elements fabricated as described in Section 4.3.1. The cantilevers were inserted in a 3D-printed packaging (see schematics in Fig. 4.11). The electrical ground contacts were wired to the top of the 3D-printed packaging with a 80- $\mu\text{m}$ -thick Cu wire. The high-voltage wiring was made with 80  $\mu\text{m}$ -thick Cu wires that were connected to the buried Pt electrode. This prevented sparking and damage to the measuring equipment.

The electric field was applied to the cantilevers in a periodic manner, first the electric field was applied to the lower cantilever and then to the upper one. This was made possible with a Arduino Uno driven Relay switch. Arduino was connected to the PC and programmed by a Labview program.

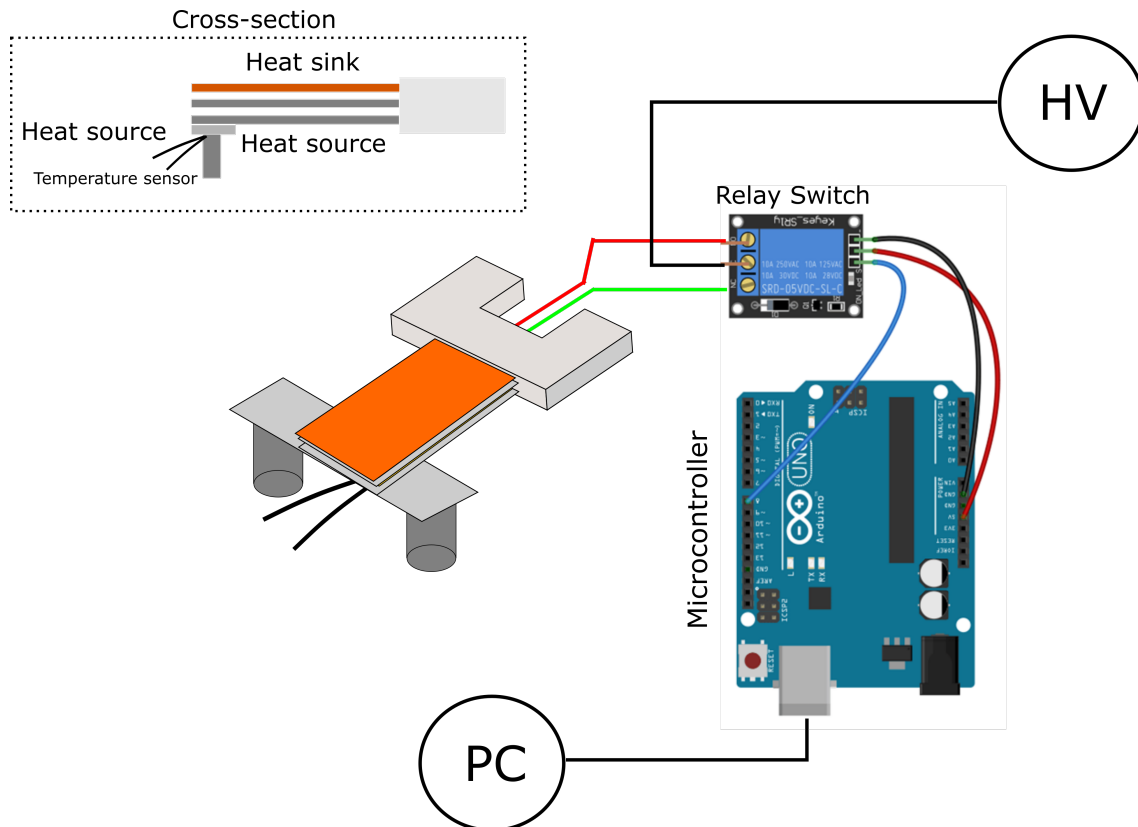


Figure 4.12: Driving set-up for the proof-of-concept device. The device consisting from two cantilever elements was connected to a relay switch. The relay switch was controlled via a Arduino Uno microcontroller programmed by a Labview-made application.

## Chapter 5

# Results and Discussion

### 5.1 Feasibility and Performance Evaluation of Proof-of-Concept Device by Modelling

*Initially, we analysed the concept of the cooling device using numerical modelling. The elements used in the simulation were based on the work of Uršič et al.[110]. The device operation was simulated using different numbers of elements (i.e., cantilevers) and different boundary conditions that mimic realistic conditions. This work was published in Applied Physics Letters, Issue 109, Page 143508, Year 2016 with the following co-authors: Đ. Juričić, M. Santo Zarnik, B. Malič, Z. Kutnjak, and T. Rojac.*

#### 5.1.1 An idealistic model of the device

We investigated how the number of elements ( $n$ ) influences the overall EC temperature span in the device which is shown in Section 2, Fig. 2.1. We built models of the devices with three, five and ten cantilevers (these cantilevers are subsequently referred to as the “elements”, since we modelled only their thermal aspect, not electro-mechanical, e.g., bending under field application). We first investigated an ideal case where any heat exchange with the environment is neglected and where the thermal contacts between the elements are ideal. This means that we assumed no contact resistance between the elements during the time period of the contact and a contact area equal the whole area of the elements.

After building the numerical model, we simulated the device with three elements and investigated the temperature in the middle of each EC element during the first operation cycle consisting of successive contacts between 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> element. While the temperature of the first element was increased, a simultaneous contact was made with the second element. These two steps were used as a part of the simulation procedure that emulated the application of the electric field to the first element and thus its EC effect. In this way the first element exchanged the generated EC heat with the second element. After  $t_c$  elapsed, the contact was closed and the first element cooled by  $\Delta T_{EC}$ . The second and third elements followed the same procedure. The third element had no upper neighbour to further transfer the generated heat, so even after heating and cooling, the temperature of the third element remained the same as it was at the beginning of its cycle.

Figure 5.1 shows the results of the simulations of the device with three elements under ideal heat-transfer conditions as described in the introduction of this chapter. The results clearly show that in the first cycle, i.e., after the final contact with the last, 3<sup>rd</sup> element, a temperature span of 0.18 K is established across the EC device between the first and the last element. If the simulation procedure is repeated, starting again with the first element, the temperature span across the device continues to increase. However, the heat exchange

stopped and the device reached a steady state after several cycles when the temperature span between the element neighbours became larger than the EC temperature change of a single element. r

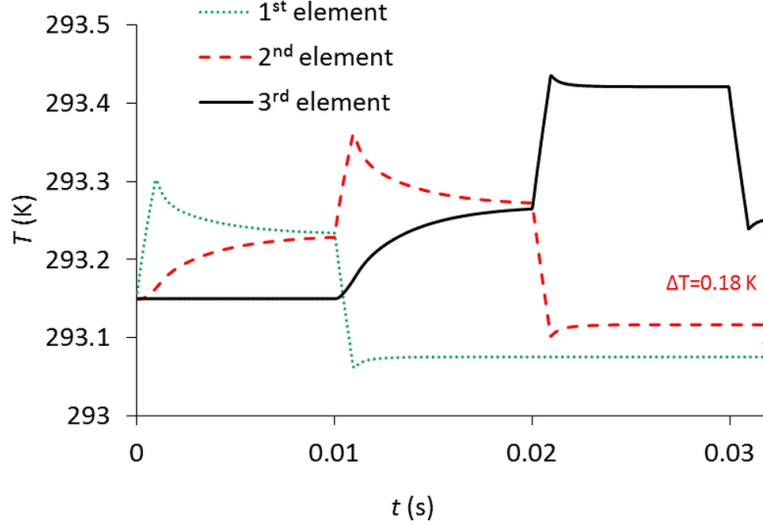


Figure 5.1: Time-dependant operation of the device with three EC elements. The green shows the temperature of the first element, while red and black show the temperature of the 2<sup>nd</sup> and 3<sup>rd</sup> element, respectively.

In the next step, we investigated how repeated excitations of the elements (cycles) affect the temperature span in a device with three, five and ten elements (Fig. 5.2). In the device with three elements the temperature span converges to  $\Delta T = T_{\text{last}} - T_{\text{first}} = 0.32$  K after six cycles. The device with five elements reaches a steady  $\Delta T = 0.56$  K after eight cycles. The  $\Delta T$  further increases with the number of elements, and the device with ten elements reaches  $\Delta T = 1.32$  K after thirty cycles. A rough estimation is that such temperature span would lead to a heat flux of  $31 \text{ mW/mm}^2$  [97] which is lower than measured in the device by Ma et al. [76] ( $30 \text{ mW/cm}^2$ ).

### 5.1.2 Towards a more realistic model

Fig. 5.3 shows the temperature span between the hot and cold sides of the device under ideal and realistic heat-transfer conditions. As shown in Fig. 5.3 (circles), the converged temperature span between the first and last elements in ideal heat-transfer conditions follows a linear relationship with the number of elements. This is due to the ideal heat-transfer conditions assumed in these initial simulations. Aiming towards a more realistic picture of the cooling performance of the device, we next simulated the device operation in a realistic environment, including: i) the heat exchange between the elements and surroundings (air and the element holders), and ii) the partial overlapping of the elements (see the bottom schematic in Fig. 5.3). The heat exchange with the air was modelled using Fourier's law. The characteristic thermal diffusion length was calculated as [97]:

$$d = \sqrt{\alpha \cdot t_c} \quad (5.1)$$

The air diffusivity ( $\alpha$ ) was taken from the literature [72], while the air temperature was 293.15 K. The heat exchange with the Al holders was calculated in a similar way.



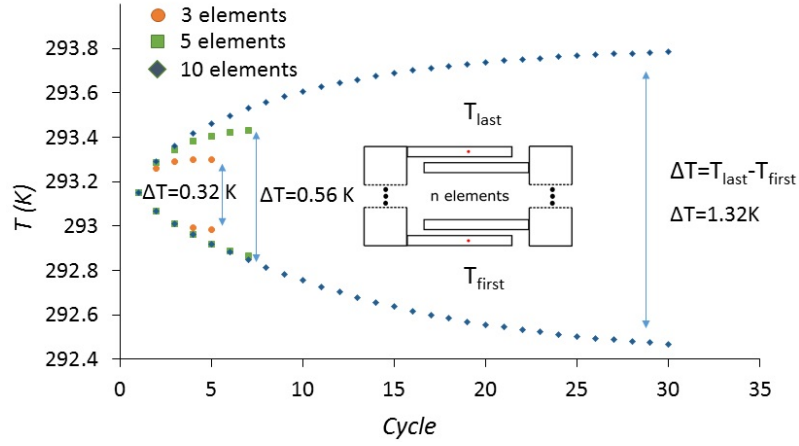


Figure 5.2: Temperature difference between cold and hot side of the device (i.e., between the first and last element in the cascade; see inset) for devices with different number of elements.

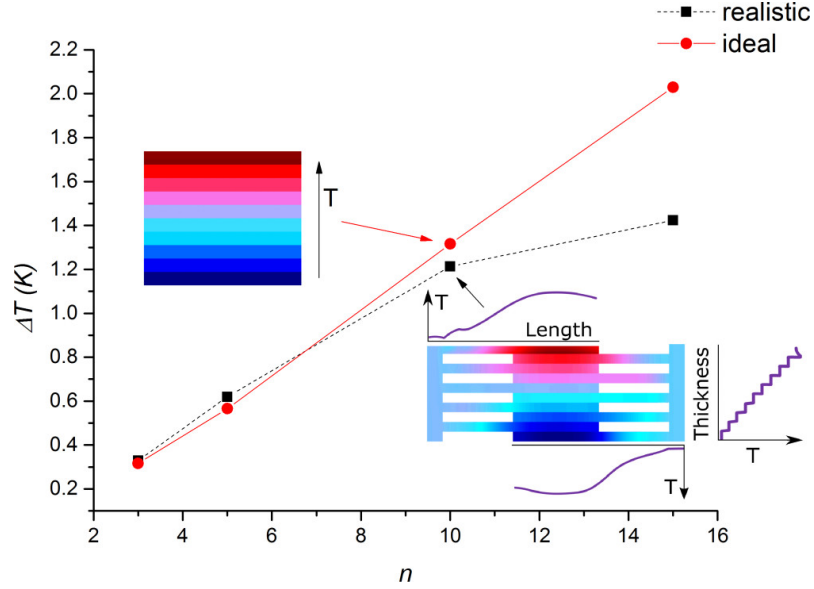


Figure 5.3: Temperature gradient between the cold and hot side as a function of number of elements modelled in ideal and realistic conditions. The insets show the simulated final temperature distribution in the device for these two heat-transfer conditions. The dark-blue colour represents the lowest temperature and the dark-red the highest.

Fig. 5.3 (squares) shows the dependence of the converged  $\Delta T$  on the number of elements,  $n$ , for realistic conditions. In these realistic models,  $\Delta T$  increases with the number of elements up to ten elements, in which case the trend is similar to that predicted for ideal conditions (Fig. 5.3, circles). With a further increase of  $n$  above ten elements,  $\Delta T$  deviates from the linear trend. This is due to the longer idle time of the elements during which they do not contribute to the heat transfer across the device. In fact, the time needed to perform one operation cycle of the device was indeed increased due to the larger number of elements in the device, operating in sequence (one after the other). In addition, the minimum number of cycles for the temperature span to converge increases with the number

of elements (see Fig. 5.2), thus prolonging the total operating time of the device. Both of these effects lead to an increased idle time of the cantilevers, allowing heat exchange between the elements and holders as well as air. Overall, this reduces the effectiveness of the refrigerator. The partial element overlapping during contact, on the other hand, leads to an inhomogeneous distribution of the temperature in the elements along the lateral direction (compare the temperature distribution in the insets of Fig. 5.3), so reducing the effective cooling area.

To reveal the important features of the realistic device, we further introduced in the realistic model the contact resistance between the elements as a critical parameter that determines the performance of the device. In the literature we found values for the contact resistances (in the case of low-pressure contacts) ranging from  $10^{-2}$  m<sup>2</sup>K/W to  $10^{-6}$  m<sup>2</sup>K/W [111]–[113]. We used these values in our model as  $R_{\text{contact}}$  (see Equation 4.1) and simulated the temperature span ( $\Delta T$ ) at a finite contact resistivity, which is plotted in Fig. 5.4 as the ratio to the ideal, zero contact resistivity ( $\Delta T_{\text{ic}}$ , as calculated in the previous example with ten elements; Fig. 5.3, squares).

By using a contact resistance of  $10^{-6}$  m<sup>2</sup>K/W no differences were observed compared to the ideal case; the regeneration factor ( $\Delta T/\Delta T_{\text{EC}}$ ) is approximately 6. By increasing  $R_{\text{contact}}$ , the  $\Delta T/\Delta T_{\text{ic}}$  ratio reduces; at  $10^{-3}$  m<sup>2</sup>K/W the values fall drastically below 0.2 and the regenerative factor falls to 1. Thus, liquid interfaces, carbon-nanotube coatings and other surface-engineering methods that ensure a good thermal contact should be considered when designing this type of refrigerator [111]–[113].

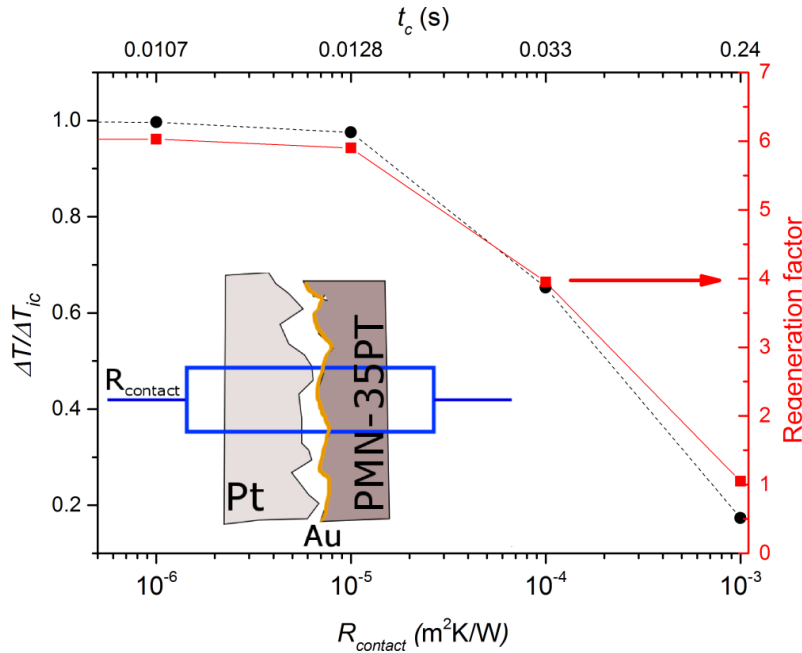


Figure 5.4: Ratio of the temperature span between the first and the last element in the array for a finite contact resistance ( $\Delta T$ ) and that for the ideal contact with no resistance ( $\Delta T_{\text{ic}}$ ) as a function of the contact resistance ( $R_{\text{contact}}$ ) between the cantilevers. On the secondary horizontal axis the corresponding change of  $t_c$  with the  $R_{\text{contact}}$  is shown. The dependence of the regeneration factor on the contact resistance ( $R_{\text{contact}}$ ) is shown on the secondary (right) vertical axis. The dashed line is drawn as a guide to the eye. The schematic shows Pt and PMN-35PT in contact with the indicated  $R_{\text{contact}}$ .

In this chapter we develop a numerical model describing the EC response of the cooling

device under consideration. The results of the numerical modelling show the device design is feasible. A significant benefit of these devices is the amplification of the EC response in terms of the final temperature span between the cold and hot sides of the device with an increasing number of elements (Fig. 5.1). The model also showed that increasing the number of elements has a practical limit related to the idle time of the cantilevers during which a heat transfer occurs to the environment (Fig. 5.2). An optimum number of elements should thus be considered. As the model predicts, a parameter limiting the performance of the device is the contact resistance between the elements (Fig. 5.4). A good thermal contact (large contact area, small thermal resistance) should thus be engineered to maximize the refrigeration performance of the devices.

## 5.2 Electrical, Thermal, EC and EM Properties of PMN-100xPT Ceramics

After showing the feasibility of the device design by numerical modelling in the previous chapter, we have next undertaken the search for the most suitable material for our device among the PMN-100xPT compositional series. For this purpose, we analysed all the relevant properties, including the electrical, thermal, electrocaloric and electromechanical, which are presented individually in the following subsections. These properties were finally incorporated into useful figures of merit to facilitate the material selection (presented in chapter 5.3).

### 5.2.1 Electrical properties

We begin the chapter by reporting the small-signal dielectric permittivity and dielectric loss. We analysed all the compositions ( $x = 0, 0.1, 0.2, 0.3, 0.35, 0.4$ ) at 1 kHz as shown in Fig. 5.5. PMN has the maximum of dielectric permittivity (real part,  $\epsilon'_r$ ) at  $-20^\circ\text{C}$  and a peak value of  $\epsilon'_r$  of 17765. By increasing the content of PT the maximum in  $\epsilon'_r$  is shifted towards higher temperatures, PMN-10PT's peak is at  $45^\circ\text{C}$ . PMN-20PT, PMN-30PT, PMN-35PT follow. PMN-40PT has the peak value of  $\epsilon'_r$  at the highest temperature, i.e.,  $220^\circ\text{C}$ . The maximum values of  $\epsilon'_r$ , room temperature values of  $\epsilon'_r$  and of dielectric losses ( $D$ ) are summarized in Table 5.1.

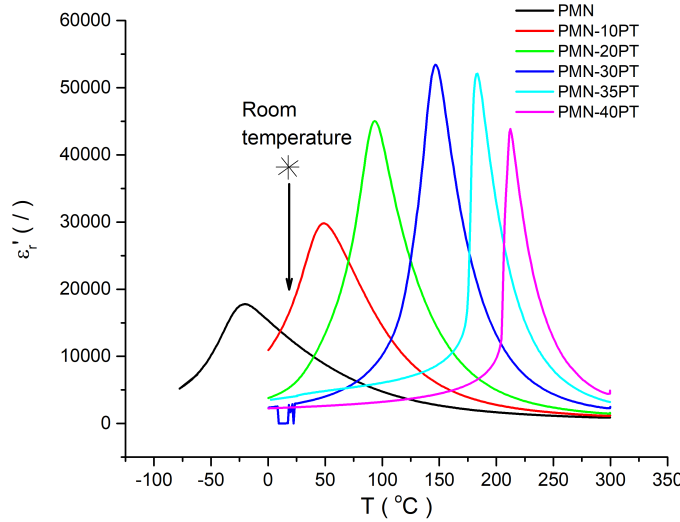


Figure 5.5: Dielectric permittivity at 1 kHz for all PMN-100xPT samples. The arrow indicates the room-temperature values.

The device will be tested at room temperature, and thus we will focus on the material properties at this temperature. At room temperature PMN has a dielectric permittivity of 13914, which is slightly lower than previously reported by Papet et al. [64] where they measured the value of 14700 at RT. This difference could be due to the large temperature sensitivity of the dielectric constant in combination with the difficulty in controlling the temperature around room temperature during the measurement. PMN-10PT also possesses a high dielectric permittivity with the values of  $\epsilon'_r$  of 14840. The compositions  $x > 0.1$  exhibit a significant drop in permittivity. For example, PMN-35PT had  $\epsilon'_r = 3000$ , similar

values were measured in Refs. [67], [114]. PMN and PMN-10PT have the anomaly closest to room temperature. Interestingly, the PMN-10PT exhibits the highest electrical losses among all the analysed compositions, while PMN has the lowest.

Table 5.1: The dielectric properties of PMN-100xPT samples at 1 kHz. The maximum dielectric permittivity ( $\epsilon'_{rmax}$ ) and temperature of the maximum are shown in the first column. The dielectric permittivity and dielectric loss ( $D$ ) values at room temperature are summarized in the second and third columns.

| Material | $\epsilon'_{rmax}$ (at $T$ ) | $\epsilon'_r$ at RT | $D$ at RT |
|----------|------------------------------|---------------------|-----------|
| PMN      | 17765 (-20 °C)               | 13914               | 0.0006    |
| PMN-10PT | 29809 (45 °C)                | 14840               | 0.0562    |
| PMN-20PT | 45053 (94 °C)                | 2503                | 0.0229    |
| PMN-30PT | 53379 (146.5 °C)             | 1840                | 0.0204    |
| PMN-35PT | 52102 (183.4 °C)             | 3000                | 0.0139    |
| PMN-40PT | 43849 (212 °C)               | 2893                | 0.0118    |

To analyse the electrical properties of the compositions in depth, we additionally measured the unipolar  $P(E)$  hysteresis of the PMN-100xPT,  $x = 0, 0.1, 0.2, 0.3, 0.35, 0.4$ . We analysed the loops in the electric field range up to 60 kV/cm and a frequency of 20 Hz. The high fields were used as we expected such field conditions in the actual cooling devices. The samples were poled prior to measurements by cycling them with a unipolar field up to 60 kV/cm. The results are shown in Fig. 5.5. Note that for each electric field, three loops are shown, measured consecutively by applying the same field amplitude (see field waveform in Section 4.2.2, Fig. 4.4b).

PMN was characterized first, the  $P(E)$  loops are shown in Fig. 5.6a. At lower field ( $<10$  kV/cm) the relationship between the  $P$  and  $E$  was linear with little hysteresis. With increasing field ( $>10$  kV/cm), however, saturation is observed, which is consisted with previous reports [84], [115]. Looking at the third electric field cycle, the polarization reached  $28 \mu\text{C}/\text{cm}^2$  at 60 kV/cm. Remanent polarization is not observed, as expected for a canonical relaxor such as PMN.

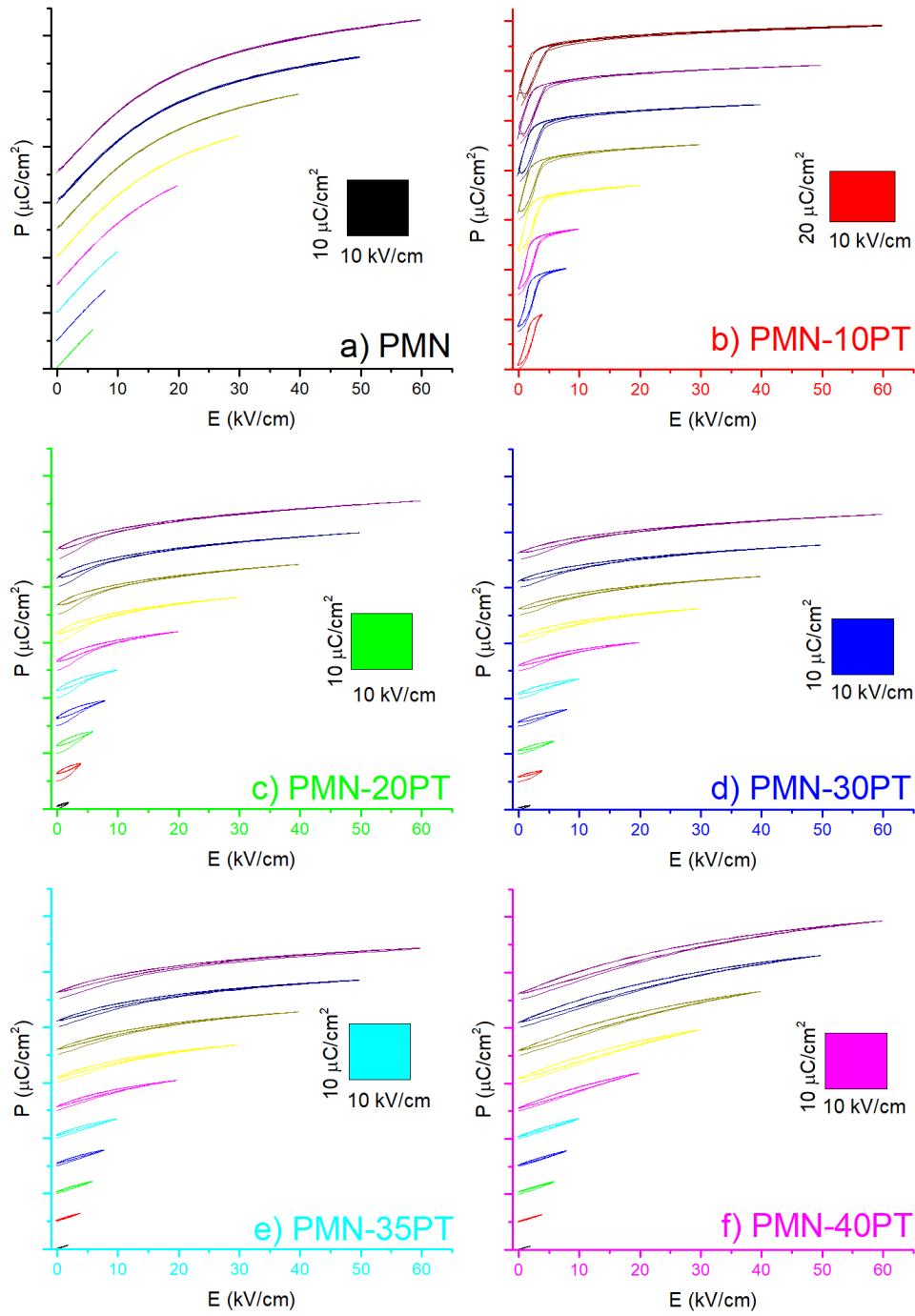


Figure 5.6: Polarization ( $P$ ) versus electric field ( $E$ ) for PMN-100xPT compositions up to 60  $\text{kV}/\text{cm}$ . The loops were measured with three unipolar electric field cycles at frequency of 20 Hz (waveform shown in Materials and Methods, Fig. 4.4b). Measured  $P(E)$  loops are plotted one above the other for clarity. Edges of the coloured square give polarization and electric field scales.

At low fields PMN-10PT has a hysteretic polarization response that is maintained at higher fields (Fig. 5.6b). As the field amplitude was increased, the polarization response started to saturate. This saturation appears more abruptly with the field when compared to PMN (see the break in the loop slope at 60 kV/cm in Fig. 5.6b and compare the same 60 kV/cm loop for PMN in Fig. 5.6a). Although PMN-10PT should be at room temperature in the ergodic relaxor phase [116], [117], similar to PMN, it shows a much higher hysteretic  $P(E)$  response and a more abrupt polarization saturation when compared to PMN. A possible explanation is the proximity of the dielectric peak (43 °C, Ref. [36], [118]) and the structural phase transition (2 °C, Ref. [118], [119]). Such abrupt  $P$  changes were also observed in materials with electric-field-induced phase transformations [39], [120]–[122].

As compared to PMN and PMN-10PT, in PMN-20PT the electric field-induced polarization change is drastically decreased to 10.5  $\mu\text{C}/\text{cm}^2$  at 60 kV/cm (see Fig. 5.6c). A generally lower  $P$  response is also observed in other composition with  $x > 0.2$ . This change in the  $P(E)$  behavior in compositions with  $x > 0.1$  can be attributed to the gradual formation of the ferroelectric order and to the concurrent shift in the permittivity maximum away from room temperature with increasing  $x$  in PMN-100xPT [123]. The emergence of the ferroelectric order is clearly reflected in the dielectric permittivity as a function of temperature and frequency. Kelly et al. [67], for example, showed that the permittivity peaks of compositions with low PT content ( $x < 0.2$ ) are broader, close to room temperature and show a frequency dispersion typical for relaxors. In contrast, as the content of PT is increased ( $x > 0.2$ ) the permittivity peaks shifts to higher temperatures and becomes sharper and less frequency dispersive, which is characteristic for ferroelectric-paraelectric phase transitions. The gradual formation of the ferroelectric order with increasing PT content was directly observed by piezoresponse atomic force microscope [124]. In that study the authors showed a gradual transition from a microstructure consisting of small and irregular polar regions to more regular ferroelectric domains with increasing PT content.

This point is further analysed in Fig. 5.7 for a virgin (as-sintered, unpoled) PMN-20PT sample. Here, we observe that during the first electric field cycle there is a change in  $P$  measured in PMN-20PT that is comparable with that of PMN and PMN-10PT at 60 kV/cm (see Fig. 5.6,  $P_{max} = 28 \mu\text{C}/\text{cm}^2$ ). High  $P$  change during the first cycle in virgin PMN-20PT is related to the poling process which causes permanent orientation of the dipoles and domains in the material inducing a state of remanence,  $P_r$  [7]. In the succeeding cycles we see a smaller  $P$  response consistent with the unipolar loops in Fig. 5.6c; the dipoles oriented in the first cycle do not contribute to the switching process in the 2<sup>nd</sup> and 3<sup>rd</sup> cycle any more, leading to smaller  $P$  changes (only 6  $\mu\text{C}/\text{cm}^2$  as shown in Fig. 5.7). Changing the direction of the electric field would switch the dipoles in the direction of  $E$ -field and a large  $P$  would again be observed; however, again only in the first poling cycle. Thus, we see that with unipolar excitation of ferroelectric materials the  $P$  is smaller as compared to relaxors due to the formation of long-range polar order during the initial poling cycle [125], [126].

Similar behaviour, as shown in Fig. 5.7, during the first poling cycles were observed in virgin samples for the rest of the compositions, which lean towards a ferroelectric nature ( $x = 0.3, 0.35, 0.4$ ). In this study, however, we will only investigate the response of the poled samples because this is the state of the material which most closely resembles the conditions in actual EC cooling devices.

The next sample we analysed is PMN-30PT. The change in polarization was  $P = 8.5 \mu\text{C}/\text{cm}^2$  at 60 kV/cm (Fig. 5.6d) which is slightly lower than in PMN-20PT (10  $\mu\text{C}/\text{cm}^2$ , Fig. 5.6b). An interesting feature which can be observed in PMN-20PT and PMN-30PT is the difference in  $P$  in the first and the subsequent two cycles ((shown in Fig. 5.6 c and d)). We can see that during cycle 2 and 3 we have a slightly higher  $P$  at zero field (when

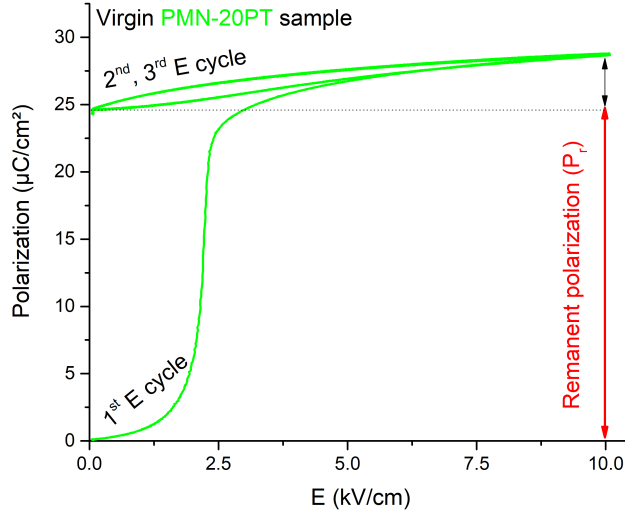


Figure 5.7: Response of a virgin PMN-20PT excited with three unipolar  $E$ -field cycles of magnitude of 10 kV/cm.

reducing field to zero after reaching the maximum) compared to that measured in the first cycle. While the different zero-field polarization measured after the first and subsequent cycles may be affected by various mechanisms, such as, e.g., the  $E$ -field induced phase transition, shown to occur in PMN-30PT [127], a similar behaviour in compositions  $0.1 \leq x \leq 0.4$  suggests that it originates from domain back-switching. This means that in the first cycle the material is prone to poling, thus showing a smaller polarization change  $P$  during subsequent cycles [128].

In Fig. 5.6e it can be observed that the PMN-35PT exhibits a slightly larger  $P$  as PMN-30PT ( $10.3 \mu\text{C}/\text{cm}^2$  at  $60\text{kV}/\text{cm}$ ). This is most probably due to the proximity of the morphotropic phase boundary, which is the region of high responsivity of materials [26], [129]. In fact, compositions in the region from 0.32 to 0.37 of PT exhibit high dielectric and piezoelectric properties at room temperature [67]. According to the phase diagram for PMN-100xPT reported by Singh et al. [66], at  $x = 0.32$  a boundary exists separating two monoclinic phases ( $M_A$  and  $M_C$ ), while at  $x = 0.37$  there is another boundary separating the monoclinic  $M_C$  and tetragonal phase. It was previously explained ([28]) that the coexistence of different crystal symmetries at the boundary leads to flattening of the energy profile for polarization rotation, leading to enhanced properties.

PMN-40PT had an even higher  $P$  than the compositions analysed before, the  $P$  is  $14.3 \mu\text{C}/\text{cm}^2$  at  $60 \text{ kV}/\text{cm}$  as shown in 5.6f. We tentatively ascribe this to the tetragonal crystal structure, which has a larger  $E_C$ , meaning that the response will begin to saturate at higher electric fields [130]. The larger  $E_C$  and response saturating at higher fields is due to the stiffer elastic properties of the tetragonal structure in which the deformation of the crystal lattice occurs in the longitudinal direction in contrast to rhombohedral, where shear deformation is responsible for a large portion of the induced strain.

In the next step, the measured  $P(E)$  data was used to evaluate the electrical efficiency of the materials under consideration by calculating the recoverable energy density and energy loss density using the methodology described in Chapter 1, Section 1.2.2, Fig. 1.14 plots the stored energy  $W_S$  calculated from the third  $E$ -field cycle for each field magnitude using



the area above the  $P(E)$  hysteresis (see Fig. 1.14). PMN and PMN-10PT are superior in electrical storage compared to other compositions, primarily due to the large induced  $P$  change by the electric field. PMN-10PT has an energy-storage capacity of  $1.7 \text{ J/cm}^3$  at  $60 \text{ kV/cm}$ , which is comparable with the highest values observed in bulk ceramics [131]–[133]. Compositions  $x > 0.1$  showed significantly smaller values, which corresponds to the lower polarization values measured in these samples (see Fig. 5.6). For example, PMN-35PT at  $60 \text{ kV/cm}$  exhibited an energy-storage density of only  $0.38 \text{ kJ/cm}^3$ .

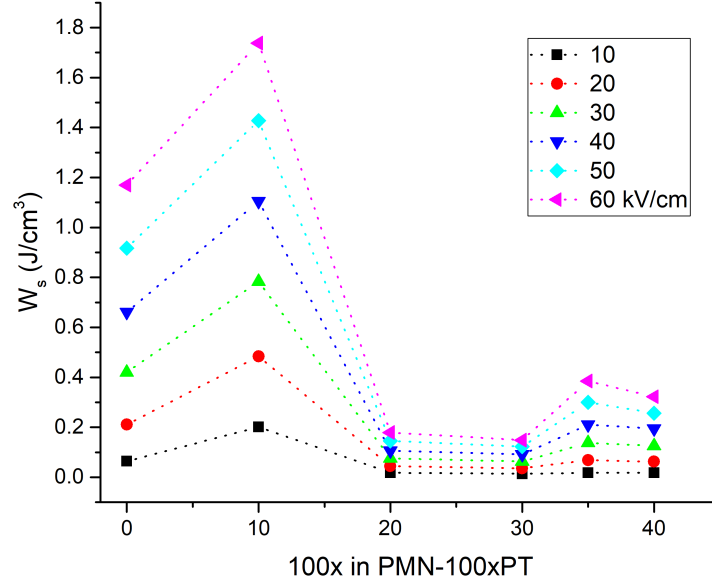


Figure 5.8: Energy storage capacity ( $W_S$ ) of PMN-100xPT samples calculated for different electric field amplitudes. The lines between the points serve as a guide to the eye.

Next, we evaluated the energy-loss density  $W_L$  by determining the hysteresis area on poled samples up to  $60 \text{ kV/cm}$  (third cycle; see also Fig. 1.14). Early studies by Härdtl et al.[62] divided the loss of ferroelectric materials into electrical and mechanical. Sources of electrical losses were further separated into: i) so-called “microstructural losses” arising from the grain boundaries, pores and secondary phases, ii) lattice defects which occur due to the anharmonic behaviour of the crystal lattice due to point defects, and iii) domain-wall motion iv) electrical conductivity. However, studies were mainly focused on weak-field (subswitching) responses. A broader overview of the physics behind the electrical losses was recently conducted by Liu et al. [88]. The modern classification divides the losses into intrinsic and extrinsic. The intrinsic losses are related to the crystal lattice, for example, polarization elongation, rotation and compression. Extrinsic losses are related to domain-wall motion, grain size, defect diffusion, crystal phase, phase transformations and impurities.

The values of  $W_L$  calculated using Equation 1.7, Section 1.2.2 are presented in Figure 5.9. Note that in all compositions the electrical resistivity was relatively high. In general, the samples had a resistivity  $> 10^{12} \Omega\text{m}$  and thus the contribution of leakage currents to electrical loss can be neglected.

Pure relaxor PMN exhibits the lowest electrical losses, which is due to the low hysteresis, probably because of the absence of a ferroelectric phase and thus domains and

dissipative domain-wall contributions. PMN-10PT had a large hysteresis loop which leads to large electrical losses. The estimated loss at 60 kV/cm was  $0.047 \text{ J/cm}^3$ . This could be due to the proximity of the structural (polar-to-nonpolar,  $2^\circ\text{C}$ , Ref. [118], [119]) phase transformation, which could be stimulated with the application of the electric field [88]. PMN-20PT, PMN-30PT and PMN-35PT exhibit similar losses,  $0.015 \text{ J/cm}^3$ . In comparison, the losses in PMN-40PT at 60 kV/cm were higher, i.e.,  $0.034 \text{ kJ/cm}^3$ .

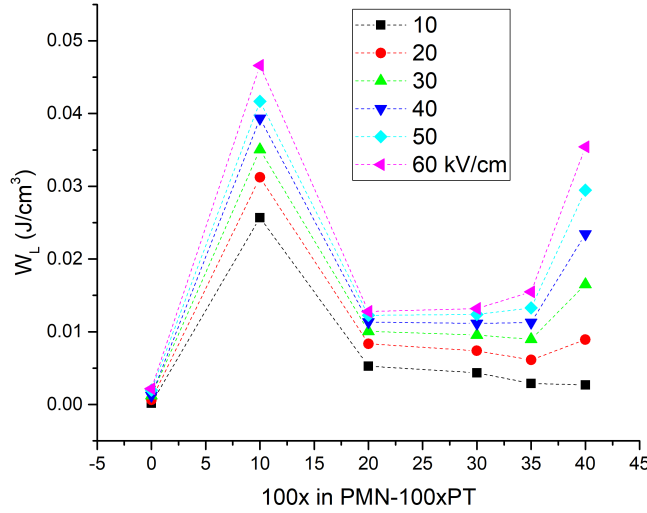


Figure 5.9: Energy loss ( $W_L$ ) of PMN-100xPT samples calculated for different electric field amplitudes. The lines between the points serve as a guide to the eye.

We finally calculated the electrical efficiency of the material ( $\zeta$ ) using an equation considering both  $W_S$  and  $W_L$ . The ratio illustrates the percentage of energy that can be recovered [85]:

$$\zeta = 100\% - \frac{W_L}{W_S} \cdot 100\%. \quad (5.2)$$

The  $\zeta$  values for the analysed compositions are plotted in Fig. 5.10. It is evident that PMN possesses the best ratio between losses and stored energy, the  $\zeta$  stays above 99 % even at 60 kV/cm. In PMN-10PT the  $\zeta$  drops and exhibits larger losses as in PMN, especially at low electric field values. We can understand this by observing the  $P(E)$  loops of PMN-10PT in Fig. 5.6b; at 4 kV/cm the material possesses a strongly hysteretic response; however, at larger fields, for example, 40 kV/cm, the initial wide hysteresis is still observed but saturation also emerges, which is non-hysteretic. The high-field non-hysteretic behaviour reduces the ratio between the losses and stored energy. This is why we see a reduction of losses with increasing electric field. Similar behaviour is observed in the rest of the compositions.

Comparing the relative loss values to the literature, we can observe that losses below 10 % are typical for relaxor-like materials [134], while losses at the level of 30 % are usually observed in classic ferroelectrics [133].

In this section we have analysed in detail the polarization response, hysteresis and electrical stored energy of the six studied PMN-100xPT compositions. The different behaviour was tentatively attributed to processes occurring in the material under electric-field ap-

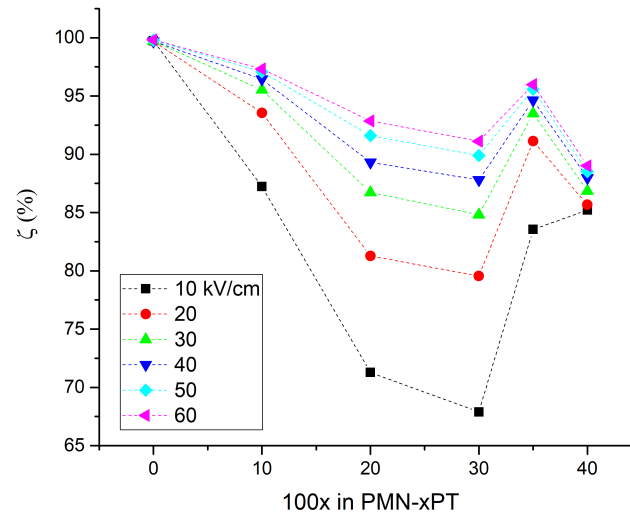


Figure 5.10: Material efficiency of PMN-100xPT samples calculated for different electric field amplitudes as a ratio between energy loss density and energy storage density. The lines between the points serve as a guide to the eye.

plication. The data show that relaxor PMN exhibits the lowest electrical loss and best electrical efficiency, which is relevant for the EC cooling device.

### 5.2.2 Electromechanical response

Simultaneously with the polarization measurements (shown in Section 5.2.1) we also measured the longitudinal electromechanical response (denoted as  $s_3$ ). The electromechanical behaviour of the ceramics is an important parameter to be considered in the design of the cantilever device as it determines the cantilever deflection under applied field and thus thermal contacts between the cantilevers in the cascade (see Fig. 2.1).

Fig. 5.11a shows the  $s_3(E)$  response of PMN. At fields lower than 10 kV/cm the strain follows an electrostrictive quadratic relationship (see Section 1.2 for explanations); however, at higher electric fields the strain significantly deviates from the quadratic field relation due to strain signal saturation. Saturation effects emerge at 20 kV/cm, like observed in the  $P(E)$  response (Fig. 5.6) confirming the coupling between polarization and strain as discussed in Section 1.2.

The  $s_3$  versus electric field for PMN-10PT was analysed next (see Fig. 5.11b). At low fields (<5 kV/cm), PMN-10PT at first exhibits a steep increase in the strain, which is strongly hysteretic. Saturation of the strain response is observed at fields >5 kV/cm. In the saturated region the strain response is hysteresis-free. The initial jump in response and wide hysteresis are identical to the observed  $P$  changes under electric field in Fig. 5.6b.

The strain behaviour of PMN-20PT shown in 5.11c again shows the distinct difference between compositions with structural polar-to-nonpolar phase transition below room temperature (PMN and PMN-10PT, Figures 5.11a and b) and above room temperature (PMN-20PT, PMN-30PT, PMN-35PT, PMN-40PT, Figures 5.11c, d, e and f). The latter resemble the strain response of typical ferroelectric materials, like PZT (See Section 1.1.2, Fig. 1.4) [9].

To further analyse the longitudinal strain response, we plot in Fig. 5.12 the maximum longitudinal strain ( $s_3^{max}$ ) as a function of the amplitude of the electric field ( $E_0$ ) and the coefficient of the maximum strain at a given electric field amplitude ( $s_3^{max}/E_0$ ). For comparison, we added on the plots (see red crosses in Fig. 5.12) the values of the direct  $d_{33}$  coefficient measured using a standard Berlincourt piezometer. The  $d_{33}$  values provide indirect information about the  $P_r$  and long-range order in the material (see Equation 1.3).

The maximum longitudinal strain measured on PMN was 0.11 % at 60 kV/cm. The coefficient  $s_3/E_0$  was the largest, i.e., 220 pm/V, at the electric field of 30 kV/cm. The  $s_3/E_0$  decreases after 30 kV/cm due to before-mentioned saturation effects. Similar values were obtained by Nomura et al.[115] at somewhat lower electric fields, i.e., they measured 240 pm/V at 10 kV/cm. The authors, however, did not report the  $s_3/E_0$  values at electric fields above 15 kV/cm. From the polarization (Fig. 5.6a) and strain (Fig. 5.11a) data we can calculate the electrostrictive  $Q$  coefficient of our PMN sample. The  $Q$  at 10 kV/cm is  $0.016 \text{ m}^4/\text{C}^2$ , which is consistent with the literature data [8]. Worth mentioning is that we also measured the direct piezoelectric response on PMN after the polarization and strain measurement using a Berlincourt piezometer. No response could be measured within the uncertainty value of 1 pC/N. Since  $P_r$  in PMN is macroscopically equal to zero this result is consistent with the equations in Section 1.2.

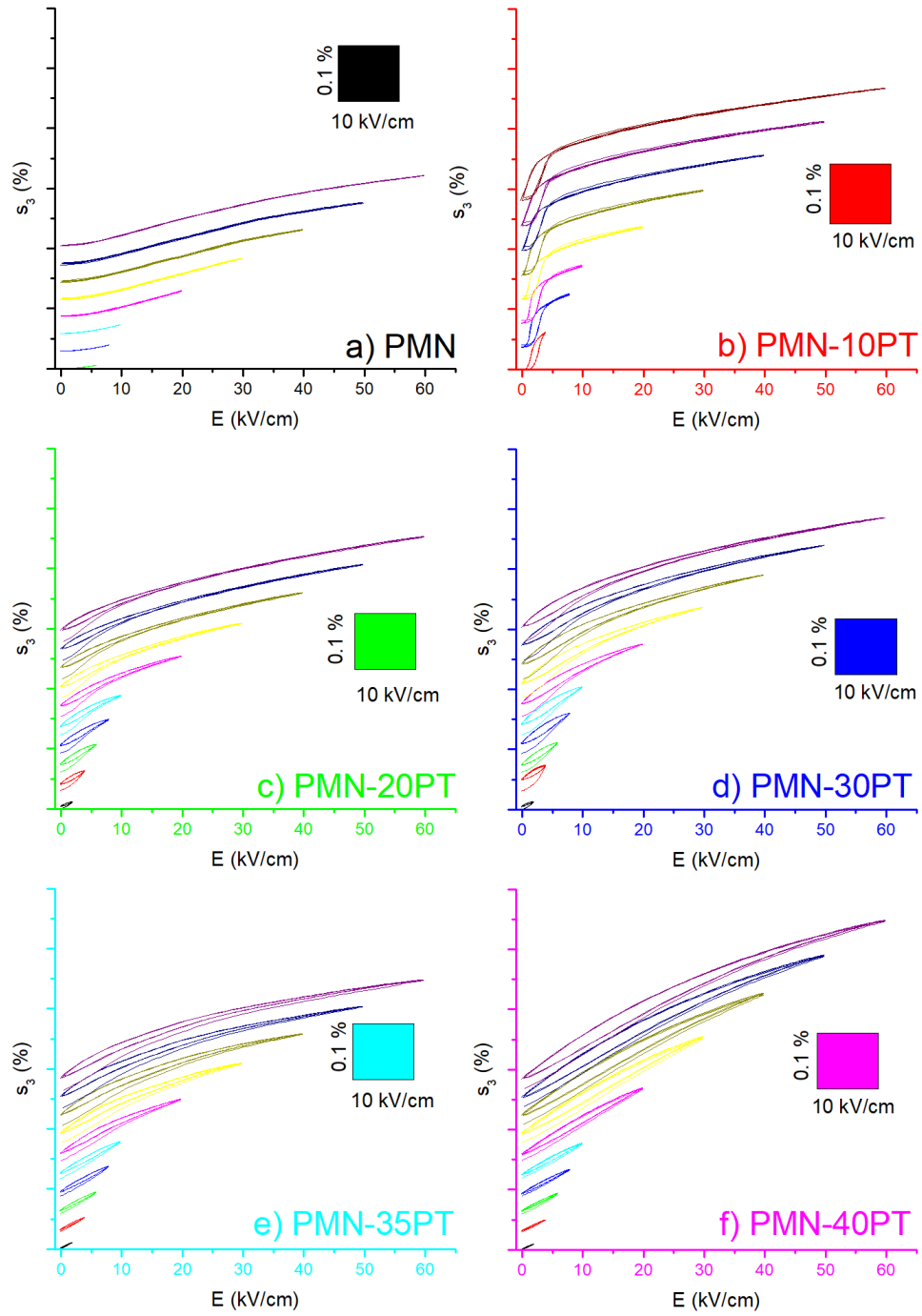


Figure 5.11: Longitudinal strain ( $s_3$ ) versus electric field hysteresis loops for PMN-100xPT compositions. The loops were measured with three unipolar electric field cycles at frequency of 20 Hz (waveform shown in Materials and Methods, Fig. 4.4b). Measured  $P(E)$  loops are plotted one above the other for clarity. Edges of the coloured square give polarization and electric field scales.

As seen in Fig. 5.12b, strain in PMN-10PT raises abruptly at fields  $< 10$  kV/cm, resulting in values of up to 1600 pm/V at an electric field of 6 kV/cm. However, the values saturate quickly with increasing field and after 20 kV/cm the coefficient drops to 300 pm/V (at 60 kV/cm). The maximum longitudinal strain measured was 0.19% at 60 kV/cm. The exceedingly large  $s_3^{max}/E_0$  values measured at low fields are consistent with the report by Zhao et al. [135] where the maximum coefficient was obtained at 3 kV/cm.

The giant  $s_3^{max}/E_0$  measured on PMN-10PT is 230-times larger than the  $d_{33}$  measured directly with Berlincourt piezometer (7 pm/V). This can be explained by inspecting Equation 1.3 in Section 1.1.2. The electromechanical response of the material is a function of dielectric constant and polarization. Fig. 5.6b shows that upon application of a small electric field the  $P$  in PMN-10PT raises abruptly (e.g.,  $22 \mu\text{C}/\text{cm}^2$  at 4 kV/cm). Such a large induced  $P$  in combination with high  $\epsilon_r'$  leads to a high electromechanical response. On the other hand, the absence of remanent polarization and long-range polar order under zero-field conditions in PMN-10PT explains the low  $d_{33}$  measured directly with the Berlincourt piezometer. Nonetheless, the non-zero direct  $d_{33}$  value after high field application indicates that a small remanence is still present.

The maximum strain achieved in PMN-20PT at 60 kV/cm was 0.15 %. The values of  $s_3/E_0$  reach a maximum of 550 pm/V at 6 kV/cm (see Fig. 5.12c). At fields higher than 6 kV/cm the values decrease reaching a value of 250 pm/V at 60 kV/cm. Despite the small  $P$  values measured during  $E$ -field cycles (see Fig. 5.6c), the electromechanical response is relatively high (Figs. 5.11c) compared to PMN (Fig. 5.11a). This can be ascribed to the remanent polarization induced in the material within the virgin cycle showed in Fig. 5.7. The direct  $d_{33}$  measured on a piezometer was 265 pm/V, which is significantly higher than in PMN-10PT, implying that the  $P_R$  is larger and that long-range order is present.

$s_3^{max}$  and  $s_3^{max}/E_0$  for PMN-30PT are shown in Fig. 5.12d.  $s_3^{max}/E_0$  has a peak value at 6 kV/cm. This value was 630 pm/V and it decreases to 300 pm/V at a maximal field of 60 kV/cm. The direct  $d_{33}$  was 303 pm/V. The response of these compositions is likely affected by the polarization rotation mechanism between two monoclinic crystal structures, as reported in Ref. [127]. PMN-35PT possessed 700 pm/V at 6 kV/cm, while in PMN-40PT the maximum value (550 pm/V) shifts to 20 kV/cm. This shift in maximum response can be attributed to the higher coercive field of this composition (in PMN-40PT  $E_c = 20$  kV/cm while in PMN-35PT  $E_c = 5$  kV/cm).

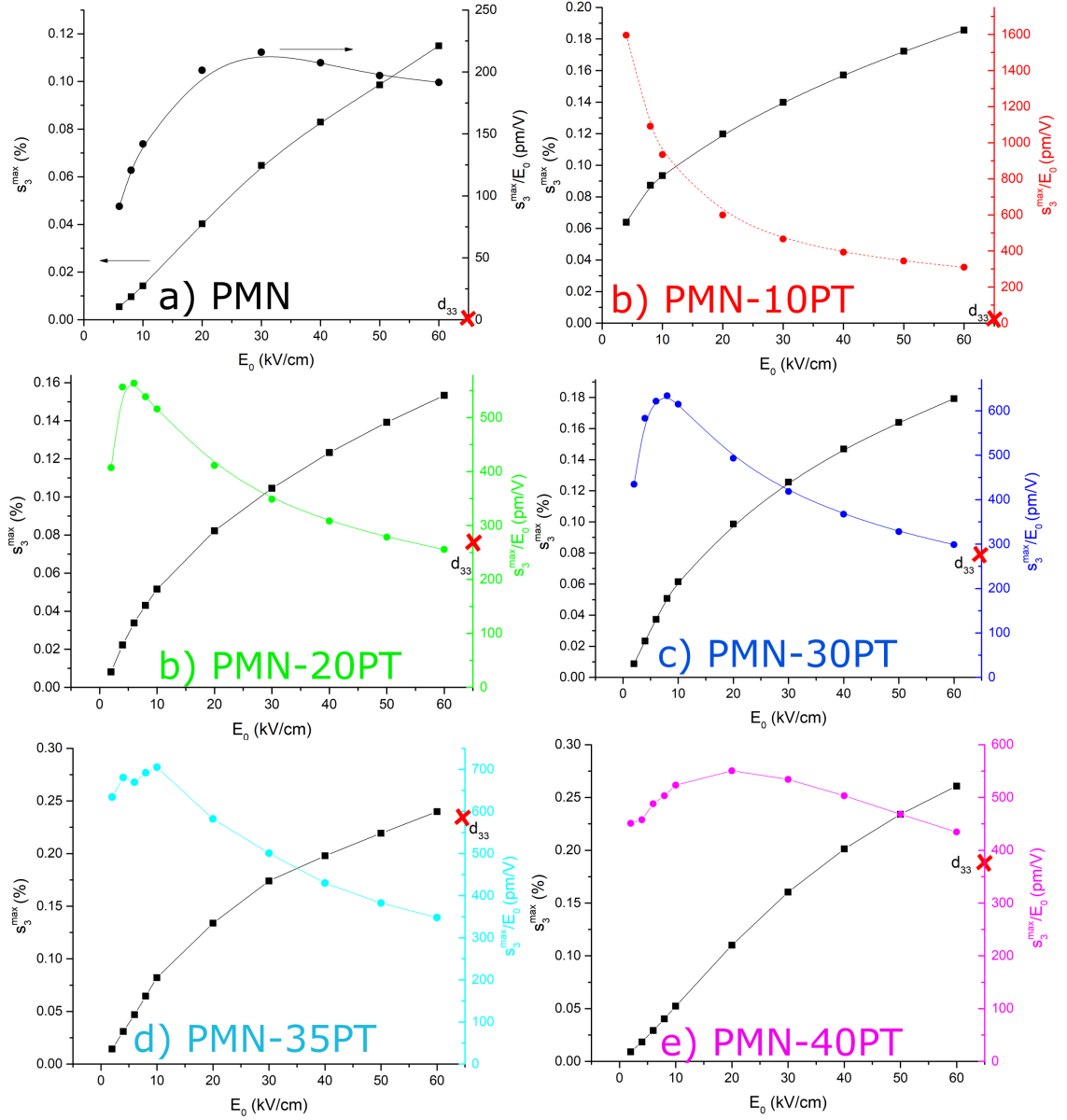


Figure 5.12: Maximum longitudinal strains  $s_3^{max}$  and  $s_3^{max}/E_0$  for PMN-100xPT compositions as a function of electric field. The lines between the points serve as a guide to the eye.

In addition to the longitudinal strain, we also measured the transverse strain  $s_1$ . Unlike in the case of the longitudinal measurements where a field frequency of 20 Hz was used, the frequency of the applied electric field for the transverse measurements was reduced to 0.1 Hz due to the limitations of the measurement method using LVDT displacement sensors. The electric field range was also altered because the sensors had limited strain sensitivity below 10 kV/cm. In addition, the maximum electric field (40 kV/cm) was limited by the observed breakdown of the samples. In fact, for  $s_1$  measurements, thicker samples were used, which were prone to breakdown under large electric fields, typically  $>40$  kV/cm.

Fig. 5.13a shows the maximum  $s_1^{max}$  and  $s_1^{max}/E_0$  coefficient for PMN as a function of the electric field amplitude ( $E_0$ ). The maximum strain is 0.027 % at 50 kV/cm, while

the maximum  $s_1^{max}/E_0$  of 55 pm/V is achieved at 30 kV/cm. Using again the comparison with the results of Nomura et al.[115], in their experiments, the maximum coefficient of 75 pm/V was measured at 15 kV/cm.

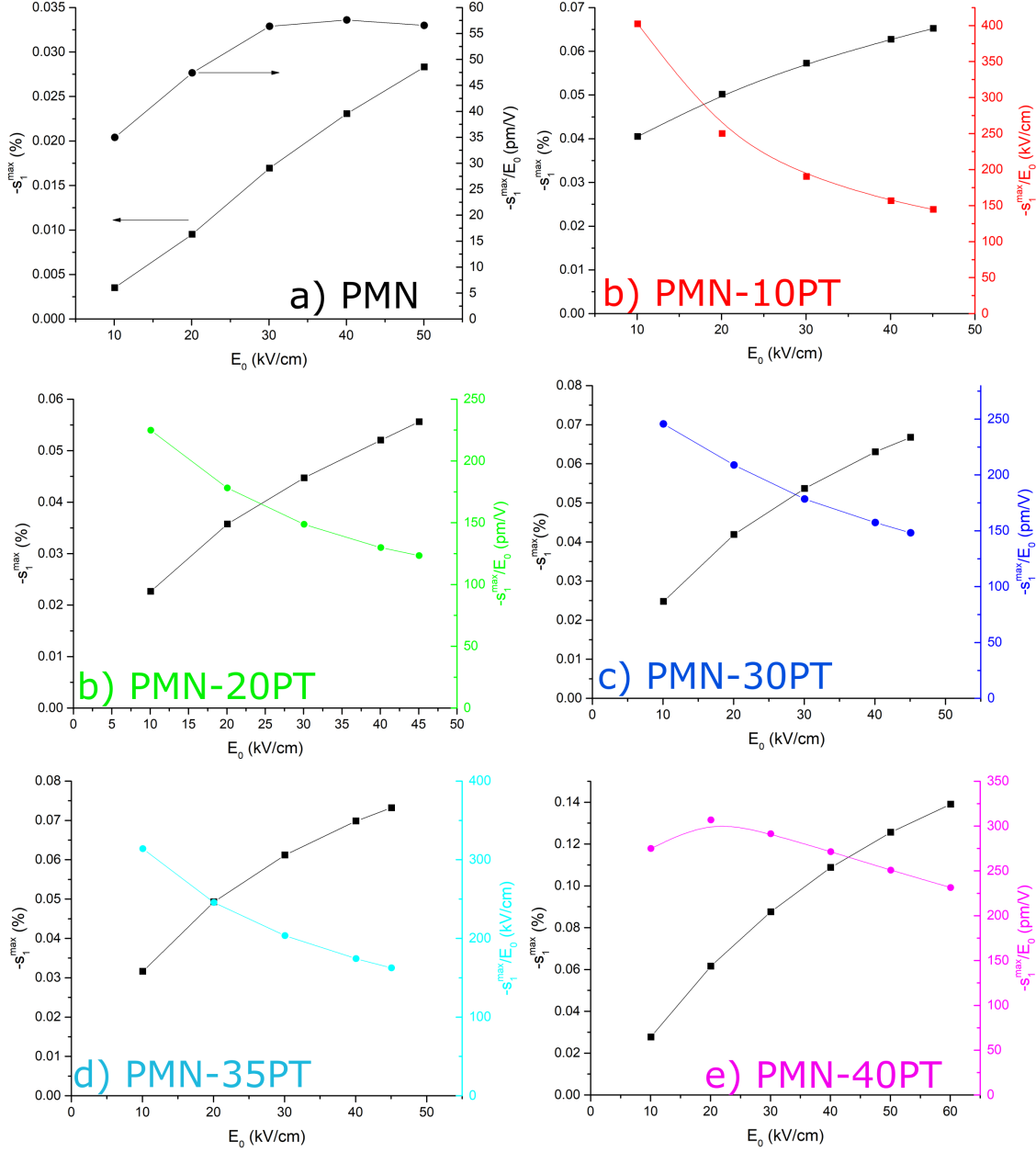


Figure 5.13: Maximum transverse strains  $s_1^{max}$  and  $s_1^{max}/E_0$  for PMN-xPT compositions as a function of electric field. The lines between the points serve as a guide to the eye.

The  $s_1^{max}$  and  $s_1^{max}/E_0$  for PMN-10PT are shown in Fig. 5.13b. The transverse strain reaches the value of 0.065 % at 45 kV/cm. The values continuously decrease with increasing field. The maximum  $s_1^{max}/E_0$  is 400 pm/V, again consistent with the work by Zhao et al. [135].

The peak value of  $s_1^{max}/E_0$  measured in PMN-20PT is 230 pm/V at 10 kV/cm and reduces to 126 pm/V at 45 kV/cm (Fig. 5.13c), while in PMN-30PT the  $s_1^{max}/E_0$  is about



250 pm/V and reduces to 150 pm/V at 45 kV/cm (Fig. 5.13d).

In the case of PMN-35PT (Fig. 5.13e) the  $s_1^{max}$  at 60 kV/cm is 0.076 in. The  $s_1^{max}/E_0$  peaks at 6 kV/cm and it is 308 pm/V. Finally, PMN-40PT shows  $s_1^{max}/E_0$  peak at 20 kV/cm and is 314 pm/V (Fig. 5.13f).

For the device developed within this work, the transverse ( $s_1^{max}/E_0$ ) EM response is crucial because it defines the deflections of the cantilevers (working in 31 mode). The values of the transverse coefficients as a function of PT content for the different field amplitudes are summed up in Fig. 5.14. PMN exhibits the lowest transverse EM response at all electric fields. The main reason is most probably the pseudocubic crystal structure and thus a purely electrostrictive response. By observing the field evolution of  $s_1^{max}/E_0$  we can see that at lower electric fields PMN-10PT and PMN-35PT exhibit the larger EM response (see black squares in Fig. 5.14). With increasing field, however, the PMN-40PT begins to surpass other compositions. Surprisingly, at high fields, PMN-10PT possesses a transverse coefficient comparable to that of PMN-35PT. In the view of device integration from the perspective of the electromechanical response, the most suitable composition is PMN-40PT as it shows the highest electromechanical transverse effects at the high electric fields that are needed to achieve a sufficiently large EC response (note that EC effect is strongly field dependent) [36]. The high response of PMN-40PT at elevated electric fields can be interpreted in terms of the tetragonal crystal structure. It is well known that the tetragonal crystal structure has a high coercive field and spontaneous polarization [130]. In  $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ , for example, at  $x=0.6$  (rhombohedral structure) the  $E_c$  is equal to 6.7 kV/cm, while in the tetragonal phase ( $x=0.45$ ) the  $E_c$  increases to 22 kV/cm [136]. This naturally leads to saturation of the EM response at higher electric fields and also large  $P_S$  values induce high electrostrictive and piezoelectric response (see Equation 1.3 in Section 1.1.2).

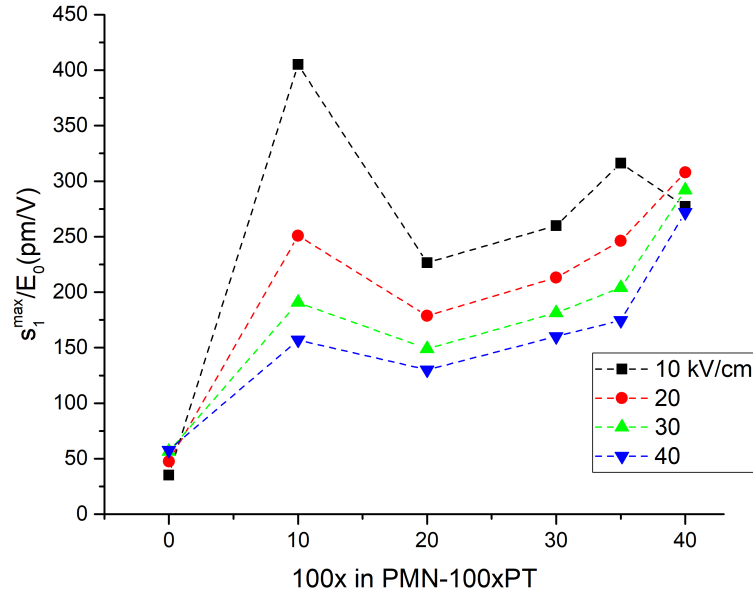


Figure 5.14: Electromechanical response ( $s_1^{max}/E_0$ ) of the analysed PMN-100xPT compositions for different field magnitudes.

### 5.2.3 Thermal properties

*The results of this study have been published in the Journal of Microelectronics, Electronic Components and Materials, Volume 45, Number 4, Page 260 in Year 2015 by Hana Uršič, Marko Vrabelj, Lovro Fulanović, Andraž Bradeško, Silvo Drnovšek, Barbara Malič.*

To estimate the heat-transport properties, the heat conductivity and heat capacity were measured at room temperature for the different PMN-100xPT ceramic compositions. The results in terms of thermal heat conductivity, heat capacity and a coefficient proportional to the characteristic time for thermalization (thermal transport coefficient) are shown in Table 5.2. The densities used in the calculation of thermal transport coefficient are given in Appendix A.1.

Table 5.2: The thermal conductivity ( $\lambda$ ) and specific heat ( $c_p$ ) for PMN-xPT ceramics and thermal transport coefficient ( $\frac{c_p \rho}{\lambda} \cdot 10^6$ ).

| Material | $\lambda$ (W/mK) | $c_p$ (J/kgK) | $\frac{c_p \rho}{\lambda} \cdot 10^6$ (s/m <sup>2</sup> ) |
|----------|------------------|---------------|-----------------------------------------------------------|
| PMN      | 1.25             | 326           | 2.031                                                     |
| PMN-10PT | 1.27             | 325           | 2.019                                                     |
| PMN-20PT | 1.29             | 326           | 1.948                                                     |
| PMN-30PT | 1.38             | 326           | 1.838                                                     |
| PMN-35PT | 1.43             | 323           | 1.743                                                     |
| PMN-40PT | 1.57             | 317           | 1.563                                                     |

As can be seen in Table 5.2, the heat conductivity ( $\lambda$ ) increases with increasing content of PT. The heat is transferred through the crystal by elastic vibrations of the crystal lattice and is limited by the defects present in the crystal lattice [137], [138]. In PMN the density of the planar defects is presumably high due to the presence of polar nano-regions. With the addition of PT the polar nano-regions grow into larger domains, causing a reduction of the density of interfaces, thus decreasing the phonon scattering.

The heat capacity ( $c_p$ ) of the analysed materials does not show an obvious trend with values very similar for compositions  $0.1 \leq x \leq 0.35$  and somewhat lower for  $x=0.4$ . In general, the heat capacity is proportional to the molar mass of the material and in our case the molar masses are within the 10 % range of the measured heat capacities.

To further estimate the heat-transport properties, we calculated the characteristic time of thermalization ( $\tau$ ) for each material. The shorter the characteristic time, the faster the heat transfer is completed, meaning that the operational frequency ( $f$ ) of the cooling devices can be increased. A high frequency of operation leads to a greater energy pumping and thus more efficient cooling.  $\tau$  can be calculated as follows [97]:

$$\tau = \frac{c_p \rho}{\lambda} \cdot l^2 \propto \frac{1}{f}, \quad (5.3)$$

where  $l^2$  is the characteristic length, i.e., the length heat has to travel. In our case  $l$  would be the thickness of the cantilever. However, to exclude geometrical parameters we will compare the materials by calculating the coefficient  $\frac{\lambda}{c_p \rho}$ . Table 5.2 shows that the thermal transport properties possessed by PMN-40PT are the highest. The lowest are in PMN. The relative difference is about 25 %. The data thus overall show that PMN-40PT possesses the best performance in terms of heat-transfer properties.

### 5.2.4 Electrocaloric response

After the electrical losses, electromechanical response and thermal transport were characterized, we proceeded with the analysis of the EC temperature response of PMN-100xPT compositions under an applied electric field. First, we studied the EC effect of the materials by applying to the samples a square electric field waveform with the frequency of 5 mHz. An illustration of the temperature response of PMN under an applied electric field is shown in Fig. 5.15. When a square electric field waveform is applied to the EC material, the material responds with a quasi-adiabatic increase of temperature. This step is called adiabatic polarization ( $\Delta T_{EC}^P$ ). In the next step, called isoelectric stage, the electric field is maintained for a longer time period (typically several tens of seconds). This allows the heat exchange with the surroundings, so the material cools ideally to its initial temperature. When the electric field is quickly removed, adiabatic depolarization ( $\Delta T_{EC}^D$ ) occurs and the material cools below the initial temperature. For the sake of our studies, we analysed the adiabatic temperature peaks during cooling and heating of the sample as denoted with red circles in Fig. 5.15.

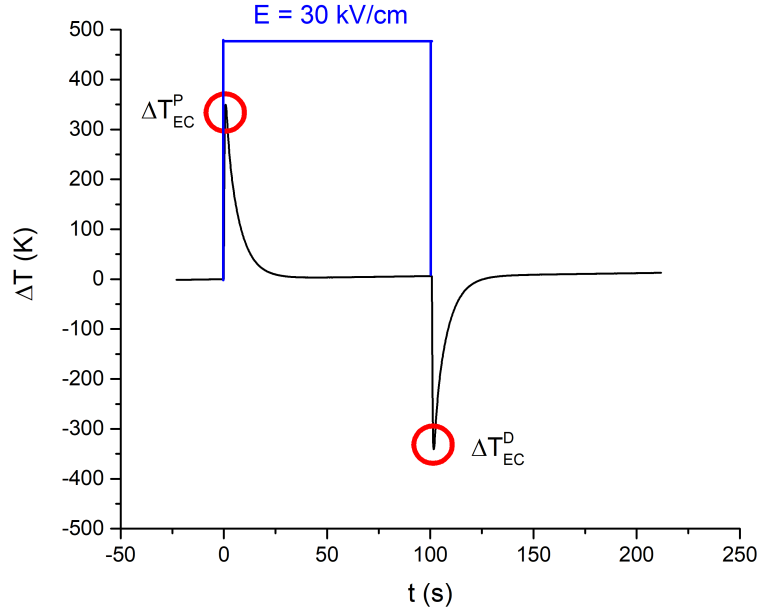


Figure 5.15: Electrocaloric effect of PMN at 30 kV/cm (black curve). Electric field used to induce EC effect is schematically depicted with blue curves. The circles denote the temperature changes during adiabatic polarization and depolarization.

The magnitude of these peaks ( $\Delta T_{EC}^P$  and  $\Delta T_{EC}^D$ ) does not correspond entirely to the true temperature change of the sample, but to a temperature change of the whole sample assembly, which includes electrical wires, thermistor, EC inactive parts of the sample and glue (used to attach the thermistor and electrical contacts to the sample). Hence, for a correct evaluation of the EC temperature change of the analysed sample and to allow a cross-comparison between the responses of different samples, a correction factor is usually implemented, which takes into account the heat absorbed by the electrical wires, glue and other EC non-active parts of the material. This correction factor is calculated as a ratio between the thermal masses that are not EC active versus the thermal mass of the

active part of the sample [38]. To allow comparisons with the literature, we adopted the correction-factor method for the cases where the field is applied for longer periods (200 s). To elucidate these points we performed numerical modelling using COMSOL Multiphysics (see Appendix 2).

Although we calculated the correction factor for each sample individually (see Table 5.3), we used a single correction factor in Fig. 5.16. Therefore, an average value of  $1.74 \pm 0.05$  was calculated from the correction factors of all the samples.

Table 5.3: Correction factors of the analysed PMN-100xPT samples.

| Material | Correction factor |
|----------|-------------------|
| PMN      | 1.7               |
| PMN-10PT | 1.76              |
| PMN-20PT | 1.76              |
| PMN-30PT | 1.72              |
| PMN-35PT | 1.69              |
| PMN-40PT | 1.74              |

In Fig. 5.16a we see that relaxor compositions (PMN and PMN-10PT) exhibit the largest EC effect. At electric field of 70 kV/cm, PMN exhibits an adiabatic temperature change during polarization and depolarization of 0.64 K. The corrected value, which is the intrinsic material response, is then calculated and estimated as 1.15 K. The EC effects of PMN-20PT, PMN-30PT and PMN-40PT, which show ferroelectric character, are according to Equation 1.1 significantly lower due to the lower polarization values observed in Fig. 5.6a. These results are consistent with the theoretical predictions, where it was postulated that materials with an established long-range polar order will not exhibit a large EC effect [139].

Already in PMN-10PT a careful observation of heating and cooling peaks reveals an asymmetry (sometimes denoted also as temperature irreversibilities [140]) between the two (see Fig. 5.16b). The magnitude of the temperature peak during adiabatic heating (0.623 K at 50 kV/cm) is 3.6 % higher compared to that measured during adiabatic cooling (0.60 K). Similar asymmetry was also observed in all the compositions with higher content of  $x$ . It is interesting to note that the asymmetry is most pronounced in PMN-40PT; the asymmetry in the peaks can be up to 9 % (at 50 kV/cm). While the origin of this asymmetry may be complex and many-featured, a possible explanation is the electrical loss mechanism, which may lead to heating of the sample during field application and is directly linked to the  $P(E)$  hysteresis area [2]. A discussion on the topic of electrical losses in connection with the EC effect will be held later in Section 5.4.3.

An interesting comparison can be made by observing the EC and electromechanical responses for the different PMN-100xPT composition. We can see in Fig. 5.16 that the EC effect drops significantly in the materials with a ferroelectric nature (PMN-20PT, PMN-30PT, PMN-35PT, PMN-40PT) in comparison to the materials with relaxor characteristics (PMN, PMN-10PT). Quite the opposite is observed in the direct piezoelectric effect  $d_{33}$  (red crosses in Fig. 5.12), which is a direct indicator of the ferroelectric long-range order; with PMN-20PT the direct piezoelectric response increases several fold with increasing PT content and stays at high levels in ferroelectric compositions (PMN-20PT, PMN-30PT, PMN-35PT, PMN-40PT). A high  $d_{33}$  reflects long-range polar order, which results in the high effective values of remanent polarization ( $P_r$ ), which according to Equation 1.3 lead to a high piezoelectric response. However, the long-range order reduces the concentration of dipoles available for switching, causing small values of  $\frac{\Delta P}{\Delta E}$  (as shown in Fig. 5.6), leading

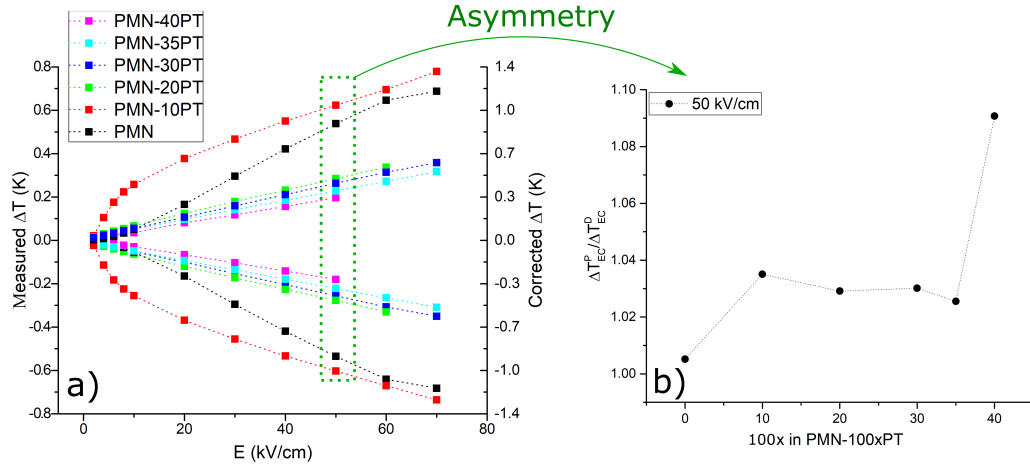


Figure 5.16: a) Magnitudes of EC effect as a function of electric field, b) the asymmetry between  $\Delta T_{EC}^P$  and  $\Delta T_{EC}^D$  at 50 kV/cm. The asymmetry is shown by calculating the ratio between  $\Delta T_{EC}^P / \Delta T_{EC}^D$ .

to a small EC temperature change according to Equation 1.5.

### 5.3 Material Selection for Proof-of-Concept Device

We have selected the optimal EC composition based on the four Figures of Merit (FOM):

- **Energy loss density -  $W_L$ .** Since the EC cooling should be efficient to compete with other cooling technologies, we have set the highest priority to this FOM [87]. The data provided in Fig. 5.9 was used to represent the electrical loss of the PMN-100xPT compositions. In addition, poor electrical efficiency causes additional problems reflected in the self-heating of the EC material, which will further be discussed in more detail in Section 5.4.3.
- **Electrocaloric response -  $\Delta T_{EC}^D$ .** The second most important figure was the temperature change during EC depolarization ( $\Delta T_{EC}^D$ ), during which the material cools below the initial temperature. The corrected values of  $\Delta T_{EC}^D$  in Fig. 5.16 were used to represent the EC effect of the analysed materials.
- **Heat transport -  $\tau$ .** The rate of the heat transfer determines the operational frequency and, consequently, the cooling power of the device. The faster the heat-transfer rate, the higher the cooling power [141]. The parameters describing the transport properties, which were incorporated in the FOM, are shown in Table 5.2.
- **Electromechanical response -  $s_1^{max}/E_0(E_0)$ .** In our opinion the transverse electromechanical coefficient is the least important FOM. The reason is that the bending of the cantilevers can be easily adjusted by tuning the dimensions of the cantilevers (see Eq. 1.4). For example, the deflection is quadratically proportional to the length of the cantilever, meaning that a low EM activity can be compensated by making the cantilevers longer. Therefore, in the final FOM (see below Equation 5.4) we have reduced the importance of this parameter by root squaring the transverse EM coefficient. The coefficient values used for the FOM calculation are shown in Fig. 5.14.

Based on the described facts we defined a simple FOM function:

$$FOM_{PMN-100xPT} = \frac{\sqrt{\frac{s_1^{max}}{E_0}} \Delta T_{EC}^D}{W_L \tau} \quad (5.4)$$

The data ( $s_1^{max}/E_0(E)$ ,  $\Delta T_{EC}^D(E_0)$ ,  $\tau$ ,  $W_L(E)$ ) obtained in Section 5.2 were compacted into the matrix form and FOM was calculated as a function of the electric field, which resulted in a plane of FOM values shown in Fig. 5.17. The derivative of the plane was taken to determine the stationary points which should correspond to the maximum and minimum values. The maximum value of FOM represent the optimally selected conditions (composition and electric field) for the device.

The FOM analysis in Fig. 5.17 shows that PMN is the most suitable material for the cooling device, seen as a peak in FOM at  $x=0$  and  $E=40$  kV/cm. For PMN the energy losses ( $W_L$ ) were the lowest, while the EC effect was comparable with PMN-10PT, which exhibits the highest EC response of all the compositions. The thermal transport properties of PMN were the worst of all compositions, but as was shown in the models and also experimentally in Section 5.6, the heat transport in our device is governed by the thermal contacts between the cantilevers. Therefore, thermal properties inherent to the composition might be less relevant than those related to the contact between the cantilevers. Lastly, the transverse EM response is also not the highest in PMN, but this does not pose as a problem since the deflections of the cantilever elements are quadratically dependant on the geometrical properties. A important benefit of electrostrictive materials is that they do not need to be poled prior to use (in contrast with ferroelectric piezoelectric materials).

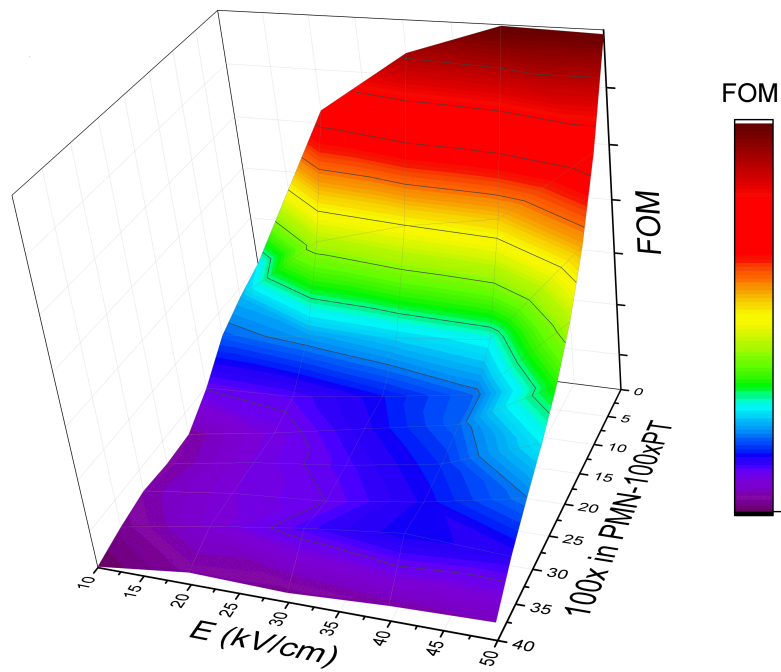


Figure 5.17: The FOM (Eq. 5.4) calculated with the data obtained in Section 5.2 and plotted versus electric field and composition  $x$ . The red colour indicates high FOM values, while blue represents low values.

## 5.4 PMN Ceramics Under Device-Like-Field-Cycling Conditions

After selecting PMN as the optimal composition within PMN-100xPT material system for the integration into the cooling device, we next analyzed the PMN EC performance using electric-field driving conditions that are expected in cooling-device environments. Considering that the EC material is expected to sustain a large number of electric field cycles with large magnitudes (to achieve large EC cooling effects) without fatigue, we were particularly interested in the field cycling stability of the EC response of PMN ceramics. The work described in this section has been published in *Acta Materialia*, Issue 169, Page 275 in Year 2019 with the co-authors: Lovro Fulanović, Marko Vrabelj, Mojca Otoničar, Hana Uršič, Alexandra Henriques, Ching-Chang Chung, Jacob L. Jones, Barbara Malič, Zdravko Kutnjak and Tadej Rojac.

### 5.4.1 Emergence of excessive heating

To remind the reader, we performed fatigue tests on PMN ceramics by driving the sample using square waveforms of 2 Hz of frequency (field hold time 0.25 s, waveform is shown in Materials and Methods, Fig. 4.5). This is further referred to as the EC cycling. After each set consisting of 1000 of such EC cycles, we performed test cycles to measure the EC response by increasing the field hold time to 200 s.

Fig. 5.18 shows two test cycles before the EC cycling (virgin, black curve) and after  $7 \cdot 10^4$  field EC cycles (red curve).

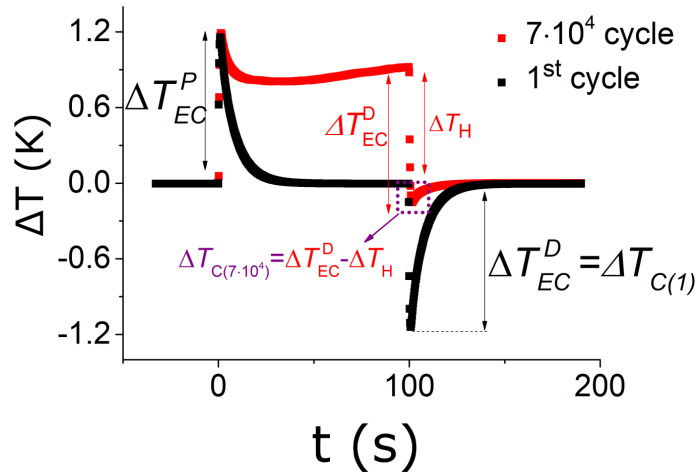


Figure 5.18: Emergence of excessive heating during the EC cycling of PMN at room temperature. EC temperature response during the first test cycle (black) and after applying  $7 \cdot 10^4$  EC cycles (red). Here,  $\Delta T_{EC}^P$  denotes the temperature change upon adiabatic polarization,  $\Delta T_{EC}^D$  denotes the temperature change upon adiabatic depolarization of the sample and  $\Delta T_H$  indicates the excessive heating emerging with EC field cycling. The effective cooling ( $\Delta T_{C(N)}$ ) is defined as the difference between  $\Delta T_{EC}^D$  and  $\Delta T_H$  at cycle number N.

The EC temperature change of 1.2 K of the virgin sample is consistent with the reported data for PMN using similar electric-field conditions. On the other hand, an obvious excessive heating ( $\Delta T_H$ ) was clearly identified during the isoelectric enthalpic heat transfer



after the sample was exposed to  $7 \cdot 10^4$  EC cycles. As is clear from the temperature response,  $\Delta T_H$  manifests itself as an offset temperature, preventing the material from cooling to its initial temperature during the isoelectric point (field hold). Therefore, the emergence of excessive heating ( $\Delta T_H$ ) with prolonged EC cycling reduces the effective cooling ( $\Delta T_C$ ) of the EC material during adiabatic depolarization ( $\Delta T_{EC}^D$ ), such that  $\Delta T_C = \Delta T_{EC}^D - \Delta T_H$ . Further cycling eventually leads to a breakdown of the sample, which was typically observed after the emergence of the excessive heating.

To quantify the data, we determined different EC parameters as a function of the number of EC cycles ( $N$ ), including the normalized EC heating effect ( $\Delta T_{EC(N)}^P / \Delta T_{EC(1)}^P$ ), normalized EC cooling effect ( $\Delta T_{EC(N)}^D / \Delta T_{EC(1)}^D$ ), normalized effective cooling ( $\Delta T_{C(N)} / \Delta T_{C(1)}$ ) and excessive heating ( $\Delta T_H$ ). The normalized values were determined relative to that at the first cycle ( $N=1$ ). All these parameters are shown in Figure 5.19 as a function of the number of EC cycles. The normalized  $\Delta T_{EC}^P$  is fairly constant up to  $6 \cdot 10^4$  cycles, after which it slightly increases. On the other hand, the normalized  $\Delta T_{EC}^D$  decreases with EC cycling up to  $6.5 \cdot 10^4$  EC cycles, after which it starts to increase. The normalized effective cooling  $\Delta T_C$  decreases during the whole cycling procedure to 10 % of the initial value. Finally, the data show that the onset of the excessive heating  $\Delta T_H$  is at  $4 \cdot 10^4$  cycles, after which the sample shows an abrupt fatigue with increasing  $N$ .

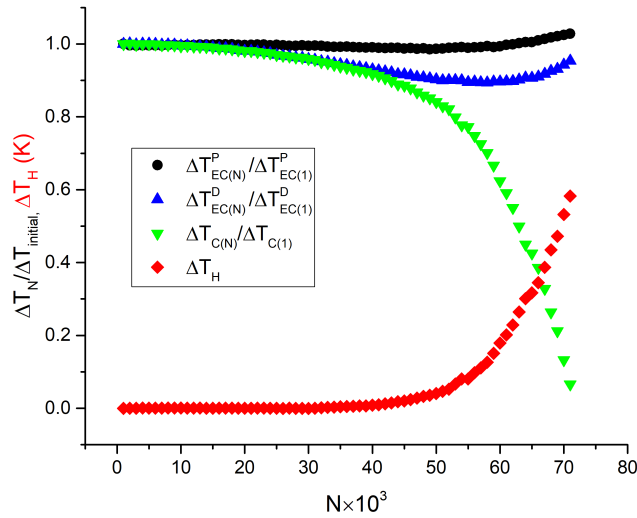


Figure 5.19: Degradation of EC response of PMN as a function of EC cycle number ( $N$ ).  $\Delta T_{EC(N)}^P / \Delta T_{EC(1)}^P$ ,  $\Delta T_{EC(N)}^D / \Delta T_{EC(1)}^D$  and  $\Delta T_{C(N)} / \Delta T_{C(1)}$  are the excessive heating, adiabatic polarization, adiabatic depolarization and effective cooling normalized on the first EC cycle ( $N=1$ ).  $\Delta T_H$  is the absolute value of excessive heating.

So far we have shown and analysed the data related to the EC effect of PMN measured during the test cycle. In addition to that, we also directly monitored the temperature of the sample during the 2-Hz EC cycling. The results are shown in Fig. 5.20. Here, the black curve shows the temperature of PMN during the initial EC cycling, i.e., between the first cycle and EC cycle number 1000, while the red curve shows the temperature of PMN between EC cycle number  $6.9 \cdot 10^4$  and  $7 \cdot 10^4$  (where significant self-heating effects were observed). Unlike the behaviour during the initial EC cycling (black curve) where an average temperature rise ( $\Delta T_R$ ) above the initial temperature is 0.125 K, the sample

after  $6.9 \cdot 10^4$  EC cycles develops a progressive increase in its average temperature, slowly converging with an increasing number of EC cycles, reaching the final value of  $\Delta T_R = 0.760$  K. We attribute this temperature evolution to the excessive heating (see Figure 5.19, red curve), which contributes to the total heating of the sample, becoming even larger than the EC cooling effect itself (hence a steady increase in the average sample temperature is observed, Figure 5.20, red curve). The increase in temperature during 2-Hz-EC cycling shows similarities to the self-heating observed in ferroelectrics with high electrical losses [89]. The self-heating will be discussed in detail in Section 5.4.3

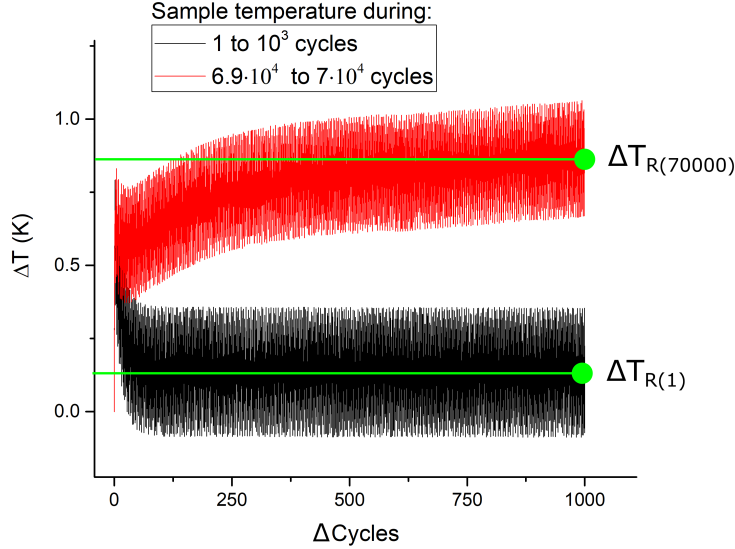


Figure 5.20: Temperature variations as a function of the number of EC cycles; the black curve shows the temperature variations during initial cycling, i.e., between the first and EC cycle number 1000, while the red curve shows the temperature variations between EC cycle number  $6.9 \cdot 10^4$  and  $7 \cdot 10^4$ . An average temperature rise ( $\Delta T_R$ ) during the two EC cycling periods (denoted in  $\Delta T_R$  in brackets) was determined as shown by the green horizontal lines.

To further analyse the self-heating, we compare in Fig. 5.21,  $\Delta T_H$  measured during test cycles (see Fig. 5.18), along with the average temperature measured during EC cycling ( $\Delta T_R$ , see Fig. 5.20). The onset of  $\Delta T_H$  clearly occurs at the cycle number  $4 \cdot 10^4$ , while  $\Delta T_R$  increases throughout the whole cycling procedure with a break in the slope close to  $4 \cdot 10^4$  cycles where  $\Delta T_H$  starts to increase abruptly. This indicates that we have two contributions to the fatigue denoted and colour coded as regime I and regime II in Fig. 5.21. The first contribution (regime I) manifests as an increase in the average temperature of the sample which occurs already in the initial cycles and can be clearly visible as a steady increase in  $\Delta T_R$  up to  $4 \cdot 10^4$  cycles. The second contribution (regime II) manifests as an offset in temperature during test cycle ( $\Delta T_H$ ), clearly appearing at  $4 \cdot 10^4$  cycles and further raising with increasing number of cycles. This effect also contributes to an abrupt increase in  $\Delta T_R$  above  $4 \cdot 10^4$  cycles.

The steady increase of temperature in regime I is probably due to the asymmetry in the adiabatic heating and cooling, which is increasing with the cycle number, as shown in Fig. 5.19. We see in this figure that the adiabatic cooling is reduced to 0.9 of the pristine value, while heating roughly stays equal to the initial value. This effectively means that as the number of cycles increases the sample heats during adiabatic polarization up more

than it is cooled during adiabatic depolarization, leading to an increase in the average  $T$  of the sample as cycling proceeds. In the upcoming Section 5.4.1.4 we will investigate and show that the rise of asymmetry is related to the gradual formation of the ferroelectric order in PMN with field cycling. The origin of heating in regime II, which is of a Joule heating nature, will be analysed in the next section.

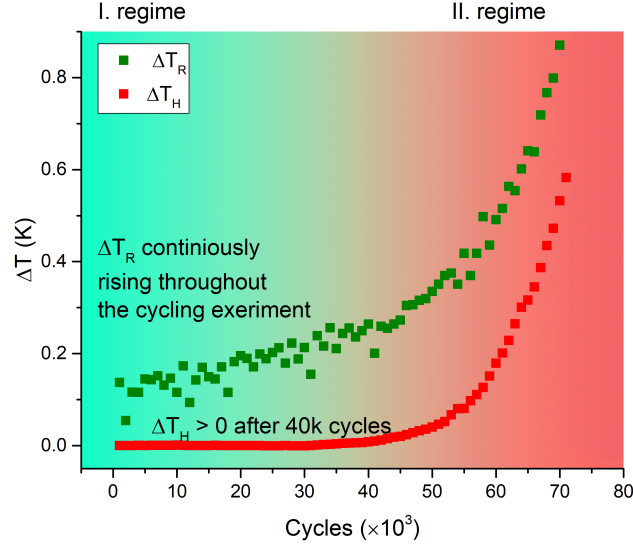


Figure 5.21: Excessive heating as a function of number of EC cycles. The red curve shows the  $\Delta T_H$  values measured during test cycle and the green the temperature rise ( $\Delta T_R$ ) during 2-Hz cycling.

#### 5.4.1.1 Origin of increased electrical conductivity

To identify the source of  $\Delta T_H$ , which significantly diminishes the effective cooling ability of the PMN, we monitored the electrical current during every test cycle simultaneously with the temperature change of the sample. Note, that due to the previous sample's breakdown, we here show the results on a new sample where the onset of excessive heating occurs at a somewhat lower number of cycles, i.e.,  $2 \cdot 10^4$  cycles [142].

The current-versus-time curves of PMN before and after EC cycling ( $2.8 \cdot 10^4$  cycles) are shown in Fig. 5.22. These curves are characterized by sharp peaks, when the field is either applied or removed, which are related to the polarization and depolarization currents, respectively (see, e.g., Figure 5.22a, black curve).

While the field is maintained at a constant value, the electrical current in the first test cycle (virgin) is practically zero (Figure 5.22a, black curve), confirming the insulating nature of the PMN sample. In contrast, the current of the fatigued sample (Figure 5.22a, red curve) continues to increase during the isoelectric stage until it reaches a nearly steady value of 216 nA, suggesting that a significant leakage current flows through the sample. At this plateau, i.e., as the current averages over the last 10 s of field holding (see  $I_L$  on Figure 5.22a), we define the leakage current, which is plotted as a function of EC cycles in Figure 5.22b. Note in this figure that during the first EC cycle number  $1.9 \cdot 10^4$  the leakage current  $I_L$  is close to zero (i.e., below the nA range), however, it increases dramatically with further cycling, reaching a value of 216 nA after  $2.8 \cdot 10^4$  cycles. This corresponds to

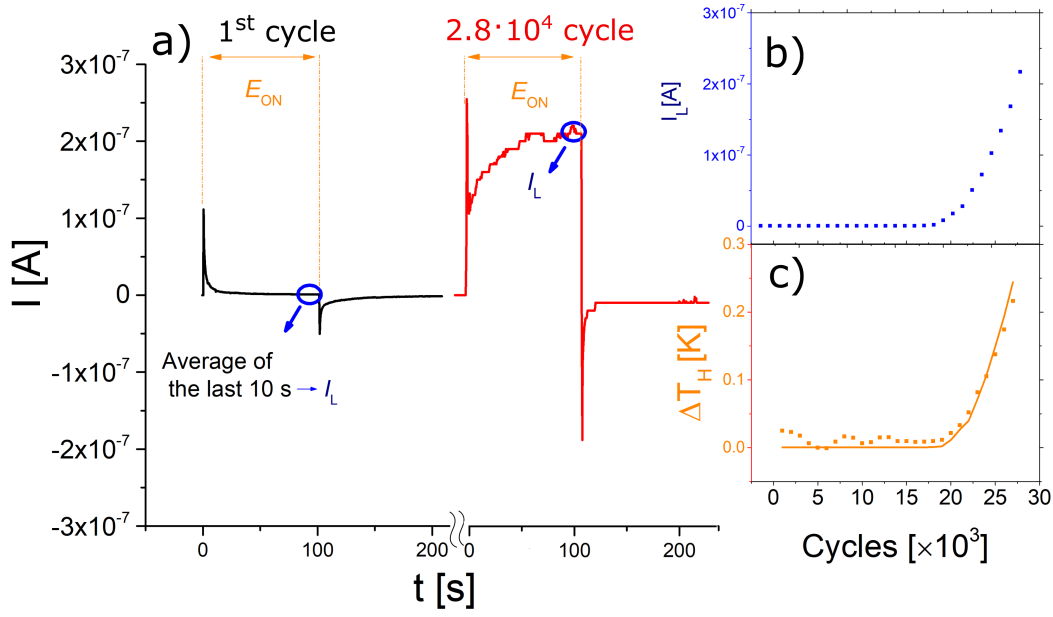


Figure 5.22: Correlation between electrical current and Joule heating observed during test cycles. The current values were measured at electric field ( $E_{ON}$ ) of 70 kV/cm at room temperature. a) Electrical current versus time measured during the first test cycle (black) and after 2.8·10<sup>4</sup> EC cycles (red), b) average electrical current ( $I_L$ ) versus number of EC cycles ( $I_L$  was determined from current points in the last 10 s before switching off the field; see arrows in panel (a)) and c) temperature change due to excessive heating ( $\Delta T_H$ ) plotted versus number of cycles; dots correspond to measured data, while the solid line corresponds to the calculated data (see text for details).

an approximately three-orders-of-magnitude decrease in the specific electrical resistivity of the PMN, i.e., from 10<sup>14</sup> Ωm (virgin) to 6.4·10<sup>8</sup> Ωm (after 2.8·10<sup>4</sup> EC cycles).

To correlate the excessive heating with the measured leakage current, in Figure 5.22c we plot  $\Delta T_H$  as a function of EC cycles (squares). It should be noted that the leakage current (Figure 5.22b) and  $\Delta T_H$  (Figure 5.22c) show the same trend as the function of EC cycles, suggesting that the excessive heating developed after 1.9·10<sup>4</sup> EC cycles is indeed has a Joule origin, thus related to the observed increased electrical conductivity of the sample during cycling. To confirm this correlation, we modelled the excessive heating using the Joule-heating model reported in Refs [58], [143], from which we calculated the excessive heating ( $\Delta T_H$ ) from the measured leakage current data ( $I_L$ ). This equation assumes that the heat generated at a specific cycle number ( $N$ ) is caused by leakage currents flowing through the sample. The total heat generated, in part, heats up the sample and, in part, dissipates into the surroundings:

$$\alpha A \Delta T + mc_p \frac{dT}{dt} = UI_{L(N)}. \quad (5.5)$$

In the equation  $\alpha$  is the heat-transfer coefficient,  $A$  is the surface of the sample,  $m$  is the mass of the sample,  $c_p$  is the specific heat of the sample,  $U$  is the voltage applied to the sample,  $I_{L(N)}$  is the leakage current and  $T$  is temperature.

Figure 5.22c confirms that the calculated  $\Delta T_H$  values (full line) fit well with the measured  $\Delta T_H$  values (squares). The small deviations are most probably due to the temper-

ature dependence of the used input parameters (i.e., the heat-transfer coefficient, specific heat capacity) and due to the simplifications associated with the time variation of the electrical currents (i.e., only an average value of the leakage current  $I_L$ , determined from data points of the last 10 s before switching off the field, was used in the model). The results thus demonstrate that the excessive heating of PMN during EC cycling develops due to a reduction in the electrical resistivity of the sample.

To explore the observed increase in the electric current developed during EC cycling on a local scale, we present in Fig. 5.23 the conductive atomic-force microscopy (c-AFM) maps of the virgin and cycled samples. The virgin sample shown in Fig. 5.23a exhibits a low level of local current signal mainly reflecting the electrical noise from the AFM pre-amplifier (typically 1 pA) [144]. It is clear in Figure 5.23b, however, that the cycled sample ( $N = 3 \cdot 10^4$ ) exhibits an increased current signal (white regions), particularly at the grain boundaries, suggesting an elevated grain-boundary conductivity in the fatigued samples. This is consistent with the increased current measured macroscopically in the cycled samples with  $N > 2 \cdot 10^4$  (see Figure 5.22). Therefore, we attribute the origin of the Joule heating and thus the EC fatigue behaviour of the PMN to an increase in the grain-boundary conductivity, progressively building up during the EC cycling.

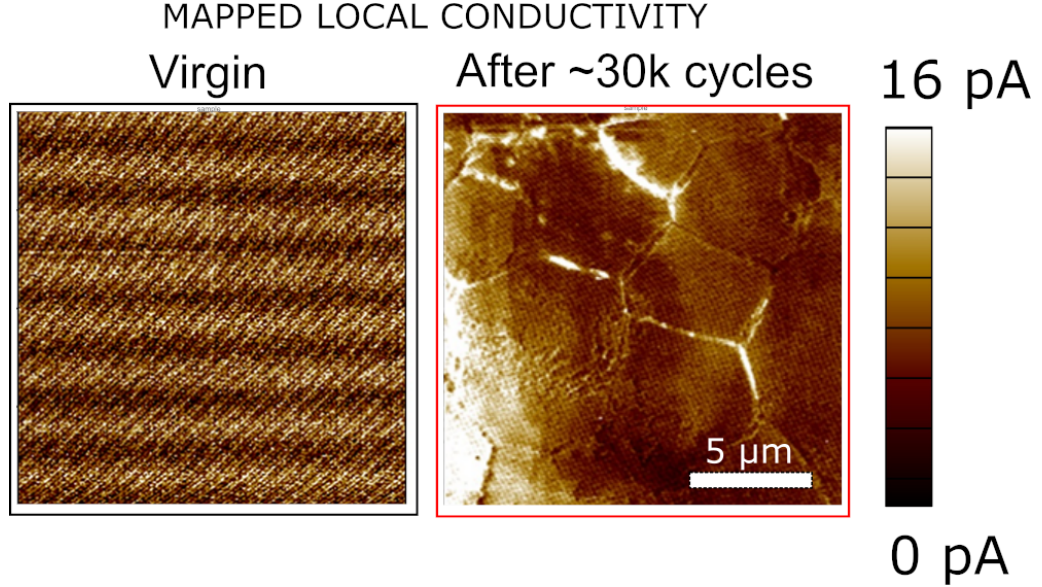


Figure 5.23: Conductivity mapping with the cAFM. a) the virgin sample b) sample with notable Joule heat cycled to  $3 \cdot 10^4$  cycles.

#### 5.4.1.2 Rejuvenation of the fatigued state

The literature reports on several cases where degraded properties of samples cycled with unipolar fields could be rejuvenated by heating the fatigued samples at elevated temperatures [91], [145], [146]. We thus conducted EC fatigue tests on PMN at room temperature and checked for rejuvenation. The results are shown in Fig. 5.24. After the sample exhibited a notable degradation in the EC properties, we stopped the cycling and heated the sample to 115 °C for 30 min. After this heating step, the sample fully regained its initial effective cooling capability, i.e., the Joule-heating effect vanished (see arrows in Fig. 5.24). This was also confirmed with cAFM imaging, i.e., upon rejuvenation the grain boundaries showed again a resistive behaviour (the c-AFM image of the rejuvenated sample is not shown as it actually reflects current noise similarly as observed for the virgin sample in

Fig. 5.24a).e. We have repeated this process several times. In each case the effective cooling of PMN was fully rejuvenated. The results indicated that the degradation is fully reversible by heating the sample, probably suggesting a redistribution of charge defects responsible for the increased grain-boundary conductivity of fatigued samples (further discussion is provided in Section 5.4).

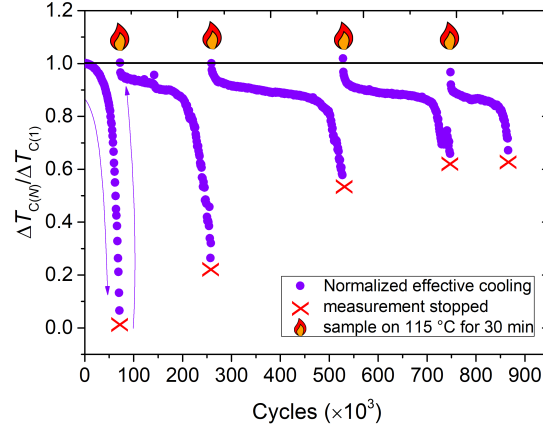


Figure 5.24: Rejuvenation experiments. A sample was cycled, fatigued and rejuvenated several times. The plot shows the effective cooling normalized ( $\Delta T_{C(N)}$ ) on the initial value of effective cooling ( $\Delta T_{C(1)}$ ). Red  $\times$  symbol shows where the cycling was paused and flame symbol represents the moment the samples was rejuvenated. Arrows indicate the degradation and the rejuvenation of the samples.

### 5.4.1.3 EC cycling at 50 °C

To further investigate the temperature dependence of the EC fatigue behaviour of the PMN we performed cycling experiments at a slightly elevated temperature of 50 °C (Figure 5.25). Under identical electric-field driving conditions to those used at room temperature, the sample did not exhibit any significant Joule heating effects, even after  $5.5 \cdot 10^5$  EC cycles (note that the Joule heating during room-temperature cycling appeared at within  $10^5$  EC cycles, Fig. 5.18). The magnitudes of the adiabatic polarization and depolarization, which are 1.4 K, remained constant and the effective cooling was thus close to unity throughout the whole cycling procedure. In the literature several reports demonstrate that the fatigue at elevated temperatures is very often less severe [147], [148]. This is ascribed to the lower spontaneous polarization values and larger mobility of domain walls. However, in addition to thermal effects, other origins may be responsible for the absence of the fatigue associated with Joule heating when cycling PMN at 50 °C. These other possibilities, related to the transformation to a ferroelectric phase, are described in detail in the following chapter.

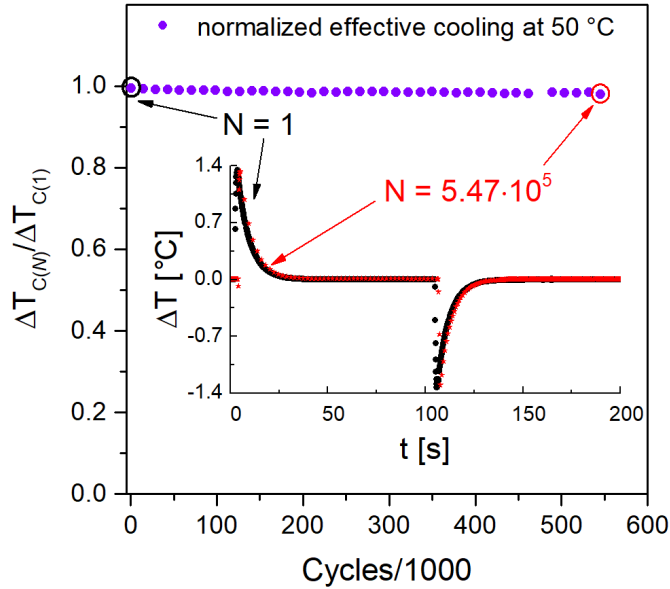


Figure 5.25: EC properties of PMN cycled at 50 °C. The normalized effective cooling ( $\Delta T_{C(N)}/\Delta T_{C(1)}$ ) stays unchanged upto  $5 \cdot 10^5$  cycles. The insets shows the initial EC response in time domain and EC response after  $5 \cdot 10^5$  cycles.

### 5.4.1.4 Electric-field-induced ferroelectric phase

As seen from the increase in the average temperature of the sample during EC cycling (green curve in Fig. 5.21) we can identify two sources of heating in PMN. One is the increased leakage current which leads to Joule heating in regime II in Fig. 5.21. Joule heating does not allow the sample to cool down to initial temperature during isoelectric, enthalpic heat transfer, which lowers the effective cooling and provokes the increase of the average sample  $T$ , particularly after  $4 \cdot 10^4$  EC cycles (compare the two curves in Fig. 5.21). The second source of heating is observed already from the beginning of the cycling where the average sample  $T$  slightly raises up to  $4 \cdot 10^4$  EC cycles (green curve in Fig. 5.21, regime I). The steady increase is ascribed to the asymmetry between the heating and cooling, which

causes accumulation of the heat and thus heating of the sample. Note that up to about  $4 \cdot 10^4$  cycles we can exclude the heating due to the increased electrical conductivity. The other possibility to explain the behaviour in regime I and which contributes to electrical loss are phase transformations and ferroelectric domains [63], [89], [149].

Since at room temperature PMN is in an ergodic relaxor phase the presence of ferroelectric/ferroelastic domains and domain walls are in principle not expected. However, the high electric fields used in this study opened a possibility of field-induced structural changes [150], [151].

To investigate this possibility *in-situ* X-Ray diffraction analysis was employed. We analysed the diffraction patterns at room temperature and 50 °C as a function of the electric field cycles (*in-situ*), as shown in Fig. 5.26. The structural evolution by cycling at room temperature reveals a progressive splitting of the  $111_{pc}$  peak during cycling, implying the emergence of a rhombohedral-like phase. We note that a shoulder adjacent to the main  $111_{pc}$  peak is already observed after 1000 cycles (Figure 5.26a, 950-1000) and further evolves into a clear peak with increasing EC cycling (Figure 5.26a, 4950-5000), suggesting that the phase transformation to the rhombohedral phase is progressive. In contrast to this room-temperature cycling, when the field cycling is conducted at 50 °C (Figure 5.26b), no major differences can be observed in the XRD patterns throughout the entire cycling procedure. Within the resolution limit of the method, the symmetry remains pseudo-cubic, with no tendency for rhombohedral distortion, confirming that only the RT cycled PMN was subjected to a field-induced phase transformation to the rhombohedral-like state. This is consistent with the observed fatigue behavior emerging during RT cycling and its absence during cycling at 50 °C, suggesting that the phase transformation is the origin of the fatigue.

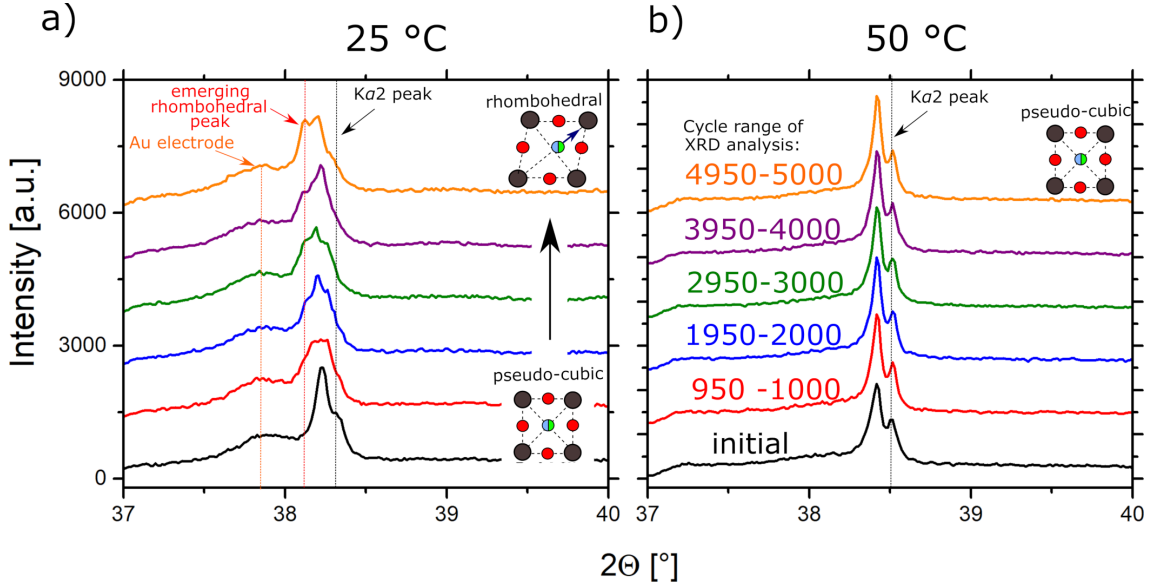


Figure 5.26: *In-situ* XRD pattern recorded during EC cycling at a) room temperature and b) 50 °C. The insets schematically show crystal structure as inferred from the XRD patterns. The numbers in panel b represent the cycle interval in which the XRD pattern was recorded.

To investigate whether the electric-field induced ferroelectric phase is metastable, we recorded XRD patterns after cycling (at zero-field conditions). Figure 5.27 shows XRD pat-



terns after 1 (black) and 30 (red) minutes from the moment the electric-field was switched off. After 1 minute the  $111_{pc}$  peak splitting is still clearly visible, indicating the presence of the rhombohedral phase. In contrast, after 30 minutes, the splitting disappears, confirming the relaxation of the rhombohedral phase back to the initial pseudo-cubic phase characteristic for virgin samples. The observed metastability complies with the observed rejuvenation of the fatigued samples (see Fig. 5.27).

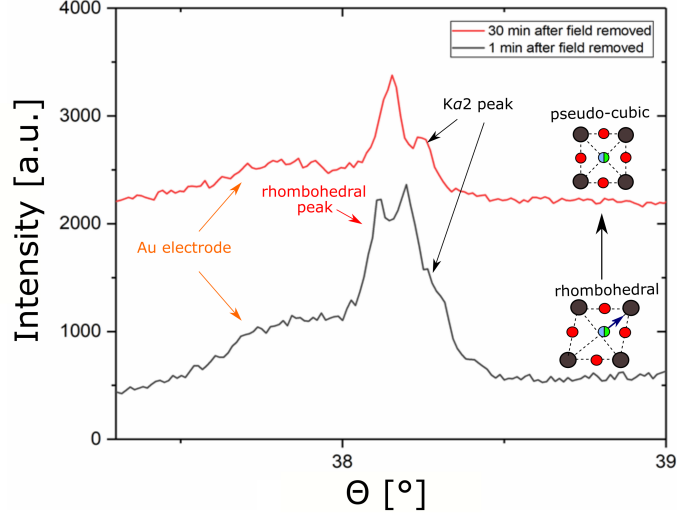


Figure 5.27: Room-temperature XRD patterns recorded one minute and 30 minutes after cycling.

To investigate the manifestation of the ferroelectric phase at the microscopic level, we studied the virgin and fatigued sample with a piezo-response force microscope (PFM). Figure 5.28 shows the PFM out-of-plane amplitude images of the virgin and fatigued samples (after  $1.1 \cdot 10^5$  cycles). The small features observed in the amplitude PFM image of the virgin sample can be attributed to clusters of electromechanically active polar nanoregions (PNRs), as previously suggested for Pb-based relaxor materials [124], while in the cycled sample larger areas are observed. The latter is an indication of the coalescence of the PNRs into ferroelectric domains, consistent with the appearance of a rhombohedral lattice distortion during cycling (Fig. 5.26).

Figure 5.28b shows the PFM phase hystereses of the virgin and fatigued sample. The black and red crosses in Figure 5.28a show the locations of the local hysteresis-loop measurements. While the virgin sample shows no hysteresis, the EC cycled samples exhibit a hysteretic response, typical for ferroelectric domain switching. At the local level, PFM thus confirms the switching characteristic of the ferroelectric phase in the cycled sample.

Such a coalescence of PNRs to ferroelectric-domain-like structures under an applied electric field was previously observed by PFM and PMN-10PT crystals by Bokov et al. [117]. However, they could not unambiguously confirm that this is not a surface effect. In the upcoming text we will illustrate that in our case this transformation to ferroelectric phase is indeed a bulk phenomenon.

Despite indicating the development of a ferroelectric rhombohedral phase in PMN during EC cycling, we note that both XRD and PFM are surface-sensitive methods. To show that the observed changes during cycling are not confined to the surface of the samples, we next analysed polarization vs. electric field  $P(E)$  and strain vs. electric field  $x(E)$  hystereses loops during EC cycling of PMN along with the direct piezoelectric response.

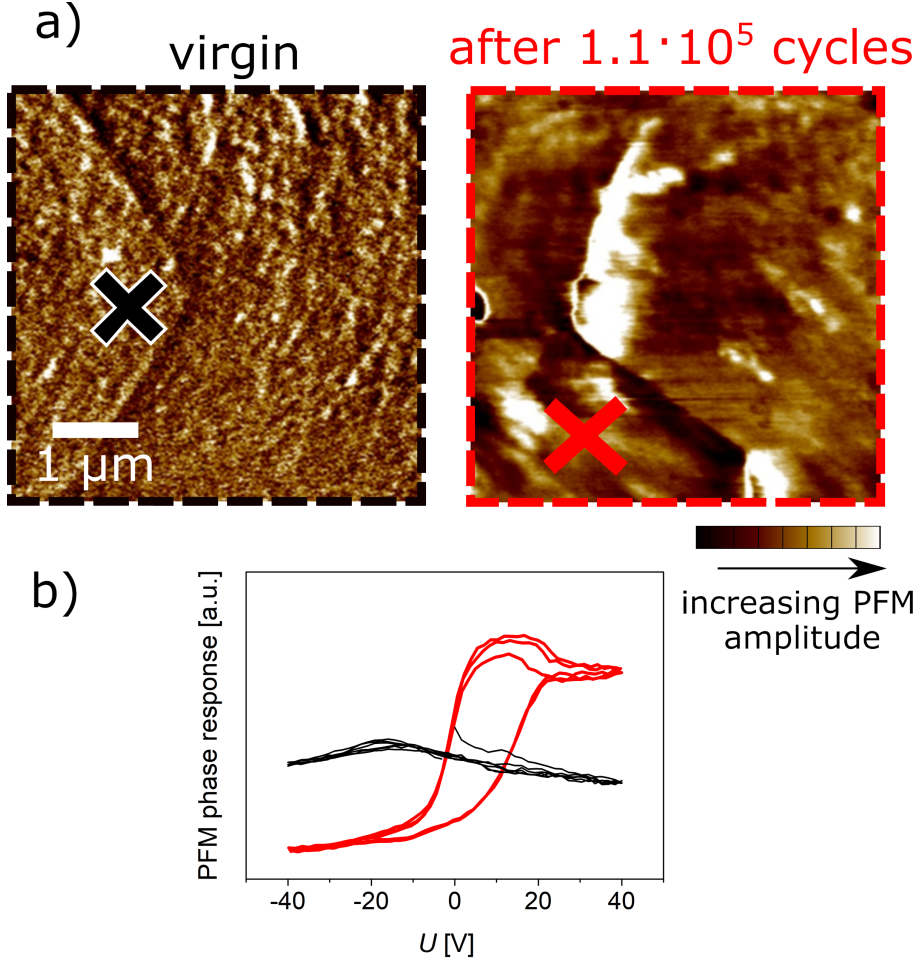


Figure 5.28: PFM response of the virgin and cycled PMN sample. a) PFM out-of-plane amplitude image of the virgin (black-left) and cycled sample (red-right). b) PFM phase hysteresis loop obtained on a virgin (black) and cycled (red) PMN sample at the location depicted with a cross in the two samples in panel a.

The hysteresis loops of the virgin PMN sample (Fig. 5.29a, black) show features typical for the relaxor behavior of this material, i.e., a saturated and weakly hysteretic  $P(E)$  loop with a maximum polarization of  $30 \mu\text{C}/\text{cm}^2$  along with a quadratic-like  $x(E)$  loop that saturates at higher fields (Figure 5.29b, black). This strain-field loop corresponds to the electrostrictive response of ergodic PMN. In contrast, the  $P(E)$  loops measured after  $10^4$  cycles (Figure 5.29a, red) show distinct features of ferroelectric switching, marked by the appearance of hysteresis in both the polarization and strain response. While the hysteresis in the  $P(E)$  loop can be in part affected by the increased leakage current observed in fatigued samples (see Fig. 5.22b), a more indicative signature of the appearance of a ferroelectric phase can be seen in the typical butterfly-like  $x(E)$  hysteresis loop (Figure 5.29b, red), characteristic for the switching of ferroelectric/ferroelastic domain walls. The strain loops thus change from an electrostrictive-like quadratic response, typical for PMN, to that resembling the responses of ferroelectric/ferroelastic materials.

Finally, measurements of the direct piezoelectric response confirmed that the virgin sample is piezoelectrically inactive ( $d_{33}=0 \text{ pC/N}$ ), as expected for ergodic PMN, while a clear and large direct piezoelectric response ( $d_{33}=200 \text{ pC/N}$ ) was measured immediately

after exposing the sample to  $10^4$  EC cycles. This last results truly confirm that a ferroelectric phase develops during EC cycling and that unipolar EC cycling at some point poles the samples.

The gradual formation of ferroelectric long-range order also explains the heating of the sample within the regime I; it was shown in Section 5.2.4, Fig. 5.16b that ferroelectric materials due to the ferroelectric losses exhibit an asymmetry in the temperature change during adiabatic polarization and depolarization. We have shown in this Section that also in PMN this asymmetry develops with cycling (Fig. 5.19) and leads to an accumulation of heat and self-heating (Fig. 5.20) effects that are detrimental to the cooling properties of EC materials.

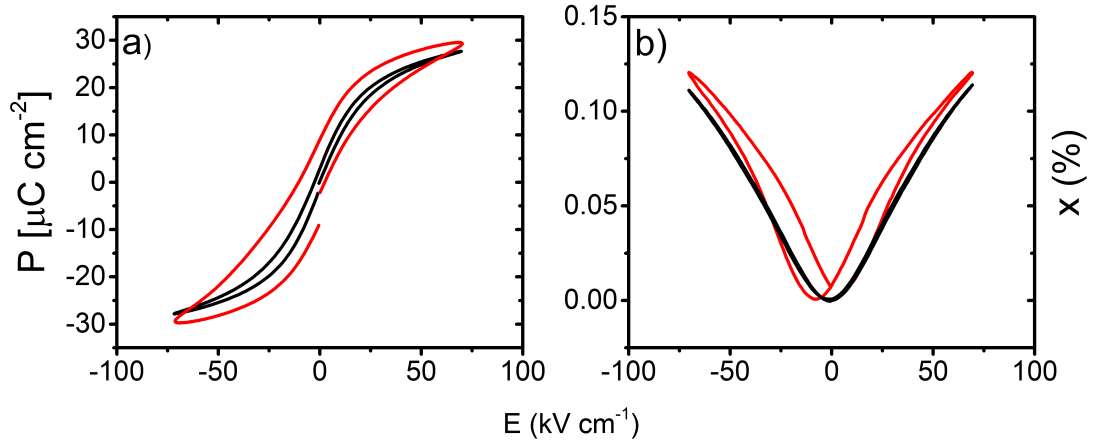


Figure 5.29:  $P(E)$  and  $x(E)$  loops measured before (black) and after fatigue (red,  $10^4$  cycles) in PMN.

#### 5.4.2 Mechanisms responsible for the EC fatigue in PMN

In this section we explain the possible mechanisms leading to the fatigue of PMN during EC cycling. As stated in Section 5.4.1.1, we observed two regimes of fatigue: first is present from the first cycle and is manifested as an asymmetry between the adiabatic heating and cooling (regime I in Fig. 5.21). This mechanism most probably stems from the field-induced phase transition to a ferroelectric phase. The formation of long-range order reduces the portion of the material cooperating in the switching process, which significantly changes the EC effect. The second mechanism occurs later (regime II in 5.21), in the case shown before, at  $4 \cdot 10^4$  cycles; this mechanism has a Joule origin, meaning we can ascribe it to the change of resistivity of the material. Agglomeration of point defects at the grain boundaries is often discussed as a typical symptom of fatigue in ferroelectrics that are cycled using unipolar electric fields [145], [152], which was also used in our study. This scenario assumes that the field-induced surface polarization charges at the grain boundaries are not entirely screened during cycling, due to the random grain orientation inside the ceramic grain matrix, resulting in depolarizing fields that act as a driving force for point-defect migration. As the field cycling continues, electrostatic and elastic driving forces drive the defects to cumulatively agglomerate at the grain boundaries, presumably resulting in an increased boundary conductivity and domain-wall pinning effects [15], [153], [154].

We propose here that a similar mechanism governs the fatigue behaviour in PMN cycled at room temperature. Our results suggest that the key element of the fatigue is

the cycling-induced phase transformation to a rhombohedral ferroelectric phase. Once this phase appears, the presence of the spontaneous polarization can induce effects, such as the agglomeration of point defects at the grain boundaries, previously observed in, e.g., ferroelectric  $\text{Pb}_{0.99}[\text{Zr}_{0.45}\text{Ti}_{0.47}(\text{Ni}_{0.33}\text{Sb}_{0.67})_{0.08}]\text{O}_3$  cycled using unipolar fields [145]. In the reverse scenario, it might also be the case that the agglomerated defects stabilize the ferroelectric domains inside the grains, possibly explaining the unusual metastability of the ferroelectric phase in ergodic PMN under off-field conditions (see Fig. 5.27; an analogy is the imprint in hard ferroelectrics, which is stabilized by defect ordering).

In addition, the temperature and time-dependent rejuvenation under field-off conditions (see Fig. 5.24) is consistent with the defect depletion from grain boundaries and thus the transition to a resistive grain-boundary state, as observed by c-AFM (see Fig. 5.23). Conversely, driving the PMN at 50 °C, where no phase transition occurred (Fig. 5.25), reduces the tendency for fatigue, probably because of the absence of any spontaneous polarization. This is consistent with the fatigue resistance of a number of relaxor materials, such as  $\text{Pb}_{0.905}\text{La}_{0.095}(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$  and  $0.91\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3\text{-}0.06\text{BaTiO}_3\text{-}0.03\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$  [155]. Interestingly, in the ergodic relaxor  $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$  a similar excessive heating as a result of EC cycling was observed; in this material a similar relaxor-to-ferroelectric transition as in PMN is expected [94]. It is thus tempting to infer that the field-induced phase transformation to the ferroelectric phase, initiating the migration of defects and increasing the conductivity of the sample, could be a more general fatigue mechanism in ergodic relaxors under conditions which induce a ferroelectric-like state.

Since according to our results the fatigue behavior of PMN appears to be tightly linked to its field-induced ferroelectric phase transformation, we propose here a tool for determining the field excitation conditions for PMN in EC refrigerators, i.e., the  $E$ - $T$  diagram [150]. This diagram is plotted in Figure 5.30 using the herein measured EC responsivity of PMN as the main parameter ( $\Delta T_{EC}^D/E$ ).

Two observations can be made from the  $E$ - $T$  diagram. First, a significant increase in EC responsivity is observed in the region corresponding to the previously published  $E$ - $T$  diagrams and, second, the region of increased EC responsivity is progressively smeared with increasing temperature (see the red area broadening at higher temperatures). The latter corresponds to the so-called Widom line, characteristic for supercritical regimes and representing the region where maximum coefficients are measured due to the continuous, supercritical change of response parameters, such as polarization.

In analogy to the pressure-temperature phase diagram of water, the Widom line represents the extension of the first-order phase-transition line [156], present below the critical temperature  $T_{cr}$  (in PMN single crystal  $T_{cr} = 230$  K along [111] direction [150]). A close inspection of the  $E$ - $T$  diagram shows that cycling at room temperature with 70 kV/cm of field magnitude indeed overcomes the maximum in the EC responsivity. Due to the steep Widom line, however, this is not the case when the same field is applied at 50 °C (see arrows in Fig. 5.30). Recent atomistic studies showed that driving PMN with high electric fields in the supercritical regime should provoke the growth of polar clusters on the nanoscale. Due to the steep nature of the Widom line (see Fig. 5.30), such growth becomes increasingly difficult as the temperature is further increased above  $T_{cr}$ . Based on the  $E$ - $T$  diagram presented in Fig. 5.30 and Ref. [157], we may thus assume that cycling above the Widom line (room-temperature case) may lead to more extensive growth of polar clusters during cycling as compared to driving conditions when this line is not crossed (50 °C case). Such field-induced growth of nanopolar correlations in PMN may influence the stabilization of the ferroelectric phase and could thus provide an explanation for the experimentally observed emergence of this phase while cycling PMN at room temperature.

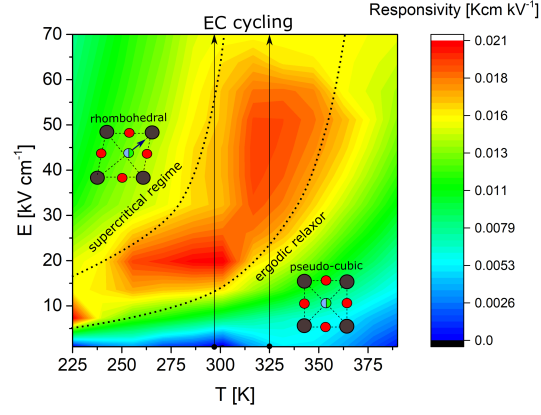


Figure 5.30: Electric field vs. temperature ( $E$ - $T$ ) diagram for PMN. The vertical arrows show the trajectories of the field excitation for the fatigue tests performed at room temperature and 50 °C. The dotted line delineate the ergodic relaxor and supercritical ferroelectric state. The color scale indicates the magnitude of the responsivity.

The proposed concept using the  $E$ - $T$  diagram is thus consistent with the observed ferroelectric phase, responsible for the fatigue behaviour, which emerges during cycling at room temperature, but not at 50 °C.  $E$ - $T$  diagrams can thus provide a useful guideline to predict the behaviour of the PMN under field cycling and could possibly be adopted for determining the excitation conditions of EC materials on a more general basis.

### 5.4.3 Contribution of ferroelectric phase and conductivity to self-heating

*The results of this study were published in APL Materials, Issue 7, pages 071111-1/6 with co-authors: Ana Hedl, Lovro Fulanović, Nikola Novak, Tadej Rojac.*

In this section we will investigate in detail the effect of ferroelectric long-range order and Joule heating on the temperature response in cooling-device-like electric-field conditions. Since the ferroelectric phase and the Joule heating in the fatigued PMN are metastable and thus difficult to accurately characterize, in addition to PMN we also use two model materials to study the mentioned phenomena: soft and hard PZT. The reason is that the response of soft PZT is dominated by domain switching and domain-wall displacements where the Joule heating effects are expected to be negligible due to the intrinsically low electrical conductivity of this PZT variant. On the other hand, hard PZT shows a reduced contribution from switching and domain-wall displacements, while exhibiting elevated electrical conductivity in the investigated temperature range (room temperature to 75 °C). The two PZT variants are thus ideal material candidates for the study of the different mechanisms, possibly leading to self-heating effects during EC cycling. Adding PMN to the study where domain structure is absent, we should be able to designate the effect of domain walls and Joule heating on the EC temperature response of the analysed materials.

For the purpose of the study, we used PMN, Nb-doped  $\text{Pb}(\text{Zr}_{0.75}\text{Ti}_{0.25})_{0.99}\text{Nb}_{0.01}\text{O}_3$  (denoted as PZT75/25-Nb) and undoped  $\text{Pb}(\text{Zr}_{0.75}\text{Ti}_{0.25})\text{O}_3$  (denoted as PZT75/25). PZT75/25-Nb possess soft properties, while PZT75/25 resembles hard characteristics, similar as in acceptor doped PZT compositions. This hardening in undoped PZT75/25 is evidenced by pinched polarization-electric field loops, aging, de-aging by electric-field cycling and quenching, and elevated electrical conductivity (for details regarding these features in PZT75/25 see Ref. [153]). Considering that in PZT75/25-Nb the hysteresis is largely controlled by domain switching, while in undoped PZT75/25 the hysteresis may be additionally influenced by the electrical conductivity, particularly at low driving frequencies, it is expected that these two mechanisms will be reflected in the self-heating effects under unipolar EC-like field driving conditions.

Fig. 5.31 shows the EC response of PMN, PZT75/25-Nb and PZT75/25 ceramics by applying a single electric-field square waveform with a holding period of 100 s. While the EC responses of the three samples were fully characterized in the temperature range between 28 °C and 65 °C (see the following discussion), in Fig. 5.31 the EC effects of PMN and PZT75/25-Nb are shown for room temperature, while the response for PZT75/25 is shown for 65 °C to illustrate the effect of the increased electrical conductivity of the latter, which strongly increases at higher temperatures.

As expected, PMN exhibits the largest EC effect where the temperature change of the adiabatic polarization and depolarization are the same, i.e., 612 mK (Fig. 5.31a). In contrast to PMN, the polarization and depolarization temperature peaks of PZT75/25-Nb (Fig. 5.31b) are not of the same magnitude, i.e., the adiabatic polarization temperature change is 99 mK, while that of the adiabatic depolarization is 89 mK, thus 11 % lower. We note that such asymmetry is, in principle, expected to lead to self-heating effects during continuous field cycling, as the sample (when thermally isolated) effectively heats more than it is cooled during each EC cycle. The asymmetry can be understood in terms of the domain switching occurring during the adiabatic polarization of PZT75/25-Nb, which is partially irreversible (i.e., resulting in remanence), thus leading to a lower polarization change as the field is reduced to zero (hence, the temperature change during depolarization is lower than that during polarization). Applying an electric field above the coercive field to a ferroelectric material, in fact, causes poling, which involves several mechanisms contributing to the energy loss and heat dissipation; in PZT75/25-Nb this is typically switching and domain-wall displacements [10].

The EC response of the third studied material, i.e., PZT75/25, is shown in Fig. 5.31c. Similar to the response of PZT75/25-Nb, we also observed an asymmetry between the adiabatic polarization (168 mK) and depolarization peaks (143 mK), resulting in a relative difference between the two peaks of 17 %. In contrast to PZT75/25-Nb, however, the temperature of the PZT75/25 sample clearly increases during the isoelectric regime (i.e., at constant field; see the progressive temperature increase in Fig. 5.31c between 25 s and 100 s). This phenomenon can be attributed to Joule heating arising from the increased electrical conductivity of the sample and has been previously observed in PMN after a large number of EC cycles (see Fig. 5.18, red curve). Considering the temperature change of the adiabatic depolarization of 143 mK, this bias temperature of 126 mK related to Joule heating, diminishes the effective cooling effect down to only 17 mK (see arrows in Fig. 5.31c). Finally, we note that both the observed asymmetry in the EC heating/cooling temperature response and the Joule heating are expected to have a detrimental effect on the EC response during electric-field cycling conditions as the accumulated heat may lead to an uncontrollable rise of the sample temperature.

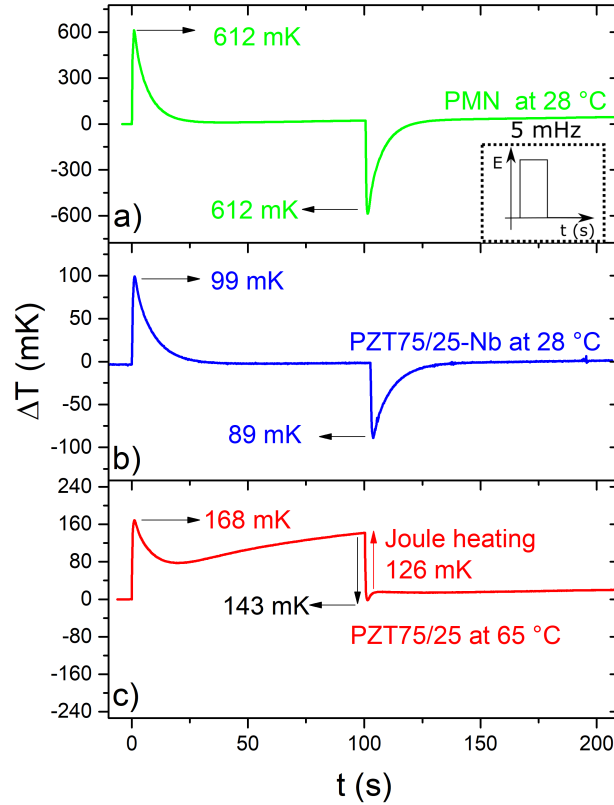


Figure 5.31: Comparison of the EC response in three different EC materials, relaxor PMN, donor-doped ferroelectric PZT and undoped ferroelectric PZT.

To investigate the origin of the pronounced Joule heating effects in PZT75/25, we analysed the electrical conductivity of the sample by measuring the temperature dependence of the DC electric-current-voltage ( $I$ - $V$ ) characteristics, from which we estimated the activation energy of the conduction mechanism (Fig. 5.32). This was done by determining the resistivity of the sample from the current-versus-time curves measured at constant field (30 kV/cm) and at different temperatures, as shown in Fig. 5.32a. The abrupt jumps during

application ( $t=0$  s) and removal of electric field ( $t=1800$  s) are due to polarization and depolarization of the sample. The current points averaged during the last 10 s (1790 s to 1800 s) of the measurement were used for the calculation of the resistivity. The resistivity values were then fitted using the Arrhenius equation, which is often used to describe thermally induced processes:

$$R = Ae^{-\frac{E_a}{kT}}, \quad (5.6)$$

where  $R$  denotes the resistance of the sample,  $A$  is a constant,  $E_a$  is the activation energy,  $k$  is the Boltzmann constant and  $T$  is the temperature. By rearranging it, we arrive at a linear equation that can be used to calculate  $E_a$  from our experimental data:

$$\ln(R) = -\frac{E_a}{kT} + \ln(A). \quad (5.7)$$

We can see from equation 5.7, that  $\ln(R)$  is in a linear relationship with  $1/T$ . Thus, by plotting  $\ln(R)$  versus  $1/T$  and extracting the slope of the line, we can calculate the  $E_a$  of the process. Consistent with the literature data, the activation energy of 1.05 eV (see Fig. 5.32b) can be attributed to the long-range migration of oxygen vacancies, and thus ionic conductivity [15], [153], [154]. This is consistent with early studies on undoped PZT where the p-type conductivity contribution was not observed below 350 °C in high-T (700 °C) quenched samples [158]. However, based on a more recent impedance analysis on PZT [159], for our case, a contribution from p-type conduction to the total conductivity cannot be ruled out.

Finally, we note that, in contrast to PZT75/25 with elevated conductivity, no effects of Joule heating could be observed in PMN and PZT75/25-Nb up to the maximum measured ambient temperature of 75 °C, consistent with their insulating nature (specific electrical resistivity  $>10^{11}$  Ωm in the analysed temperature region).

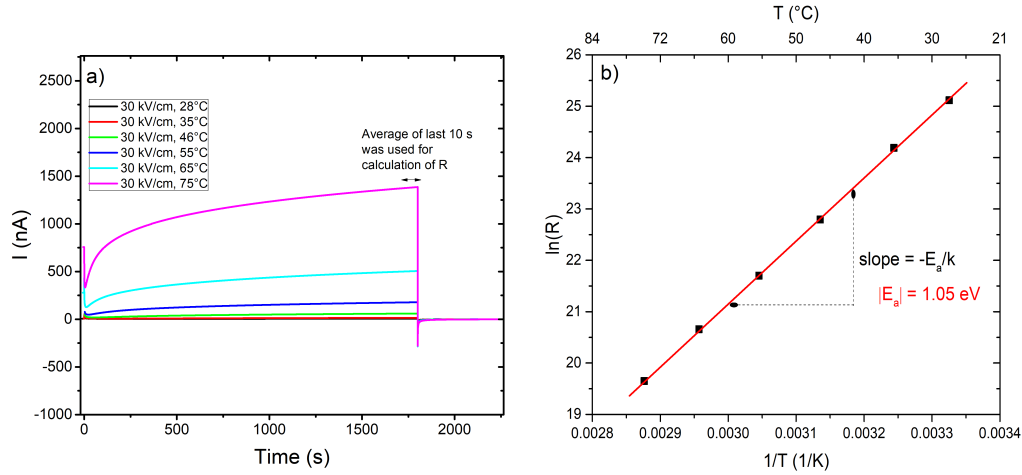


Figure 5.32: a) Current ( $I$ ) vs. time ( $t$ ) plots for hard PZT at different temperatures. The marker indicates the range for calculation of an average values used in the b) Arrhenius plot, logarithm of resistivity is plotted as a function of the inverse temperature. With the plot we estimated that the activation energy ( $E_a$ ) of resistivity is 1.05 eV.

We have so far shown the EC response of the three different ceramic materials using one field cycle with a long period (100 s), which, in terms of period excitation, would



correspond to 5 mHz of frequency. Since the EC effect is meant to be exploited in refrigeration devices whose cooling power is proportional to the operation frequency, the actual excitation frequencies are expected to be much higher than 5 mHz [141]. To illustrate the dynamic temperature response of the three materials, we thus monitored continuously the average temperature of the samples upon prolonged cycling (up to 500 of cycles) using square-like electric field waveforms of 30 kV/cm and frequencies in the range from 0.6 to 10 Hz. Fig. 5.33 shows the temperature evolution of PMN, PZT75/25-Nb and PZT75/25 during such cycling at a frequency of 4 Hz and the same ambient temperatures as those reported in Fig. 5.31. The data represent the actual (uncorrected) temperature of the sample as it evolves during field cycling.

The temperature of PMN (green curve in Fig. 5.33) abruptly increases in the first 1 second of field cycling, followed by a decrease and final convergence after 23 s of cycling to a temperature that is 40 mK higher than the initial temperature of the sample, i.e., before cycling (this temperature difference is denoted as  $\Delta T_R$  and is subsequently referred to as the temperature rise). The final, steady temperature is a result of the attained equilibrium between the heat generated by the sample, most likely related to hysteresis losses of PMN (see Section 5.2.1, Fig. 5.6a showing slim hysteresis loops of PMN), and its dissipation to the environment.

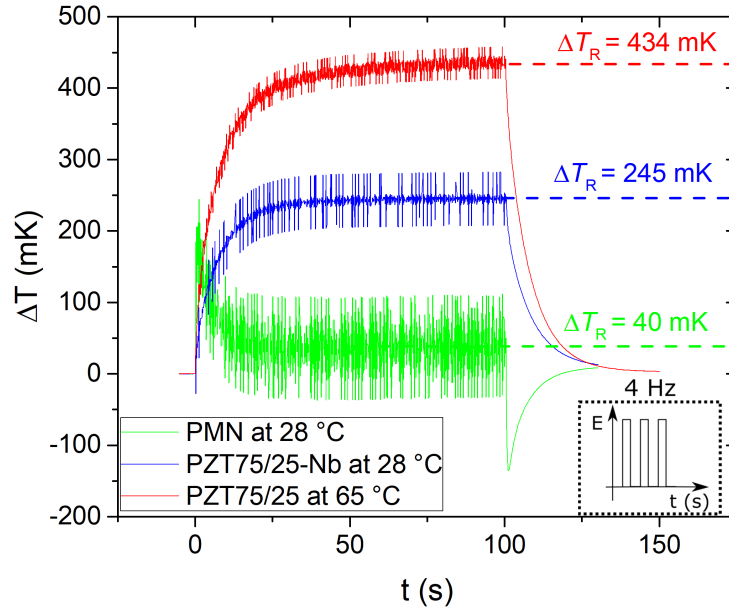


Figure 5.33: Temperature evolution during electric-field cycling of PMN, PZT75/25-Nb and PZT75/25 using 4 Hz of unipolar square waveform. The temperature rise, i.e., the difference between the initial (prior to cycling) and final (steady-state) temperature of the sample (denoted as  $\Delta T_R$ ) is 40 mK, 245 mK and 434 mK for PMN, PZT75/25-Nb and PZT75/25, respectively.

The result is qualitatively similar to the unfatigued PMN in Fig. 5.18, black curve. The temperature of PZT75/25-Nb and PZT75/25 initially increases during cycling, reaching a steady state after 30 s of cycling. The responses of the PZT75/25-Nb and PZT75/25 resemble that observed in the fatigued PMN in Fig. 5.20, red curve. The temperature rise ( $\Delta T_R$ ) is 245 mK for PZT75/25-Nb and 434 mK for PZT75/25, which is expected

considering that in PZT75/25, besides the self-heating related to the asymmetry between the adiabatic polarization and depolarization, additional self-heating effects arise due to a large Joule-heating effect (compare Figs. 5.31b and c).

After showing the self-heating effects, we further analyse the temperature response of PZT75/25-Nb and PZT75/25 during cycling as a function of both temperature and frequency. The frequency dependence of the temperature rise ( $\Delta T_R$ ) and energy loss density ( $u$ ) in PZT75/25-Nb for different ambient temperatures is shown in Fig. 5.34. The energy-loss density  $u$  was calculated from the measured temperature rise  $\Delta T_R$  using a heat-balance equation in which it is assumed that the energy loss is responsible for the self-heating of the sample while it is partially dissipated to the sample environment. When the thermal equilibrium is reached all the loss energy is dissipated in air via heat convection and radiation. From the temperature rise (equilibrium temperature) the electrical loss can be calculated:

$$u = \frac{1}{fV}(T_R - T_0)(\alpha A + \varepsilon\sigma A(T_R^2 + T_0^2))(T_R - T_0), \quad (5.8)$$

here the  $f$  is the frequency of excitation,  $T_0$  is the ambient temperature,  $V$  is the volume of the active part of the material,  $\alpha$  is the heat-transfer coefficient,  $\varepsilon$  is the emissivity of the material,  $\sigma$  is Stefan's constant,  $A$  is the surface of the sample available for the transfer of heat to the surroundings.

As shown in Fig. 5.34a,  $\Delta T_R$  increases almost linearly (with increasing frequency, while the energy-loss density (Fig. 5.34b) slightly decreases with increasing frequency at all the measured ambient temperatures (28, 54 and 63 °C).

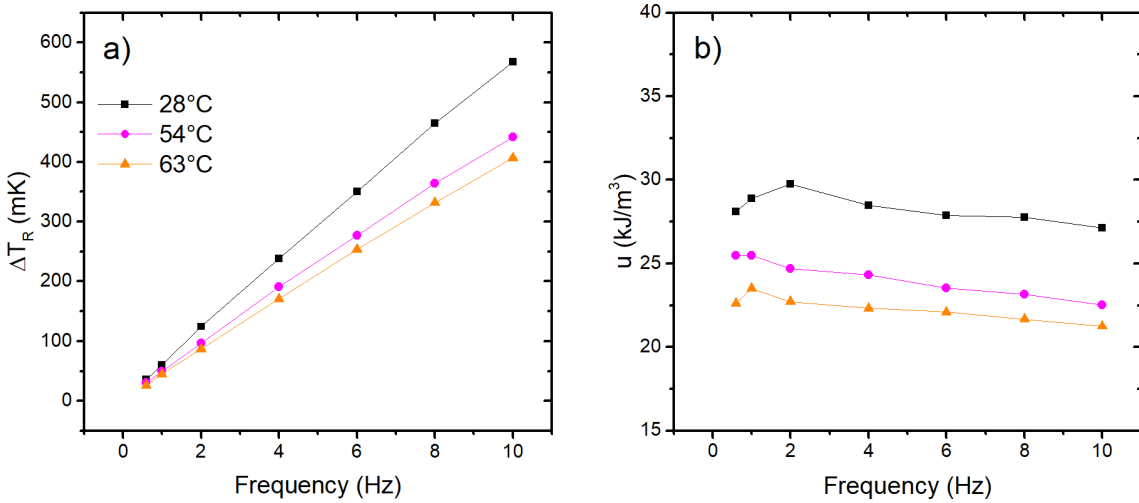


Figure 5.34: a) Temperature rise ( $\Delta T_R$ ) and b) corresponding calculated energy loss density ( $u$ ) as a function of electric-field cycling frequency for PZT75/25-Nb determined at different ambient temperatures.

The increase of  $\Delta T_R$  with increasing frequency can be explained by the number of cycles per unit of time. As the driving frequency is increased, the material responds with a larger number of EC cycles per unit time where each such cycle is characterized by the energy-loss density  $u$ . The total (accumulated) excess heat generated is thus larger at higher frequencies, leading to an increased self-heating effect and temperature rise  $\Delta T_R$ . We propose that the origin of the self-heating is the observed asymmetry between the adiabatic

polarization and depolarization (see Fig. 5.31 for PZT75/25-Nb), stemming from domain-wall displacements and switching. Increasing the ambient temperature results in a reduced  $\Delta T_R$  and energy-loss density, which can be associated with a decreased coercive field at higher ambient temperatures. The decreased coercive field leads to slimmer hysteresis loops and thus a smaller area and losses [160].

In a similar manner as for PZT75/25-Nb,  $\Delta T_R$  and  $u$  were obtained for the PZT75/25 sample (Fig. 5.35). Here,  $\Delta T_R$  increases with increasing frequency; however, in comparison with PZT75/25-Nb the relationship is evidently non-linear (Fig. 5.35a). Besides, with increasing ambient temperature,  $\Delta T_R$  increases (Fig. 5.35b), thus showing an opposite trend to that observed in PZT75/25-Nb (5.34b). At ambient temperatures of 55 and 65 °C, the energy-loss density  $u$  of PZT75/25 shows a strong increase in the low-frequency range (below 2 Hz; Fig. 5.35b), which is not observed in insulating PZT75/25-Nb (see Fig. 5.34b). This low-frequency dispersion of  $u$  can therefore be attributed to the conductivity in PZT75/25, which is likely governed by the slow, kinetically restricted, long-range, oxygen-vacancy migration, dominantly contributing to the loss  $u$  and thus the self-heating effects when the driving field excitations are slow (i.e., low driving frequencies).

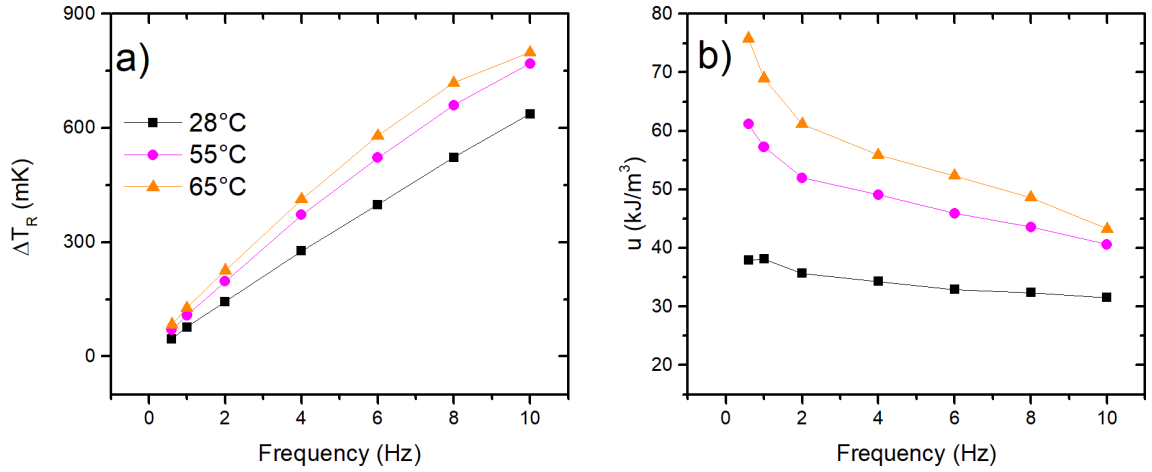


Figure 5.35: a) Temperature rise ( $\Delta T_R$ ) and b) corresponding calculated energy loss density ( $u$ ) as a function of electric-field cycling frequency for PZT75/25 determined at different ambient temperatures.

To link the self-heating effects ( $u$ ) of PZT75/25-Nb and PZT75/25 to the energy-loss density ( $W_L$ ), represented by the hysteresis area of the  $P(E)$  response, we next analyse and compare the  $P(E)$  loops of these two samples. Since the hysteresis loop can hardly be constructed from a square-waveform field signal, which was used for the self-heating investigations, and to emulate the driving conditions expected in EC refrigerators (Fig. 5.34 and 5.35), the  $P(E)$  loops were instead measured with conventional sinusoidal unipolar waveforms. This still allows a qualitative comparison between  $P(E)$  hysteresis ( $W_L$ ) and energy loss  $u$  determined from the measured temperature rise (5.34b and 5.35b). The frequencies used for  $P(E)$  hysteresis measurements were 0.6 Hz (solid lines in Fig. 5.36) and 10 Hz (dashed lines in Fig. 5.36).

As shown in Fig. 5.36a, the  $P(E)$  loops of PZT75/25-Nb show a typical hysteresis, commonly related to domain-wall switching and displacements under an applied field. Note that the hysteresis shows little frequency and temperature dependence, which is consistent with the behavior of the calculated energy-loss density  $u$  shown in Fig. 5.34b. In fact, similar to the behavior of the energy-loss density  $u$ , the hysteresis also slightly decreases

(within 15 %) with increasing frequency and temperature. In contrast, PZT75/25 shows a strong temperature dependence of the hysteresis area, particularly at 0.6 Hz (i.e., the hysteresis area at 0.6 Hz increases for 220 % at 65 °C, relative to that at 28 °C). Since a dominant portion of the losses in PZT75/25 at low driving frequencies is due to the electrical conductivity, it is apparent that the losses can be to some extent prevented by increasing the excitation frequencies (note the smaller hysteresis measured at 10 Hz (Fig. 5.36b), consistent with the smaller  $u$  as the frequency is increased (Fig. 5.35b)). For example, in PZT75/25 at 65 °C and 10 Hz the losses are almost 4-fold smaller than at 0.6 Hz. Nonetheless, even when the effect of the conductivity is diminished by increasing the frequency, the losses are larger in PZT75/25 as in PZT75/25-Nb.

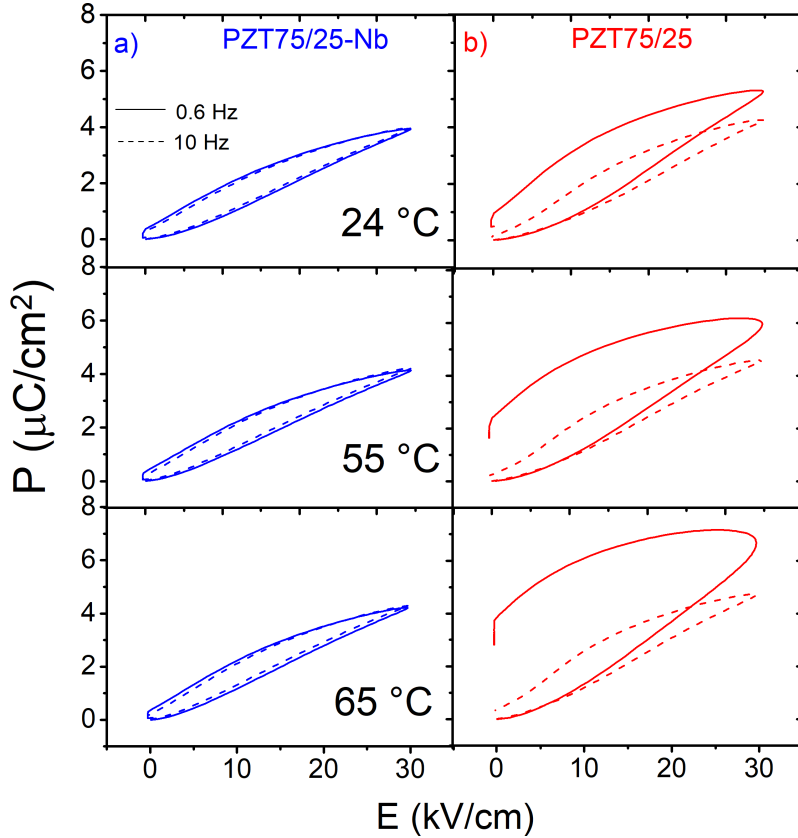


Figure 5.36:  $P(E)$  loops of a) PZT75/25-Nb and b) PZT75/25 measured at 0.6 Hz (full curves) and 10 Hz (dashed curves) and at temperatures of 24, 55 and 65 °C

In this section we illustrated how domains, ferroelectric long-range order and Joule heating contribute to the electrical losses and affect the temperature response of EC materials. We showed that Joule heating reduces the effective cooling, while ferroelectric domain motion induces an asymmetry in the response. This asymmetry and also the Joule heating lead to severe self-heating, which can be several times larger than the EC effect of the material; for example, for undoped PZT, compare the red curves in Fig. 5.31 where  $\Delta T_{EC}^D = 143$  mK and in Fig. 5.33, where the self-heating  $\Delta T_R = 434$  mK. The results thus show the key role of energy losses on the EC behavior under constant field driving, which should be seriously considered in the implementation of EC materials into cooling devices.

## 5.5 Multifunctional Properties of PMN Cantilevers

*After modelling, characterizing the PMN-100xPT ceramics, selecting the optimal composition and performing fatigue tests under EC cycling conditions expected in a cooling device, in the next step we fabricated the multifunctional cantilevers intended to operate in the refrigerator. The fabrication and characterization of the cantilever, before their integration in the actual device, is shown in the following section.*

### 5.5.1 Microstructural properties

In order to find the optimal sintering conditions, we sintered the laminated tapes in the form of PMN/Pt/PMN plates at 1000, 1100 and 1200 °C. The evolution of the microstructure (cross-section) with increasing sintering temperature is shown in Fig. 5.37. The plates sintered at 1000 °C were porous with a thickness of  $49 \pm 1 \mu\text{m}$  and a non-uniform electrode layer. By increasing the sintering temperature to 1100 °C, the density of the material and the uniformity of the electrode were improved. In this case the thickness of the PMN layer was reduced to  $43.8 \pm 1 \mu\text{m}$ . A further increase of the density and thus a reduction in the PMN layer thickness ( $43.4 \pm 1 \mu\text{m}$ ) was achieved at the sintering temperature of 1200 °C.

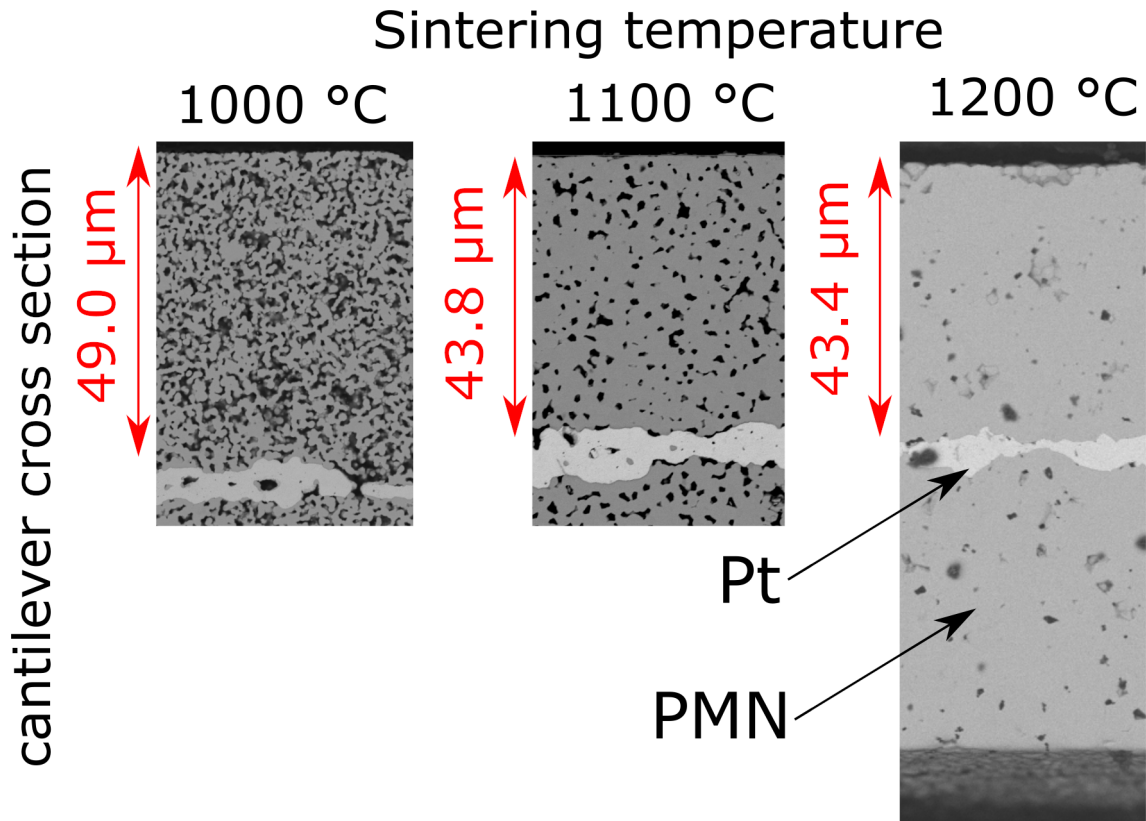


Figure 5.37: Microstructure cross-section of the PMN/Pt/PMN plates sintered at different temperatures, from left to right: 1000 °C, 1100 °C and 1200 °C. The thickness of the PMN layer is given next to the microstructure.

The XRD of the sintered tape at 1200 °C exhibited a pure perovskite crystal structure, no secondary pyrochlore phases were observed [161], as shown in Fig.5.38. The inset shows an enlarged area around the angles (25° - 30°) where pyrochlore peaks are usually observed.

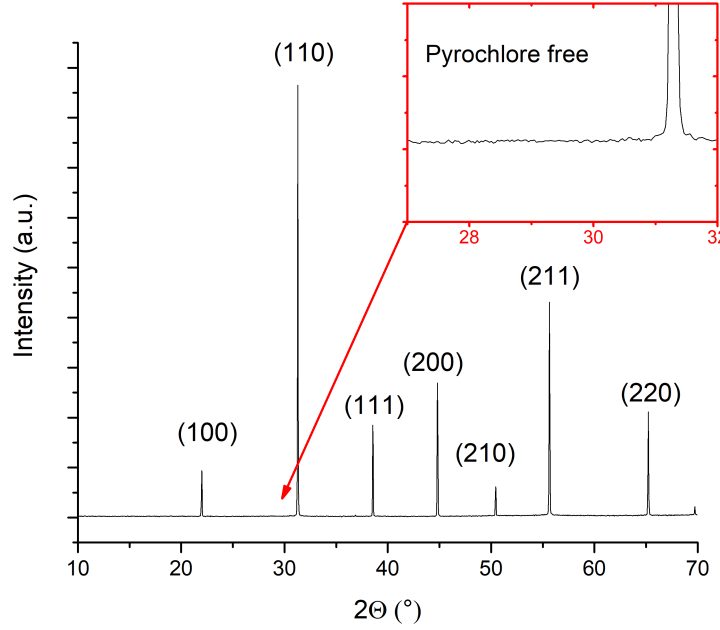


Figure 5.38: XRD of the tape sintered at 1200 °C for 2h. XRD pattern shows a pure perovskite crystal structure without any secondary phases. Miller indices are given above the diffraction peaks. The inset shows the enlarged area in which pyrochlore peaks usually appear.

### 5.5.2 Electrical properties

First, the dielectric permittivity of the circular sample (disc sample A in Fig. 4.9) was measured. The room-temperature permittivity and dielectric loss values are shown in Table 5.1. As expected, the lowest permittivity ( $\epsilon'_r = 3300$ ) and highest losses ( $\tan\delta=0.0028$ ) were measured on the sample sintered at 1000 °C due to the high porosity and poor inner platinum electrode. By increasing the sintering temperature to 1100 °C the permittivity increased (to  $\epsilon'_r=8525$ ) and losses slightly decreased (to  $\tan\delta=0.002$ ). Owing to the improved sintering behaviour and thus the dense microstructure, the highest permittivity ( $\epsilon'_r=9174$ ) and significantly reduced losses ( $\tan\delta=0.0007$ ) were achieved after sintering at 1200 °C. By comparing the permittivity of the disc sample A with that of the bulk PMN (see Table 5.1,  $\epsilon'_r$ ), we can see that the former shows a lower permittivity than the bulk and also lower losses. A possible explanation for the lower permittivity is the presence of the residual mechanical stresses in the PMN/Pt/PMN samples due to the thermal strain mismatch between the platinum and the PMN layers as well as surface effects [162].

Table 5.4: Dielectric permittivity and loss of sintered tapes measured at room temperature and 1 kHz.

| Sintering T (°C) | $\epsilon'_r$ | D      |
|------------------|---------------|--------|
| 1000             | 3300          | 0.0028 |
| 1100             | 8525          | 0.0022 |
| 1200             | 9174          | 0.0007 |

The  $P(E)$  loops of the fabricated cantilevers (Sample B in Fig. 4.9, Section 4.8) are shown in Fig. 5.39. The loops were measured in the specially designed holder shown in Fig. 4.10 in the Materials and Methods. The loops were measured in the field range from 6 kV/cm to 50 kV/cm and show little hysteresis. The saturation effects are visible above 20 kV/cm. The maximum polarization at 50 kV/cm was  $18 \mu\text{C}/\text{cm}^2$ , while in bulk ceramics at the same electric field value it was  $27 \mu\text{C}/\text{cm}^2$ . This is consistent with the lower measured dielectric permittivity in the PMN/Pt/PMN structures as compared to the bulk (compare values in Tables 5.1 and 5.4). Such a reduction of the properties in multilayered structures is usually attributed to surface effects and/or residual thermal stresses due to the thermal expansion coefficient mismatch between the different layers [162], [163].

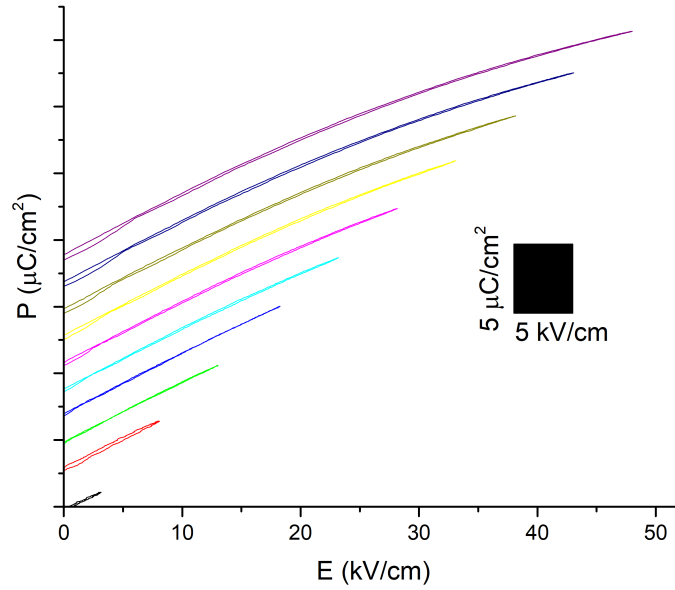


Figure 5.39: Polarization ( $P$ ) vs. electric field ( $E$ ) loops measured on the sintered tapes. The square's edge represents the scale for polarization and electric field.

### 5.5.3 Electromechanical properties

The PMN/Pt/PMN cantilever B (Fig. 4.9) was further electromechanically characterized by applying a sinusoidal electric field and monitoring using a digital microscope camera. The electric field was applied to one layer in the PMN/Pt/PMN cantilever structure which leads to large deflections (several times larger than the thickness of cantilever), as described in Section 1.1.2.1.

The results are shown in Fig. 5.40. Fig. 5.40a shows the maximum deflections ( $\delta^{max}$ ) as a function of the magnitude of the electric field ( $E_0$ ). The cantilevers bend by  $500 \mu\text{m}$  at the maximum applied field of  $30 \text{ kV}/\text{cm}$ . The insets show the strain response as a function of the applied electric field of the cantilevers, which is hysteresis free up to the maximum electric field. We can also observe saturation effects at a field of  $25 \text{ kV}/\text{cm}$  and above. Using Equation 1.4 we calculated the approximate  $s_1^{max}/E_0$  for the PMN cantilevers and compared them with the bulk values. The  $s_1^{max}/E_0$  value at  $10 \text{ kV}/\text{cm}$  is  $27 \text{ pm}/\text{V}$  which increases to  $39 \text{ pm}/\text{V}$  at  $15 \text{ kV}/\text{cm}$  and saturates at about  $45 \text{ pm}/\text{V}$  at the higher fields

(Fig. 5.40). This is lower than in bulk ceramics (see 5.14). The lower  $s_1^{max}/E_0$  are expected due to the lower  $\epsilon'_r$  (compare values in Table 5.1 and Table 5.4) and  $P_{max}$  (compare Fig. 5.6 and Fig. 5.39) measured on PMN cantilevers.

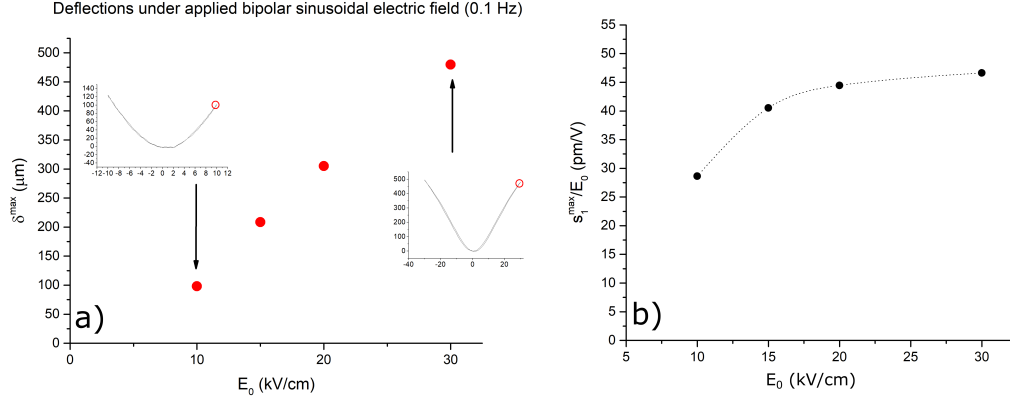


Figure 5.40: Electromechanical response of the cantilevers. a) The deflections ( $\delta$ ) of the cantilever versus electric field, b) the calculated values of transverse electromechanical coefficient by using Equation 1.4 in Section 1.4.

### 5.5.4 Electrocaloric properties

We measured the EC effect on differently shaped sintered samples. Fig. 5.41 shows the temperature changes during adiabatic polarization ( $\Delta T_{EC}^P$ ) and depolarization ( $\Delta T_{EC}^D$ ) of the cantilever B (see Fig. 4.9) as a function of the driving field's magnitude in terms of the as-measured values (left vertical axis) and the measured values corrected with the correction factor (right vertical axis). As mentioned earlier, the correction factor takes into account the heat dissipated to/from the non-active parts of the sample. The value in the case of the cantilever structure was 3.2, which is higher than in bulk PMN samples (see Table 5.3), indicating we have a larger portion of EC non-active parts of the sample. This is due to the one non-active PMN layer in the cantilever and due to the screen-printed Pt-electrode.

Considering that the focus of the EC measurements of the cantilevers is not the EC effect of the material itself, the uncorrected temperature values are the more relevant from the cooling-device point-of-view. On the other hand, the corrected EC response of the cantilever can be directly compared to the corrected values obtained in bulk PMN. The temperature change during adiabatic depolarization in bulk PMN at 60 kV/cm was 1.1 K (Fig. 5.16), while that of the cantilever was 0.8 K (Fig. 5.41). Similarly, at 40 kV/cm the bulk showed an EC cooling response of 0.7 K, while the cantilever showed 0.55 K. In general, the EC cooling effect (corrected values) is 25 % lower in the cantilever elements, consistent with a lower dielectric permittivity observed (compare Tables 5.1 and 5.4). The ratio  $\Delta T_{EC}^P$  and  $\Delta T_{EC}^D$  was close to unity (within 1 %), similar to the bulk PMN and according to the slim  $P(E)$  loops measured (Fig. 5.39). It is also interesting to note that the relationship between the electric field and the induced temperature change is more linear in the case of cantilever elements than in the bulk PMN (compare Fig. 5.16 with Fig. 5.41).



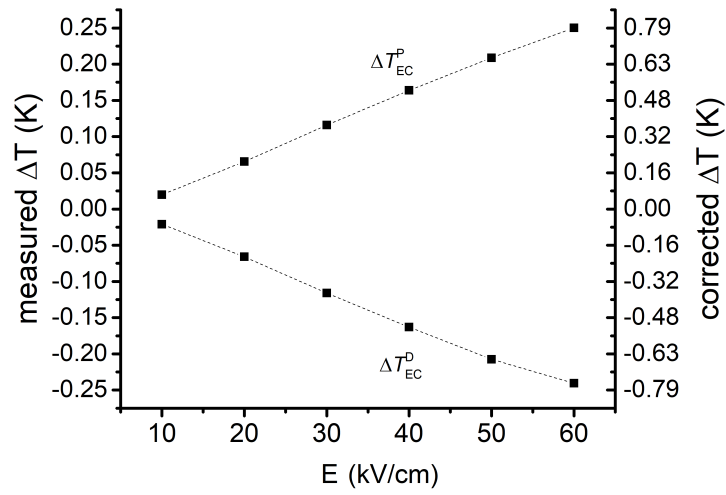


Figure 5.41: EC temperature change of the cantilever during adiabatic polarization ( $\Delta T_{EC}^P$ ) and depolarization ( $\Delta T_{EC}^D$ ). Left y-axis shows the directly measured values, while the right y-axis shows the corrected temperature changes. The correction factor was calculated using the procedure described in the Materials and Methods, Section 4.15.

## 5.6 Cooling Performance of Proof-of Concept Device

As a final step, we used the cantilevers C (Fig. 4.9) in an actual proof-of-concept cooling device. As shown in Fig. 5.42 we fabricated this proof-of-concept device with two cantilevers. The cantilevers were inserted into a 3D-printed packaging and wired with the microcontroller circuit. To test the device we had to establish a heat source and heat sink. The heat sink was a copper plate mounted above the two cantilevers in the packaging, like shown in Fig. 5.42 in the upper left image, where the bottom two cantilevers are PMN cantilever elements. The heat source was another cantilever on which a temperature sensor was mounted (shown schematically in Fig. 4.12).

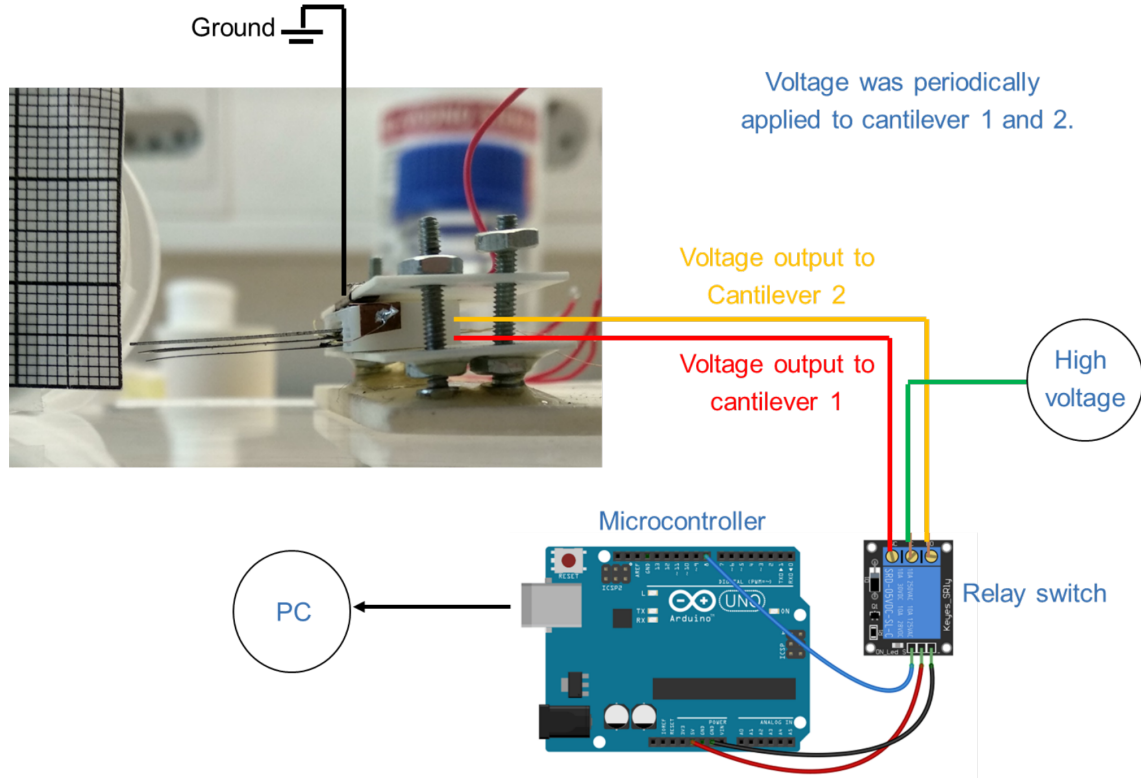


Figure 5.42: Driving set-up for the proof-of-concept device. The device was electrically wired to ground and high voltage. The high voltage was switched between cantilever 1 and 2 by a relay switch controlled by an Arduino Uno microcontroller. The microcontroller was programmed with Labview.

At first, we had to determine the optimal frequency ( $f$ ) of operation. This was done with one active element, as shown in Fig. 5.43. The electric field was applied to the cantilever and due to the applied field the cantilever bent and contacted the other, second cantilever. During the interval from  $0 - \frac{2}{f}$ , heat transfer between the two cantilevers occurred. During the time of contact, the heat was passed from the first sample to the second one. The second cantilever was passive (no applied field). When the field was removed from the first cantilever (time interval  $\frac{2}{f} - \frac{1}{f}$ ), it returned to the initial position and absorbed the heat from the heat source, which in our case was a cantilever with an attached temperature sensor.

In order to illustrate the frequency dependence of the device cooling, we plotted the normalized cooling ( $\Delta T_{HS}/\Delta T_{EC}^D$ ), where the  $\Delta T_{EC}^D$  is the uncorrected EC effect of the

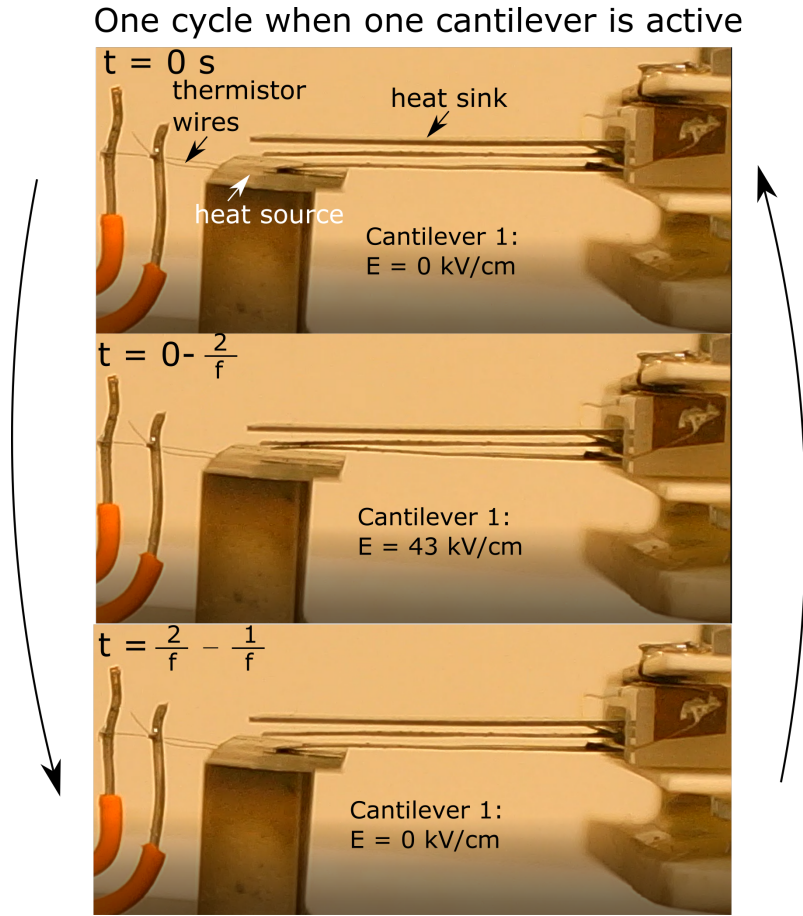


Figure 5.43: Determination of the optimum operation frequency of the driving field with one active cantilever. One cycle with one active cantilever element at 43 kV/cm. The active cantilever is in contact with the upper element for half of the cycle period ( $0-2/f$ ) and the second half of the period ( $0-1/f$ ) in contact with the heat source where the temperature is measured.

cantilever and  $\Delta T_{HS}$  (temperature on the heat source) was measured with the thermistor attached to the heat source, see Fig. 4.12 in Materials and Methods.

As shown in Fig. 5.44 the ratio between the temperature in the heat sink ( $\Delta T_{HS}$ ) and the uncorrected EC effect ( $\Delta T_{EC}^D$ ) in the cantilever is below unity; meaning the cooling effect is in general lower than the EC effect of the cantilever due to the poor thermal transfer between the cantilevers. A peak in the cooling capacity of the cantilever is achieved close to 1–2 Hz for all three applied electric fields. At best, at this peak the cooling performance is 0.35 of the EC effect of a single cantilever using the same electric field of 43 kV/cm and 50 kV/cm (red and green curves, respectively) (see Fig. 5.44). When the electric field magnitude is 30 kV/cm (red curve) the ratio is reduced to 0.27, which can be ascribed to the lower contact force (see Appendix A.3). By lowering the operational frequency of the device below 1 Hz, a dramatic drop of the cooling efficiency is observed. This is probably because the heat removed from the heat source is replaced with the heat inflow from the surroundings. A more progressive decrease in the cooling performance is observed when increasing the operational frequency from 2 Hz up to 20 Hz. In this case, a higher frequency and shorter contact time prevent effective heat transfer between the cantilever and heat source, leading to a reduced cooling ability of the device. Thus, for the given cooling device

the optimum driving frequency is 2 Hz.

As already implied in the simulations, the contact between the cantilevers plays a critical role in the device performance. Poor thermal contact will prolong the heat transfer between the cantilevers, leading to heat inflow from the surroundings and thus smaller temperature spans. The peak at 1–2 Hz significantly differs from the optimal frequency that was estimated from the simulations (100 Hz); therefore, heat regenerations do not occur, meaning the temperature spans are low.

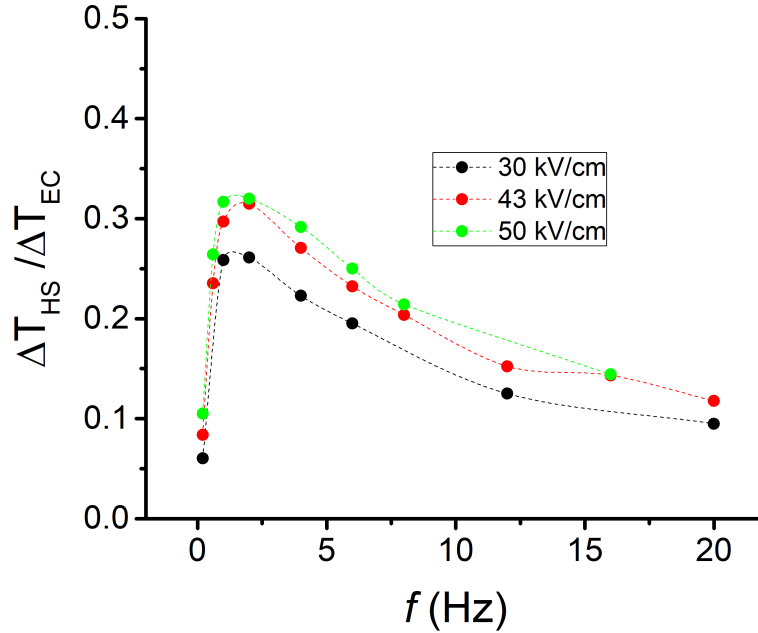


Figure 5.44: Frequency ( $f$ ) dependence of normalized cooling of the first cantilever in the proof-of-concept device. The measured temperatures ( $\Delta T_{HS}$ ) are normalized with respect to the uncorrected EC effect ( $\Delta T_{EC}^D$ ) of the cantilever at an identical electric field.

Despite the small cooling effects, we determined the optimum frequency of operation to test the device's performance with two active cantilevers (see Fig. 5.45). The first cantilever was in contact with the upper element for the first quarter of the cycle period ( $0 - \frac{4}{f}$ ) and the second quarter of the period ( $\frac{4}{f} - \frac{2}{f}$ ) in contact with the heat source where the temperature is measured. During  $\frac{2}{f} - \frac{3}{4f}$  the electric field is applied to the second cantilever, which is then in contact with the heat sink. The electric field is then reduced to zero during the period  $\frac{3}{4f} - \frac{1}{f}$  and the cantilever 2 returns to the initial position. This cycling procedure was repeated until a stable temperature was reached in the heat source.

## One cycle when two cantilevers are active

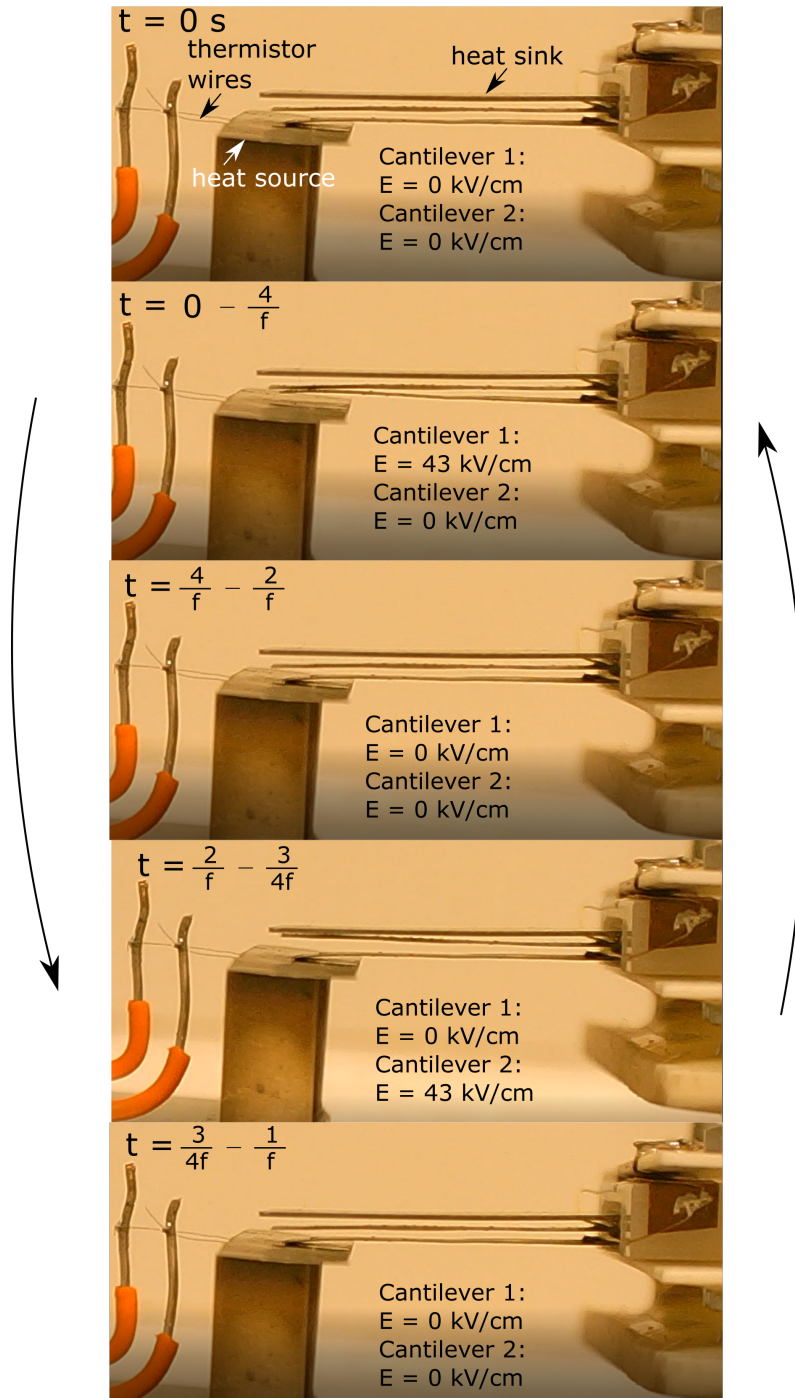


Figure 5.45: Determination of cooling capacity with two active cantilevers. One cycle with two active cantilever elements at 43 kV/cm is shown. The active cantilever is in contact with the upper element for a quarter of the cycle period ( $0 - \frac{4}{f}$ ) and the second quarter of the period ( $\frac{4}{f} - \frac{2}{f}$ ) in contact with the heat source where the temperature is measured. During  $\frac{2}{f} - \frac{3}{4f}$  the electric field is applied to the cantilever element 2, which is then in contact with the heat sink. The electric field is then reduced to zero during the period  $\frac{3}{4f} - \frac{1}{f}$ .

To provide a comparison with two active cantilevers (Fig. 5.45) we also performed measurements using one active cantilever (Fig. 5.43). The results are shown in Fig. 5.46. By cycling only one of the cantilevers, we reached a temperature change of 35 mK after 25 s. In comparison, by driving two cantilevers the temperature drop was 45 mK. With this experiment we show that the temperature span in the device could, in principle, be increased by increasing the number of active cantilever elements, which qualitatively confirms the initial model (Section 5.1). It is also evident that the heat transfer is severely limited, thus no energy regeneration is occurring, resulting in small temperature spans across the device. To improve the quality of the thermal contact the cantilever surfaces must be modified to allow a more efficient heat transfer. An attempt was made to deposit water and glycol on the surfaces of the cantilevers, and the fluids temporarily increased the heat transfer; however, after a few cycles the droplets caused a short circuit of the devices due to their conductive nature.

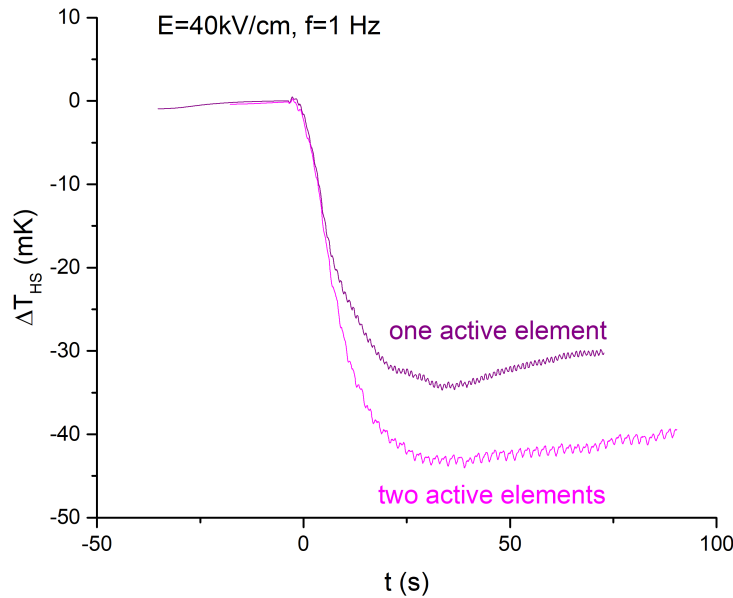


Figure 5.46: Temperature of the heat source as a function of time when one element is active (purple line) and when both elements are active (pink).

In summary, the device exhibited a relatively small temperature span for several reasons:

(i) the surface area of the contact is low due to the non-ideal flatness of the cantilevers and due to the nature of the cantilever's bending. The deflection of the cantilever is quadratically proportional to the length, meaning only a small portion of the area will have sufficient contact with the adjacent cantilever (see Fig. 5.43 when the cantilever is subjected to an electric field and makes contact with the upper cantilever only along a small area at the tip of the active cantilever). In the device designed by Ma et al. [76], this was solved by using electrostatic actuation that forces the polymer elements to "stick" to the heat sink and source, thus probably ensuring a good thermal contact. In our case, an improvement could be made with an appropriate thermally but not electrically conductive fluid in combination with so-called S-shaped cantilevers [2], [164]. The fluid would improve the contact resistance due to poor surface roughness and flatness and the

S-shaped cantilevers would increase the portion of the cantilever area in contact with the adjacent element.

(ii) the thermal mass of the samples was small compared to their area, which leads to a large thermal exchange with the surroundings, as can be inferred from Equation 5.8.

(iii) the elements used in our device, in general, consist of a large portion of EC non-active parts (one inactive PMN layer, Pt electrode, non-electroded parts of the sample). The structure could be optimized to a certain degree so it would contain a smaller passive volume.





## Chapter 6

# Conclusions

- In the scope of this PhD we have made an attempt to design, model, fabricate and characterize an EC cooling device made of multiple cantilevers of active EC materials arranged in a cascade. The cooling device was based on the coupled electrocaloric and electromechanical properties of the PMN-100xPT relaxor ferroelectric system, in which the applied electric field on individual cantilevers trigger the EC cooling effect and, at the same time, bending, which is used to make thermal contact between the cantilevers.
- To test our design idea, we have numerically modelled the behaviour of such a device. The results showed that the device is feasible and possesses properties that solve the core problem of the dielectric cooling, that is, the low intrinsic electrocaloric temperature changes. Based on the results of modelling, we concluded that the device should enhance the electrocaloric response of individual cantilevers by establishing a temperature span across the device. This span was several times larger than the EC effect of the material (i.e., individual cantilever).
- Motivated by the promising modelling results, we decided to fabricate a proof-of-concept device. We began by searching for an optimal composition within the PMN-100xPT system. The selection process followed a procedure in which electrical, electromechanical, thermal and electrocaloric properties were characterized and taken into account in the final figure-of-merit designed by taking into account all the mentioned properties. In the process of characterization, we observed several peculiarities of the analysed materials, for example, we have observed that PMN is superior to the rest of the compositions ( $x=0, 0.1, 0.20, 0.3, 0.35, 0.4$ ) in terms of electrical loss. Low electrical loss is important due to the high efficiency desired in dielectric cooling and the due to its detrimental effects in the electric-field induced temperature response. In terms of the electrocaloric effect, PMN and PMN-10PT exhibited similar response, which was superior to the rest of the analysed compositions. In terms of thermal properties (thermal conductivity, diffusivity and specific heat capacity), PMN-40PT possessed the best performance, probably because of the lower density of planar defects (larger domains) in comparison to PMN. Electromechanically, PMN-40PT also exhibited the best performance.
- Our selection based on a function, which took four Figures of Merit into account, pointed to PMN as the most suitable material for the device integration.
- The fatigue properties of PMN were then taken into consideration as EC materials are expected to provide cooling effects for a high number of electric-field cycles. We showed that cycling PMN is problematic due to the high electric fields involved (in

our case up to 70 kV/cm). Upon cycling Joule heating occurred due to the formation of a field-induced ferroelectric phase. The ferroelectric phase provided a driving force for point defects to accumulate and form conductive paths at grain boundaries. However, with careful tuning of the electric field and temperature conditions the fatigue can be avoided.

- We fabricated the PMN cantilever elements for the device by tape-casting. They were sintered and cut into tapes with dimensions suitable for cantilever elements. We optimized the fabrication to achieve dense and as-flat-as-possible cantilevers. The cantilever elements were then characterized and their properties were compared to the bulk PMN. The cantilever elements possessed lower dielectric properties and electromechanical response; this was expected, due to the surface effects and residual stresses that are usually present in thick films.
- The elements were then used in a proof-of-concept device. Despite the low temperature span (45 mK) achieved in our device, we showed that with increasing number of elements, the temperature span in the device can be enhanced. The characterization of the device's performance showed that the thermal contacts between the cantilevers are the bottleneck of this device design. Thus, surface-engineering methods should be employed to tailor the thermal contact resistivity and increase the contact area.

## Appendix A

## Appendix

### A.1 Structural and Microstructural Properties of PMN-xPT Ceramics

The densities of the analysed materials obtained with Archimedes method are shown in Table A.1. The densities vary by 0.1 kg/l, which is within 10 % of the average values of all the densities.

Table A.1: Density of the ceramics under investigation.

| Material | Density (kg/l) | Relative density (%) |
|----------|----------------|----------------------|
| PMN      | 7.79           | 95.8                 |
| PMN-10PT | 7.89           | 97.1                 |
| PMN-20PT | 7.71           | 94.8                 |
| PMN-30PT | 7.78           | 95.7                 |
| PMN-35PT | 7.72           | 95                   |
| PMN-40PT | 7.74           | 95.2                 |

The grain size of the prepared ceramics was first measured and characterized [102]. The values are shown in Table A.2. The grains are in the range from 2.9 to 7  $\mu\text{m}$ , where it is expected that the size of the grains does not significantly influence the properties of the materials [64], [162].

Table A.2: Grain size of the ceramics under investigation.

| Material | grain size                  |
|----------|-----------------------------|
| PMN      | $3.15 \pm 1.7 \mu\text{m}$  |
| PMN-10PT | $6.84 \pm 3.84 \mu\text{m}$ |
| PMN-20PT | $4.03 \pm 2.16 \mu\text{m}$ |
| PMN-30PT | $3.19 \pm 1.76 \mu\text{m}$ |
| PMN-35PT | $2.92 \pm 1.51 \mu\text{m}$ |
| PMN-40PT | $2.90 \pm 1.55 \mu\text{m}$ |

The XRD patterns of the crushed pellets of PMN-100xPT corresponded to the phase-pure perovskite, see Fig. A.1.

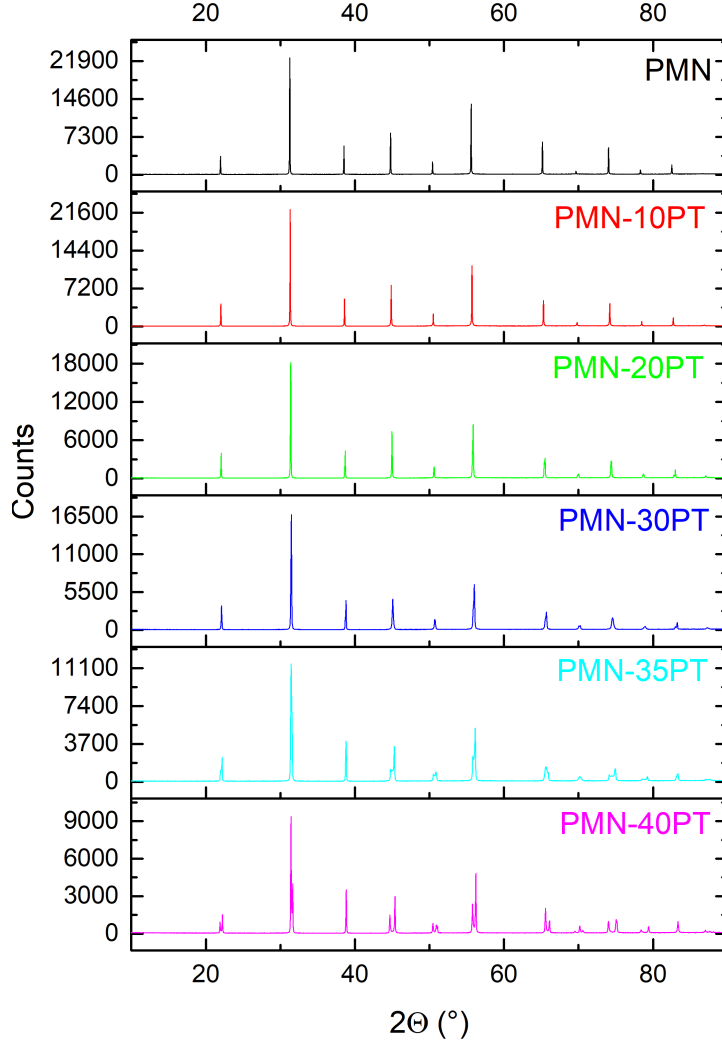


Figure A.1: XRD patterns of PMN-xPT ceramics.

## A.2 Correction Factors Determined with Finite-Element Modelling

To justify the use of a correction factor in the evaluation of the EC temperature change of the samples we analysed the case with numerical modelling [38]. The modelling was carried out with COMSOL Multiphysics.

The geometry of the typical sample was modelled in 3D as shown in Figure A.2. The largest disk represents the PMN sample. The inner circle is the electroded part of the sample. The electrical contacts of the sample are represented by a square wire glued to the sample with a square-shaped glue. The thermistor is represented by a sphere with cylindrical wires. The sample was 150  $\mu\text{m}$  thick and the 50- $\mu\text{m}$  Au electrical wires were glued to the sample with 50- $\mu\text{m}$ -thick silver layer. The radius of the thermistor end was 100  $\mu\text{m}$  while the radius of the Pt thermistor wires was 25  $\mu\text{m}$ .

We simulated the temperature change during adiabatic polarization of the PMN by applying a step-like electric field. The induced EC effect was assumed to be 0.51 K. 0.51

$K$  is the corrected value of the EC temperature response of the PMN sample at 30 kV/cm (see Fig. 5.16).

Figure A.2 shows the simulated temperature in the sample 0.5 s after the EC effect has been induced. The time (0.5 s) corresponds to the peak value of temperature in the thermistor. The colours illustrate the temperature distribution in the analysed sample (see adjacent color bar). From the temperature distribution we can observe that the temperature is lower (i) in the parts where the EC material is in direct contact with the elements which do not contribute to the EC temperature change (see red regions) and (ii) in the non-electroded peripheral area (yellow border region of the sample). In areas away from the passive elements and under electrode the temperature is higher (white regions).

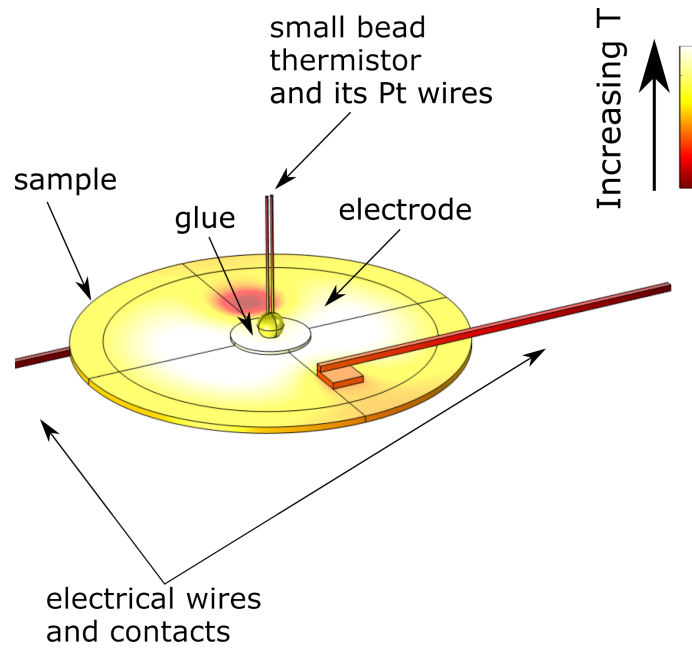


Figure A.2: Simulated temperature distribution in the sample after 0.5 s.

Figure A.3 shows the volume-averaged temperature in the thermistor plotted versus time for the first 2 s of the EC experiment. The results of the simulations illustrate two important points that must be considered in the evaluation of the EC effect. First, the data show that the maximum temperature of the thermistor at 0.5 s (vertical black line) reaches a value of 0.28 K, which is by a factor of 1.7 lower than the EC temperature change assumed in the simulations (0.51 K; dashed red horizontal line). This correction factor agrees well with that calculated by the method described in Ref. [38] and the experimental data in Fig. 5.16. Thus, it was used throughout our study.

Fig. A.3 also shows that the thermalization time of the thermistor, i.e., the time needed to equalize the sample temperature to that of the thermistor, is 0.5 s. This is consistent with the value, i.e., 1 s, found in the thermistor datasheet.

In practice, the thermalization time may vary depending on the thickness of the glue layer and position of the thermistor (see temperature gradients in the sample in Figure A.3a) and quality of the thermal contact between the thermistor and the sample.

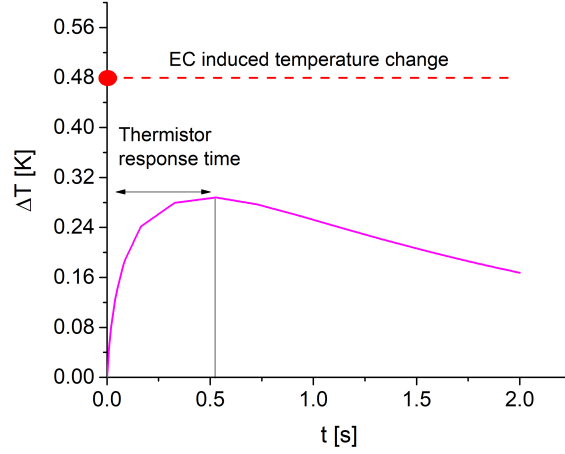


Figure A.3: Simulated volume-averaged temperature evolution on the thermistor as a function of time.

### A.3 EC and EM effect of the cantilevers

The cantilever's deflection plotted versus the EC temperature change during adiabatic depolarization is shown in Fig. A.4. The deflections are in correlation with the EC temperature change.

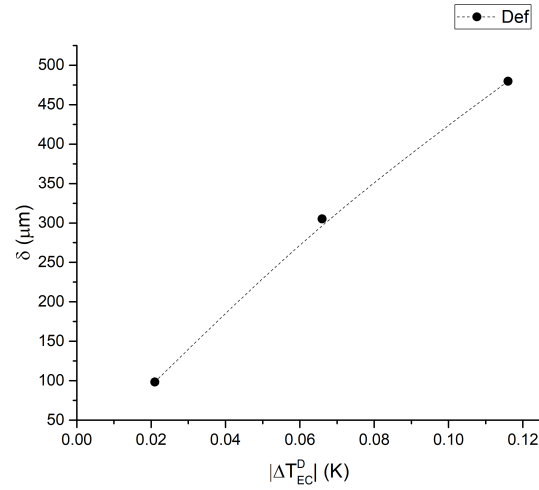


Figure A.4: Cantilever B deflections plotted versus the EC temperature change during adiabatic depolarization.

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