

RELAXOR-FERROELECTRIC-BASED CERAMIC MULTILAYER ELEMENTS FOR VIABLE ELECTROCALORIC COOLING

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Doctoral Dissertation
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KERAMIČNI VEČPLASTNI ELEMENTI NA OSNOVI
RELAKSORSKIH FERROELEKTRIKOV ZA
IZVEDLJIVO ELEKTROKALORIČNO HLAJENJE

Doktorska disertacija

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To my dear ones

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Abstract

The discovery of the “giant” electrocaloric (EC) effect (Mischenko et al., Science, 2006) triggered the interest of the scientific community due to its potential use in refrigeration technology. The magnitude of the EC effect, that is, the EC temperature change (ΔT_{EC}), depends on the chemical composition, applied electric field and temperature. The $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $x\text{PbTiO}_3$ (PMN-100xPT) solid solution has been studied for its excellent dielectric and piezoelectric properties, and it has been shown that PMN and PMN-rich solid solutions with dielectric permittivity maxima close to room temperature exhibit ΔT_{EC} that are among the largest reported for relaxor ferroelectric ceramics. The latter are in the range of a few K for electric fields close to the dielectric breakdown strength at about 100 kV/cm.

In the first part of the thesis we investigate the relation between the temperature of the maximum ΔT_{EC} ($T_{\text{EC max}}$) and the temperature of the permittivity peak (T_{m}) as a function of the electric field (E) in PMN, PMN-5PT and PMN-10PT bulk ceramics, prepared from mechanochemically synthesized powders. Both maxima, ΔT_{EC} and $T_{\text{EC max}}$, increase with increasing PT content at a given field. By applying the DC bias above the threshold field the ferroelectric state is induced, and consequently the T_{m} is strongly up-shifted with increasing electric field. Since the $T_{\text{EC max}}$ is always lower than T_{m} and the temperature gap between both maxima progressively increases with increasing DC bias, the T_{m} cannot be used as the estimation of the $T_{\text{EC max}}$. In contrast, T_{m} can only roughly mark the temperature of the upper boundary of the temperature-electric-field window where the EC responsivity ($\Delta T_{\text{EC}}/\Delta E$) is the highest.

In multilayer (ML) elements the thickness of individual layers is in the range of a few tens of μm , i.e., much lower than the thickness of bulk ceramic samples. The PMN and PMN-10PT ML elements were fabricated by tape casting. The phase composition, microstructure, low- and high-field dielectric properties of ML elements are comparable to those of bulk. Moreover, the EC responsivity of the PMN and PMN-10PT ML elements is comparable to their bulk counterparts; however, here significantly lower voltages are needed. The maximum ΔT_{EC} of 1.99 K and 2.72 K at 120 kV/cm at 62 °C and 99 °C were obtained for PMN and PMN-10PT, respectively, by both direct and indirect EC measurements. Nevertheless, at room temperature the PMN and PMN-10PT ML elements exhibit almost the same ΔT_{EC} as a consequence of the lower $T_{\text{EC max}}$ of the former. Both PMN and PMN-10PT ML elements exhibit an almost fatigue-less EC behaviour after 10^6 electric field cycles at ~ 100 kV/cm, indicating that they are a viable choice for EC cooling applications.

Povzetek

Elektrokalični (EK) pojav je po odkritju ‘ogromnega’ EK pojava pred dobrimi desetimi leti (Mischenko et al., Science, 2006) vzbudil izjemno zanimanje raziskovalcev zaradi možnosti uporabe v hladilni tehniki. EK sprememba temperature (ΔT_{EC}), ki običajno predstavlja merilo EK pojava, je odvisna od kemijske sestave, električnega polja in temperature. Volumenska keramika na osnovi trdne raztopine $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}x\text{PbTiO}_3$ (PMN-100xPT) ima odlične dielektrične in piezoelektrične lastnosti, poleg tega pa PMN in s PMN bogate trdne raztopine izkazujejo ΔT_{EC} , ki so med največjimi objavljenimi vrednostmi za relaksorske feroelektrike. Slednje dosegajo nekaj K pri električnih poljih okrog 100 kV/cm, kar je blizu prebojne trdnosti feroelektrične volumenske keramike.

V prvem delu doktorske disertacije raziskujemo povezavo med temperaturo, pri kateri doseže ΔT_{EC} največjo vrednost ($T_{\text{EC max}}$) in temperaturo maksimuma dielektričnosti (T_{m}) v odvisnosti od električnega polja (E) v volumenski keramiki PMN, PMN-5PT in PMN-10PT, ki smo jo pripravili iz mehanokemijsko sintetiziranih prahov. Tako največja ΔT_{EC} and $T_{\text{EC max}}$ pri danem električnem polju naraščata z deležem PT. Ko na vzorec pritismo električno polje, ki presega mejno vrednost, induciramo feroelektrično fazo. Posledično se T_{m} izrazito pomika k višjim temperaturam, pri čemer pomik narašča z amplitudo polja. Temperatura $T_{\text{EC max}}$ je vedno nižja od T_{m} , poleg tega se interval med obema temperaturama z naraščajočim poljem povečuje, zato T_{m} ne moremo uporabiti kot ocene za $T_{\text{EC max}}$. Nasprotno, T_{m} lahko uporabimo le kot okvirno zgornjo mejo območja z največjim EK odzivom ($\Delta T_{\text{EC}}/\Delta E$) v diagramu temperatura – električno polje.

V večplastnih elementih je debelina posamezne plasti običajno nekaj 10 μm , kar je precej manj, kot je debelina vzorcev volumenske keramike. Večplastne elemente PMN in PMN-10PT smo izdelali s tehnologijo nalivanja. Fazna sestava, mikrostruktura, dielektrične lastnosti in tudi EK odziv omenjenih elementov so primerljivi z lastnostmi volumenske keramike. Elementi PMN in PMN-10PT izkazujejo največjo vrednost ΔT_{EC} 1.99 K oziroma 2.72 K pri 120 kV/cm in pri 62 °C (PMN) in 99 °C (PMN-10PT), izmerjeno tako z direktno kot z indirektno metodo. Pri sobni temperaturi sta vrednosti ΔT_{EC} obeh sestav zelo podobni, kar je posledica nižje $T_{\text{EC max}}$, ki jo izkazuje PMN. Večplastni elementi PMN in PMN-10PT tudi po 10^6 ciklih z amplitudo polja ~ 100 kV/cm skoraj ne izkazujejo zmanjševanja EK odziva, zato lahko zaključimo, da so primerni kandidati za uporabo v hladilni tehniki.

Contents

List of Figures	xv
List of Tables	xix
Abbreviations	xxi
Symbols	xxiii
1 Introduction	1
1.1 Electrocaloric Effect	1
1.1.1 Electrocaloric cycle	2
1.1.2 Methods for measuring the electrocaloric effect.....	3
1.2 (1-x)Pb(Mg _{1/3} Nb _{2/3})O ₃ -xPbTiO ₃ Solid Solution.....	5
1.3 Electrocaloric Effect in PMN-PT	6
1.3.1 Influence of the DC bias-field on the dielectric permittivity and the relation to the EC effect	8
1.3.2 Electrocaloric stability upon electric field cycling	10
1.4 Multilayer Elements; a Viable Solution for EC Cooling	11
2 Aims and Hypothesis	15
3 Materials and Methods	17
3.1 Sample Preparation.....	17
3.1.1 Mechanochemical synthesis of the (1-x)Pb(Mg _{1/3} Nb _{2/3})O ₃ -xPbTiO ₃ powders	17
3.1.2 Sintering of bulk ceramics	20
3.1.3 Fabrication of multilayer elements	21
3.1.3.1 Slurry preparation	21
3.1.3.2 Tape casting and the fabrication of ML elements	21
3.1.3.3 Sintering of ML elements.....	22
3.2 Characterization Methods	23
3.2.1 Particle size and size distribution	23
3.2.2 X-Ray diffraction.....	23
3.2.3 Density	23
3.2.4 Inductively coupled plasma spectroscopy	23
3.2.5 Viscosity of ceramic slurries	24
3.2.6 Thermogravimetric analysis	24
3.2.7 Microstructural analysis	24
3.2.8 Dielectric spectroscopy	24
3.2.9 Polarization electric-field hysteresis measurements	25
3.2.10 Piezoelectric measurements	25
3.2.11 Electrocaloric measurements	25

3.2.11.1	Indirect electrocaloric measurements	25
3.2.11.2	Direct electrocaloric measurements via modified differential scanning calorimeter	25
3.2.12	Stability of the electrocaloric effect.....	27
4	Results and Discussion	29
4.1	PMN and PMN-PT Bulk Ceramics.....	29
4.1.1	Synthesis of PMN and PMN-PT powders	29
4.1.2	Microstructure and phase composition	32
4.1.3	Dielectric and ferroelectric properties	37
4.1.4	Dielectric permittivity under DC bias field.....	41
4.1.5	Electrocaloric effect in bulk ceramics.....	44
4.1.6	Comparison of the electrocaloric properties between PMN and PMN-PT bulk ceramics	46
4.2	PMN and PMN-10PT Multilayer Elements	51
4.2.1	Preparation of ML elements	51
4.2.2	Microstructure and phase composition	53
4.2.3	Dielectric and ferroelectric properties	58
4.2.3.1	Stress-induced ferroelectric phase in PMN-10PT ML elements	61
4.2.4	EC effect in multilayer elements.....	64
4.2.5	Comparison of the EC properties between the ML elements and bulk ceramics	67
4.2.6	Stability of the EC effect in multilayer elements.....	72
5	Summary and Conclusions	77
5.1	PMN and PMN-PT Bulk Ceramics.....	77
5.2	PMN and PMN-10PT Multilayer Elements	78
Appendix A	Indirect Measuring Method	79
Appendix B	Tape Casting and the Fabrication of Multilayer Elements	81
B.1	Slurry Preparation.....	82
B.2	Tape Casting of the Green Tape	82
B.3	From Green Tape to Multilayer Elements	84
Appendix C	Temperature versus Electric Field Contour Graphs of Electrocaloric Responsivity	85
References		87
Bibliography		97
Biography		101

List of Figures

Figure 1.1: (a) Schematic diagram of an EC cycle, showing its four stages [16]	3
Figure 1.2: Example of a ΔT_{EC} measurement, where the temperature versus time is determined by a direct measuring method.....	4
Figure 1.3: Comparison of EC temperature change (ΔT_{EC}) values measured on the same batch of multilayer elements with different set-ups.....	5
Figure 1.4: Phase diagram of PMN-xPT solid solution with $0 < x < 0.5$, ...	6
Figure 1.5: (a) EC effect (ΔT_{EC}) measured in PMN at different temperatures and electric fields up to 90 kV/cm. (b) Temperature of maximum ΔT_{EC} vs electric field (4–50 kV/cm) for PMN-PT solid solutions ($x=0-0.30$) [53].	7
Figure 1.6:(a) Shifting of T_m with increasing DC bias field (E_{DC}) for PMN-PT single crystals.....	8
Figure 1.7: a) Dielectric permittivity versus temperature measured without electric field and with DC-bias of 10 kV/cm and 25 kV/cm in PMN-10PT ceramics. b) Comparison of the dielectric permittivity upon a DC bias of 25 kV/cm and the EC effect at 28 kV/cm versus temperature [52].....	9
Figure 1.8: Normalized remanent polarization in a relaxor $0.85K_{1/2}Na_{1/2}NbO_3-0.15SrTiO_3$ ceramic as a function of applied electric field cycles, compared to a fatigue investigation on ferroelectric $(Pb_{0.88}La_{0.08})(Zr_{0.65}Ti_{0.35})O_3$ ceramics	10
Figure 1.9: a) Multilayer (ML) capacitor as an existing electronic component, which can be found on an Intel Xenon E3 processor. (b) Schematic of a ML element based on $BaTiO_3$ (BTO). (c) Optical microscope image of a ML cross-section obtained after sawing and polishing [16].....	12
Figure 1.10:The EC effect of ML elements found in the literature.....	13
Figure 3.1:Schematic presentation of the (a) PMN and (b) PMN-PT mechanochemical synthesis.	18
Figure 3.2: Tape caster with the heating zones 1 and 2 marked with a red line.....	22
Figure 3.3:ML elements placed in an alumina crucible with the $PbZrO_3$ packing powder alongside.	22
Figure 3.4: The DC bias blocking circuit for the LCR meter	25
Figure 3.5: (a) Photograph of the DSC 204 F1 modified for EC measurements. (b) Custom made lid which serves as the sample holder. (c) Bulk ceramic sample mounted onto the lid with a miniature thermistor glued in the middle of the sample.....	26
Figure 3.6:(a) The scheme of the sample holder for EC stability testing. (b) Monitoring the EC stability	27
Figure 4.1: XRD patterns of the PMN and PMN-PT powders after high-energy milling.....	30
Figure 4.2: Particle size distributions of (a) PMN, (b) PMN-5PT and (c) PMN-10PT. ...	31
Figure 4.3: XRD patterns of the PMN, PMN-5PT and PMN-10PT sintered bulk	32
Figure 4.4: a) FE-SEM micrograph of a polished PMN surface. (b) WDXS analysis of six random points.....	33
Figure 4.5: FE-SEM micrographs and WDXS analyses of the polished PMN-5PT (a, b) and PMN-10PT (c, d) surfaces.....	35

Figure 4.6: FE-SEM micrographs of thermally etched (a) PMN, (b) PMN-5PT and (c) PMN-10PT bulk ceramics. In (d), (e) and (f) the average grain size (GS) and grain size distribution plots are provided for PMN, PMN-5PT and PMN-10PT, respectively.	36
Figure 4.7: Temperature-dependent dielectric permittivity of PMN (black lines), PMN-5PT (red lines) and PMN-10PT (blue lines) bulk ceramics measured	38
Figure 4.8: P - E hysteresis loops of PMN, PMN-5PT and PMN-10PT ceramics	40
Figure 4.9: The real part of the complex dielectric permittivity (ϵ') versus temperature, measured at DC bias fields of 0 to 50 kV/cm, is shown in (a) PMN, in (b) PMN-5PT, and in (c) PMN-10PT bulk ceramics.	42
Figure 4.10: DC bias field dependence of (a) absolute values of T_m and (b) normalized values $\Delta T_m = T_m(E_{DC}) - T_m(E_{DC}=0)$ for PMN, PMN-5PT and PMN-10PT.	43
Figure 4.11: Electrocaloric temperature change (ΔT_{EC}) of (a) PMN, (b) PMN-5PT and (c) PMN-10PT bulk ceramics	45
Figure 4.12: Electrocaloric temperature changes (ΔT_{EC}) in PMN, PMN-5PT and PMN-10PT bulk ceramics	46
Figure 4.13: Temperature of the maximum ΔT_{EC} ($T_{EC \max}$) versus electric field for PMN, PMN-5PT and PMN-10PT bulk ceramics.	47
Figure 4.14: Comparison of ΔT_{EC} and ϵ' as a function of temperature at 50 kV/cm for PMN (on left) and PMN-5PT (on right).	48
Figure 4.15: The EC responsivity as a function of temperature and electric field expressed for PMN.	49
Figure 4.16: The EC responsivity as a function of temperature and electric field expressed for (a) PMN-5PT and (b) PMN-10PT.	50
Figure 4.17: (a) Dependence of viscosity on the weight percent of the dispersant oleic acid in a PMN-10PT slurry, presented for shear rates of 113, 242 and 500 1/s. (b) Viscosity as a function of the shear rate for the PMN-10PT slurry.	52
Figure 4.18: Thermogravimetry (TG) and differential thermal analysis (DTA) of the PMN-10PT green tape in the temperature range of 25 to 700 °C.	52
Figure 4.19: (a) Scheme of a ML layer with lateral dimensions. (b) Photo of a sintered ML element (PMN-10PT). The FE-SEM micrographs showing the cross-sections of (c) PMN and (d) PMN-10PT ML elements, with the layer thickness.	53
Figure 4.20: XRD patterns of the PMN and PMN-10PT sintered ML elements.	54
Figure 4.21: In (a) FE-SEM micrographs of the outer surface of the PMN ML element is presented, while the high-magnification inset reveals trace impurities at the grain-boundaries. Micrographs of the (b) polished and (c) thermally etched cross-section of the PMN ML element are shown.	55
Figure 4.22: WDXS analyses of the PMN ML element, where for each layer two points were analysed, with the exception of layer 5, where only one data point could be reliably measured.	55
Figure 4.23: (a) PMN-10PT FE-SEM micrograph of the ML's outer surface, with high-magnification view of the impurity at the grain boundaries in the inset. Micrographs of the (b) polished and (c) thermally etched cross-section are shown.	56
Figure 4.24: WDXS of PMN-10PT ML element, where for each layer two points were probed.	57
Figure 4.25: Temperature-dependent dielectric response of PMN ML element (solid line) and bulk ceramics (dashed line)	59
Figure 4.26: Temperature-dependent dielectric response of PMN-10PT ML element (solid line) and bulk ceramic (dashed line)	60
Figure 4.27: P - E hysteresis loops of (a) PMN and (b) PMN-10PT ML elements (solid line) and bulk ceramics (dashed line)	61

Figure 4.28: First derivative of ϵ' as a function of temperature for the PMN-10PT ML element	62
Figure 4.29: A simplified scheme of the thermal shrinkage of a ML element upon cooling from the sintering temperature.....	63
Figure 4.30: Calculated residual stresses with the finite-element method in PMN-10PT ML elements.....	64
Figure 4.31: ΔT_{EC} versus temperature of (a) PMN and (b) PMN-10PT ML elements	65
Figure 4.32: ΔT_{EC} comparison between PMN (black square symbols) and PMN-10PT (red circle symbols) ML elements.....	67
Figure 4.33: The ΔT_{EC} comparison between the ML elements and the bulk ceramics for (a) PMN and (b) PMN-10PT.....	68
Figure 4.34: Comparison of the electric-field-dependent $T_{EC \max}$ between ML elements (hollow symbols) and bulk ceramics (solid symbols) for PMN and PMN-10PT materials.	70
Figure 4.35: (a) Temperature change (ΔT) as a function of time (t) for bulk (black symbols) and ML (red symbols) PMN-10PT.....	71
Figure 4.36: The EC temperature change normalized by the initial ΔT_{EC} value as a function of the number of the electric field cycles for the (a) PMN and (b) PMN-10PT ML elements.....	73
Figure 4.37: Temperature dependence of the dielectric permittivity measured at frequencies between 100 Hz and 100 kHz and dielectric losses ($\tan \delta$) at 1 kHz for PMN (a,b) and for PMN-10PT (c, d) before and after cycling.	74
Figure 4.38: P - E hysteresis loops of PMN ML element before and after the electric field cycling.....	75
Figure 4.39: FE-SEM micrographs of (a) the polished and (b) thermally etched PMN ML cross-section after electric field cycling	76
Figure A.1: (a) P - E hysteresis loops measured at temperatures from 25 °C to 110 °C, at an electric field of 100 kV/cm. (b) Calculated ΔT_{EC} versus temperature at electric fields of 10 to 100 kV/cm.....	79
Figure B.1: Schematic representation of the tape-casting process [147].....	81
Figure B.2: The influence of the two-stage milling time on the final fired density. The first and the second numbers are the durations of the respective milling stages in hours [146].	82
Figure B.3: Simplified doctor-blade assembly of a tape caster.	83
Figure B.4: The multi-step process of fabricating multilayer elements, after [149].....	84
Figure C.1: The EC responsivity as a function of electric field and temperature expressed for PMN.....	85
Figure C.2: The EC responsivity as a function of electric field and temperature field expressed for (a) PMN-5PT and (b) PMN-10PT.	86

List of Tables

Table 1.1: EC temperature change, electric field and measurement temperature in PMN-rich and PMN-PT bulk ceramics (selected results)	8
Table 1.2: Reported values of the EC effect measured in ML elements	13
Table 3.1: List of chemicals used in the preparation of PMN and PMN-PT powders and green tapes.....	19
Table 3.2: List of equipment used in the preparation of PMN and PMN-PT powders, bulk and ML samples.....	20
Table 3.3: The amount of slurry additives for the PMN and PMN-10PT compositions.	21
Table 3.4: Theoretical densities (TD) of PMN and PMN-PT.	23
Table 4.1: The PMN-PT particle size limit of 10 % (d_{10}), 50 % (d_{50}), and 90 % (d_{90}). ..	30
Table 4.2: Concentrations of contaminants (Co, W and Zr) in the PMN and PMN-PT powders.....	32
Table 4.3: Density and relative density (RD) of the PMN-PT bulk ceramics.	32
Table 4.4: Results of the WDXS analyses of the PMN expressed as the average of six measurements.	34
Table 4.5: Results of the WDXS analyses for PMN-PT expressed as the average of six measurements.	34
Table 4.6: Values of $\epsilon'_{\max}$, maximum dielectric losses ($\tan \delta_{\max}$) and T_m obtained at 1 kHz in various bulk PMN and PMN-PT ceramics.....	39
Table 4.7: Saturated polarization (P_s) of various PMN and PMN-PT ceramics.....	40
Table 4.8: Results of the WDXS analyses for the PMN and PMN-10PT ML elements .	56
Table 4.9: Material properties used for estimating the residual stresses in ML elements.	62
Table 4.10: The EC effect of PMN determined via the direct (ΔT_{EC}) and indirect ($\Delta T_{EC\ IND}$) methods.	65
Table 4.11: The EC effect of PMN-10PT determined via the direct (ΔT_{EC}) and indirect ($\Delta T_{EC\ IND}$) methods.	66
Table 4.12: Comparison of the EC properties of selected PMN and PMN-PT ML elements and bulk ceramics, measured at similar electric fields.	69
Table 4.13: The EC temperature changes of ML elements expressed with and without the correction factor.....	70

Abbreviations

AC	... Alternating current
BTO	... BaTiO ₃
C1	... Capacitor 1 μ F
C2	... Capacitor 1 μ F
DMM	... Digital multimeter
DC	... Direct current
DSC	... Differential scanning calorimeter
DTA	... Differential thermal analysis
EC	... Electrocaloric
FE SEM	... Field-emission scanning electron microscope
GS	... Grain size
ICP	... Inductively coupled plasma
IPA	... Isopropanol
ML	... Multilayer
MPB	... Morphotropic phase boundary
PMN	... Pb(Mg _{1/3} Nb _{2/3})O ₃
PMN-100xPT	... (1-x)Pb(Mg _{1/3} Nb _{2/3})O ₃ -xPbTiO ₃
PSD	... Particle size distributions
PT	... PbTiO ₃
R1	... 100-kOhm resistor
RD	... Relative density
RT	... Room temperature
STDEV	... Standard deviation
TD	... Theoretical density
TG	... Thermogravimetry
WC	... Tungsten carbide
XRD	... X-ray powder diffraction
YSZ	... Yttria-stabilized zirconia
WDXS	... Wavelength-dispersive X-ray spectrometry

Symbols

D_i	... Electric displacement
d	... Sample thickness
E_{DC}	... DC bias electric field
E_{Pt}	... Elastic modulus of platinum
E_i	... Electric field vector
E_t	... Threshold field
P_S	... Saturated polarization
$T_{EC\ max}$	... Temperature of the maximum ΔT_{EC} value
T_m	... Temperature of the dielectric peak maximum
$\Delta T_{EC\ raw}$	... EC temperature change measured by a thermistor or thermocouple without correction
$\Delta T_{EC}/\Delta E$	... Electrocaloric responsivity
$\Delta T_{IND\ EC}$	... Electrocaloric temperature change determined by the indirect measuring method
ΔT_m	... Temperature difference of dielectric peak maximums without the DC bias and under the DC bias
ΔT_{EC}	... EC temperature change
ΔT	... Temperature change
X_{ij}	... Stress tensor
c_E	... Specific heat capacity
c_E^a	... Specific heat capacity of the active part
c_E^i	... Specific heat capacity of the passive part
d_{10}, d_{50}, d_{90}	... Particle size reached by 10 %, 50 % and 90 % of the particles per area
d_{33}	... Piezoelectric coefficient
m^a	... Mass of the active part
m^i	... Mass of the passive part
p_i	... Pyroelectric coefficient
$v_{cycling}$	... Frequency of electric field cycling
x_{ij}	... Strain
α_{Pt}	... Thermal expansion coefficient of platinum
α_{cer}	... Thermal expansion coefficient of PMN/PMN-10PT
ε^*	... Complex dielectric permittivity
ε'	... Real part of the complex dielectric permittivity
ε''	... Imaginary part of the complex dielectric permittivity
ε'_{max}	... Maximum of the real part of dielectric permittivity
σ_{Pt}	... Tensile stress in electrodes

σ_{cer}	... Compressive stress in ceramic layer
ΔT_{EC}	... EC temperature change
ΔT	... Temperature change
t	... Time
t_{EC}	... Relaxation time
G	... Gibbs free energy
P	... Polarization
S	... Entropy
T	... Temperature
U	... Internal energy
$\tan \delta$	... Dielectric loss
Δx	... Difference between thermal deformations of platinum electrode and ceramic layer
κ	... Thermal conductivity
ρ	... Density
τ	... Thermal time constant
ν	... Frequency

Chapter 1

Introduction

In the Introduction the fundamental phenomena and the current status of the topics relevant to the thesis are presented. Firstly, the electrocaloric effect and its thermodynamic background are discussed, alongside the electrocaloric cycle and measurement methods. The second part is focused on the $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ (PMN-PT) solid solution. The third part includes an overview of selected electrocaloric studies of the PMN-PT solid solution in the form of bulk ceramics. The relationship between the dielectric permittivity under a DC bias field and the electrocaloric effect is discussed. Moreover, the stability of the electrocaloric effect is introduced. In the last part the results of recent electrocaloric studies of multilayer elements are collected and discussed.

1.1 Electrocaloric Effect

The electrocaloric (EC) effect is a temperature change induced in a polar material by an electric field, and was first observed in Rochelle salt in 1930 [1]. The effect was small, about 0.1 K, and only since the discovery of the “giant” EC effect of 12 K measured at 480 kV/cm in ferroelectric lead zirconate titanate thin films in 2006 [2] was a major interest in the scientific community triggered.

The EC effect is defined as an adiabatic and reversible temperature change, induced by an external electric field in dielectric materials. More precisely, in polar dielectrics the polarization increases with the applied electric field, due to the partial dipole alignment, which leads to a reduction of the dipole entropy. Under adiabatic conditions, in order to maintain the total entropy unchanged, the temperature of a material increases. Conversely, when the electric field is removed, the entropy of dipoles increases as a result of the polarization reduction and the return of dipoles to the disordered state, and consequently the dielectric material cools down. Such an abrupt EC temperature change is denoted as ΔT_{EC} [3]–[5].

The thermodynamic background of the EC effect can be explained by two approaches. One is by the phenomenological theory [6], [7]; the other is by using the polarization P as function of temperature and electric field in the frame of the Maxwell equations. In agreement with the first and the second law of thermodynamics, the EC effect is described as a change in the internal energy dU of a material [6]

$$dU = X_{ij}dx_{ij} + E_i dD_i + TdS. \quad (1.1)$$

Here, X_{ij} represents the stress tensor, E_i is electric field vector and T is temperature. The strain, displacement and entropy are denoted as x_{ij} , D_i and S , respectively. Using the Gibbs free energy, G , Equation (1.1) can be rewritten as [6]

$$G = U - X_{ij}x_{ij} - E_i D_i - TS. \quad (1.2)$$

With a derivation of the Gibbs free energy (Eq.(1.2)), the relation between (S, T) and (D, E) pairs of parameters can be described by the Maxwell relations

$$\left(\frac{\partial D_i}{\partial T}\right)_{X,E} = \left(\frac{\partial S}{\partial E_i}\right)_{X,T} = p_i, \quad (1.3)$$

where p_i is the pyroelectric coefficient [6]. Equation (1.3) indicates that, numerically, the EC effect is equal to the pyroelectric effect; in other words the EC effect is its converse. At constant X and under adiabatic conditions, the EC entropy change is given by

$$dS = \left(\frac{\partial D_i}{\partial T}\right)_{X,E} dE_i. \quad (1.4)$$

By integration between the electric fields E_1 and E_2 , Eq.(1.4) becomes:

$$\Delta S = \int_{E_1}^{E_2} \left(\frac{\partial D_i}{\partial T}\right)_{X,E} dE_i. \quad (1.5)$$

The specific heat capacity at constant electric field c_E , is defined as [6]

$$c_E = \frac{T}{\rho} \left(\frac{\partial S}{\partial T}\right)_E, \quad (1.6)$$

where ρ is the density. By assuming a constant stress X , the ΔT_{EC} can be expressed as

$$\Delta T_{EC} = -\frac{T}{\rho} \int_{E_1}^{E_2} \frac{1}{c_E} \left(\frac{\partial D_i}{\partial T}\right)_E dE_i. \quad (1.7)$$

In case of the polarization P change with temperature, ΔT_{EC} is described as

$$\Delta T_{EC} = -\frac{T}{\rho} \int_{E_1}^{E_2} \frac{1}{c_E} \left(\frac{\partial P_i}{\partial T}\right)_E dE_i. \quad (1.8)$$

Thus, it is evident from Eqs. (1.6) and (1.8) that indeed large entropy changes (ΔS) are needed to obtain a large ΔT_{EC} . Ferroelectrics and relaxor ferroelectrics, or briefly relaxors, are known to exhibit a large entropy change in the vicinity of the temperature-dependent dielectric permittivity peak. Therefore, ferroelectrics such as barium titanate and lead zirconate titanate and relaxors such as lead magnesium niobate and its solid solutions with lead titanate, have been extensively studied.

1.1.1 Electrocaloric cycle

The idea of exploiting the EC effect in refrigeration technology is quite appealing. EC cooling is potentially more energy efficient, more compact and produces less noise than traditional vapour-compression systems. Moreover, it is considered environmentally friendly as it does not contain harmful refrigerants. However, currently the development of the EC-effect-based cooling technology is at an early stage.

In order to exploit the EC effect in cooling, the EC material should be subjected to a thermodynamic cycle. In other words, excess heat from a heat load has to be transferred to a heat sink, i.e., to the surroundings, via the EC material. Thermodynamic refrigeration cycles such as Carnot, Bryton, Stirling and Ericsson have been considered for EC cooling [4], [8]–[11]. In this thesis the Bryton cycle is used for explaining the EC cycle, see Figure 1.1. It consists of two cycles of adiabatic polarization and two cycles of isofield heat transfers [12]:

Stage 1, *Adiabatic polarization*: the applied electric field causes the alignment of dipoles. Due to the adiabatic process, the total entropy of the material needs to remain constant. Consequently, the material heats up to compensate for the decrease of the dipole entropy.

Stage 2, *Isofield cooling*: while the electric field is held constant the excess heat is removed from the material, i.e., transferred to the heat sink. Thus the temperature of the material can relax back to the initial temperature.

Stage 3, *Adiabatic depolarization*: upon removal of the electric field the dipoles become disordered. Thus, the thermal entropy is transferred to the dipole entropy, and consequently the material cools down.

Stage 4, *Isofield heating*: the temperature of the EC material relaxes back to the temperature of the environment, due to the heat received from the cooling object.

It should be noted that in an EC cooling device the EC cycle should be repeated numerous times, as it was already shown in first EC-demo devices [13]–[15]. Such a large number of electric field cycles represents a challenge for EC materials.

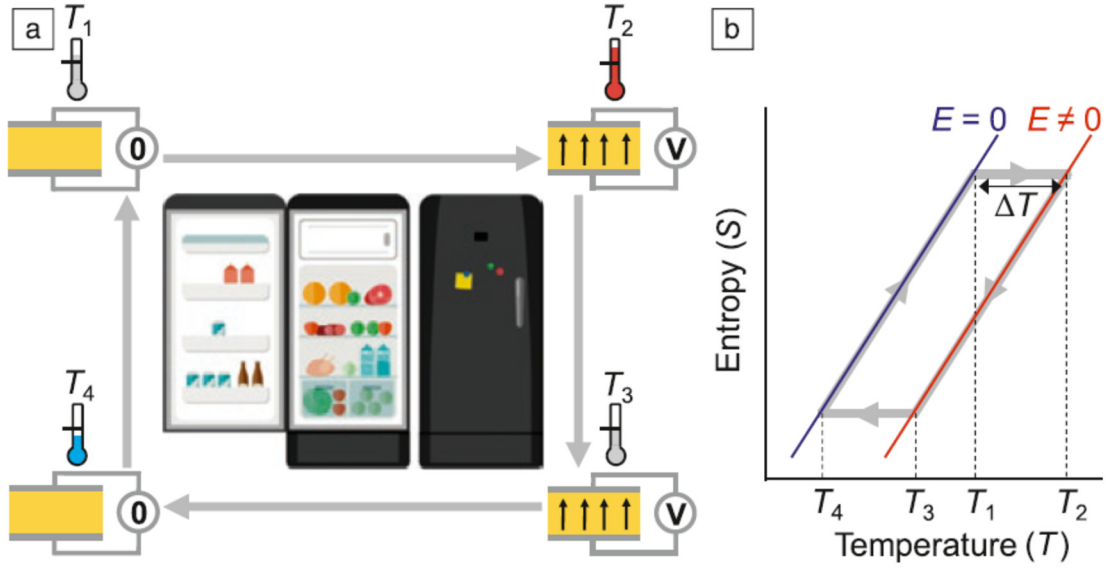


Figure 1.1: (a) Schematic diagram of an EC cycle, showing its four stages [16]: T_1 - T_2 Adiabatic polarization; T_2 - T_3 Isofield cooling; T_3 - T_4 Adiabatic depolarization; and T_4 - T_1 Isofield heating. In (b) an entropy versus temperature diagram is presented for the four stages of the EC cycle.

1.1.2 Methods for measuring the electrocaloric effect

The magnitude of the EC effect is usually expressed as ΔT_{EC} , which is determined by a direct or indirect measuring method. In the former case the temperature or the released heat of the sample at a selected electric field is measured. Such experiments are performed, for example, in adiabatic calorimeters or modified differential scanning calorimeters (DSC). In the indirect method ΔT_{EC} is calculated from the measured polarization as a function of temperature and electric field. For more details refer to Appendix A. It is accepted that the directly obtained results are more reliable, while the indirect measurement is more easily performed. However, until now none of the methods has been standardized, and thus a comparison of the EC results acquired from different laboratories cannot be reliably performed.

A commercial device for EC measurements does not exist, and so researchers have overcome this by modifying existing DSCs or by building calorimeters. Lately, infra-red cameras and scanning thermal microscopy have also been modified and used to directly determine the EC effect [17], [18]. Regardless of the set-up type the measurement procedure

is the same. First, the bath temperature has to be stabilized and then a voltage signal is applied; usually it is a step signal. At the same time the temperature of the sample rapidly changes. The duration of the applied electric field is selected to be considerably longer than the time needed for the temperature of the sample to relax back to the bath temperature. The removal of the electric field is followed by a decrease of the sample temperature. The latter relaxes back, i.e., it heats up to the bath temperature. The temperature changes should be symmetrical during the application and removal of the electric field, as can be seen in Figure 1.2.

The measuring devices can be classified according to the principles of the measured temperature or entropy changes. Therefore, the four types of EC measurements are the ones obtained in a DSC [12], [19], in a calorimeter [7], [20], [21], with an infra-red camera [17] [12], and with scanning thermal microscopy [17], [18]. In the following paragraphs, measurements performed in DSCs and calorimeters are presented:

- (I) Commercial DSCs measure the heat flow. Thus, when the electric field is quickly applied and later removed, the EC entropy or EC temperature change is calculated from the heat flow corresponding to the area of the exothermic (endothermic) peak [12], [19]. In order to establish the electric field, a voltage source needs to be implemented into commercial DSCs.
- (II) In calorimeters and other homemade thermally insulated chambers a small thermistor or a thermocouple is attached to the sample, thus upon the electric field's application and removal, the heat exchange is very fast.

In order to compensate for thermal losses due to the inactive volume of the sample, a correction factor is normally used. It takes into account the inactive part of the sample, thermocouple/thermistor, wires for high voltage and glues for connections. Details of the correction-factor calculation can be found elsewhere [7], [20], [21]. Note that also in other measuring set-ups the thermal losses that are not related to the tested material need to be compensated. For instance, in a DSC a thermal-loss correction factor has been introduced to compensate for the losses related to electrical contacts [22].

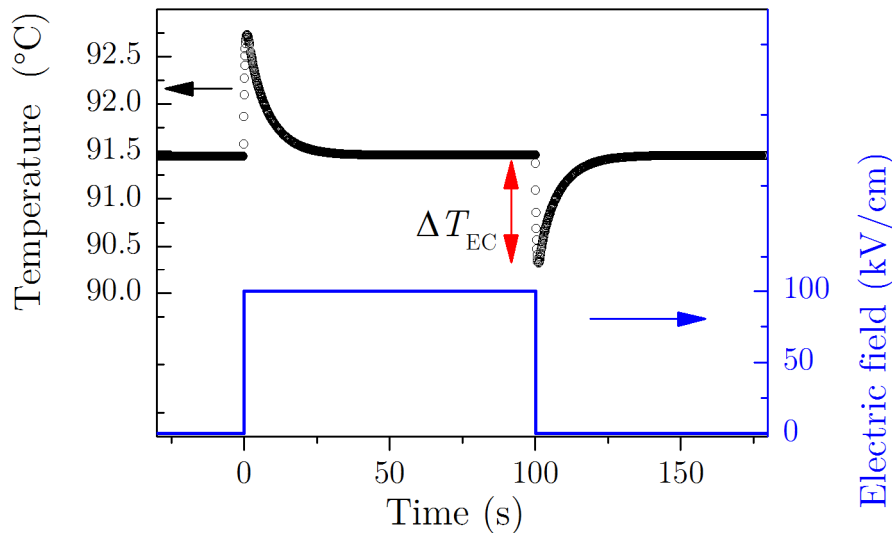


Figure 1.2: Example of a ΔT_{EC} measurement, where the temperature versus time is determined by a direct measuring method.

A comparison of different direct methods has recently been published by Molin et al. [23], see Figure 1.3. They showed that the ΔT_{EC} values determined on the same batch of samples with a thermocouple or with a thermistor differ by as much as 15 %. They explained that this could be due to an insulating glass layer on the thermistor, attached to the surface of the sample, which hinders the heat transfer. Nonetheless, in all direct measurement methods the existence of Joule heating is undoubtedly revealed, which is a key advantage over the indirect measuring method.

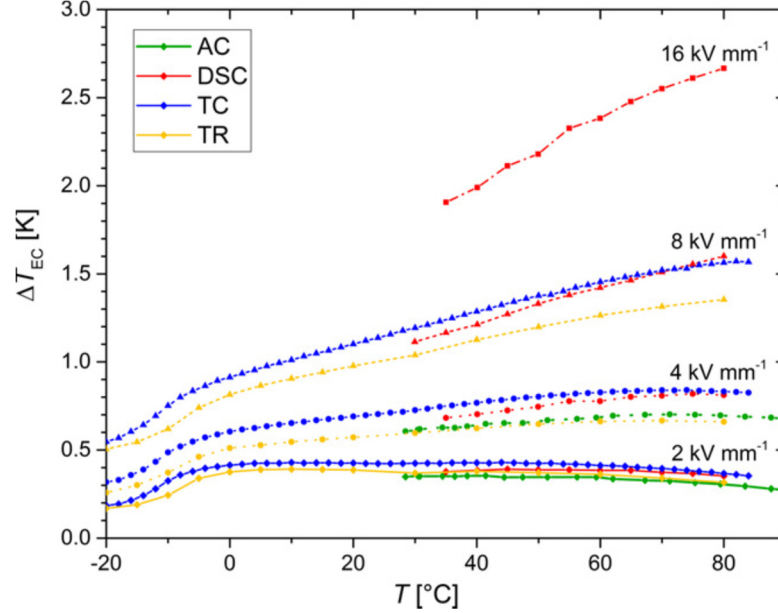


Figure 1.3: Comparison of EC temperature change (ΔT_{EC}) values measured on the same batch of multilayer elements with different set-ups (AC - quasi-adiabatic calorimetry; DSC - differential scanning calorimetry; TC - thermocouple; TR - thermistor) [23].

1.2 (1-x)Pb(Mg_{1/3}Nb_{2/3})O₃-xPbTiO₃ Solid Solution

Lead magnesium niobate Pb(Mg_{1/3}Nb_{2/3})O₃ (PMN) is one of the most studied relaxors; it was discovered by Smolenskii and Agranovskaya in 1958 [24].

PMN crystallises in a perovskite ABO₃ unit cell, in which Pb²⁺ cations are situated on the A-sites, while Mg²⁺ and Nb⁵⁺ ions occupy the B-sites in a 1:2 stoichiometric ratio. The occupation of B-sites is largely random, although there is local ordering known as chemically ordered regions [25], [26]. Polar nanoregions can be defined as nano-sized polar islands embedded in a cubic/paraelectric matrix [27]. They are formed at high temperatures, at or above ~ 530 °C [28], and upon cooling these nanoregions increase in size and merge into larger clusters [29]. The PMN is characterized by a broad and frequency-dispersive peak of dielectric permittivity versus temperature, and the peak values are about 25 000 at a temperature (T_m) of -5 °C at 1 kHz. At room temperature (RT) the P - E hysteresis loop is slim, with the saturated polarization P_s of about 25 $\mu\text{C}/\text{cm}^2$ [30].

Lead titanate, PbTiO₃ (PT), is a perovskite ferroelectric that exhibits a strong tetragonal distortion of about 6 % at RT [31]. Its Curie temperature is at 495 °C [31].

Relaxor PMN and ferroelectric PT form a solid solution (1-x)Pb(Mg_{1/3}Nb_{2/3})O₃-xPbTiO₃ (PMN-100xPT) over the whole compositional range. Thus with increasing PT content in the solid solution the relaxor behaviour is gradually suppressed, the temperature-dependent dielectric permittivity peak becomes narrower and

the P - E hysteresis loop widens. As can be observed from the PMN-PT phase diagram in Figure 1.4, the transition temperature from the polar to the non-polar (cubic) phase increases with increasing PT content from about -75 °C to about 275 °C for $x=0.5$. At RT the PMN-rich solid solution is rhombohedral for $x < \approx 0.2$. With increasing x , the structure changes to two monoclinic phases (C_m and P_m) and at $x > 0.35$ the structure is tetragonal. The morphotropic phase boundary (MPB) between the monoclinic and tetragonal phases at about $x = 0.3$ – 0.35 , is characterized by exceptionally good dielectric, ferroelectric and electromechanical properties [32]–[35].

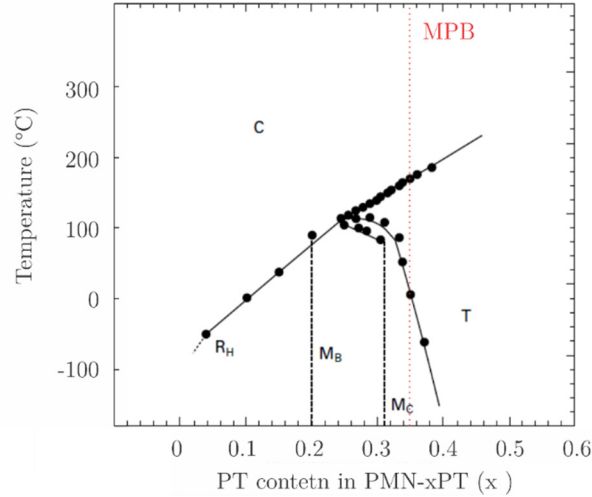


Figure 1.4: Phase diagram of PMN-xPT solid solution with $0 < x < 0.5$, where the dashed line highlights the morphotropic phase boundary (MPB) at $x \sim 0.3$ – 0.35 after [36].

Pure PMN and PMN-PT solid solutions are commonly prepared by solid-state synthesis, using the so-called “columbite” method. Note that the first step is the synthesis of the MgNb_2O_6 (Columbite), which in the next step reacts with the stoichiometric amount of PbO [37]–[39]. However, in the past other approaches have also been considered, for example, mechanochemical activation or high-energy milling [40]–[43], controlled agglomeration of precursor particles [44], [45], or the sol-gel method [46]. Regardless of the synthesis method the challenge has been to obtain pure perovskite phase without a residual thermodynamically stable pyrochlore phase, especially for the PMN and PMN-rich solid solutions.

1.3 Electrocaloric Effect in PMN-PT

The studies of the EC effect in different ferroelectrics and relaxors have been summarized in [3]–[5], [47]. Among the studied materials the PMN and PMN-PT solid solutions have been recognized as materials with exceptional EC properties. The PMN-rich compositions exhibit the largest polarization changes close to RT. There the largest ΔT_{EC} are expected, denoting PMN and PMN-rich materials as suitable candidates for EC cooling devices.

The first EC study of a PMN-10PT thin film was reported by Mischenko et al. [48] in 2006. The so-called “giant” ΔT_{EC} of 5 K was obtained at 75 °C and an electric field of 895 kV/cm. In 2009, Correia et al. [49] reported an even larger ΔT_{EC} of 9 K at 25 °C and at an electric field of 723 kV/cm in a PMN-7PT thin film. Saranya et al. [50] obtained ΔT_{EC} of 31 K at 140 °C and at an electric field of 1720 kV/cm. But at 100 °C the ΔT_{EC} was significantly smaller, but only about 4 K.

In all these studies the thicknesses of the PMN-PT films were from 210 to 260 nm. Thus, in order to induce a large EC effect, electric fields well above a few hundred kV/cm were required. However, a considerable disadvantage of thin films is the very low mass, which is not suitable for a real cooling device.

In contrast, bulk ceramics have much larger thermal masses than thin films and are thus good candidates for cooling applications. However, the dielectric breakdown strength of bulk ceramics is about an order of magnitude lower than that of thin films, about 100 kV/cm as compared to about 1 MV/cm, hence the highest achieved EC temperature changes in bulk ceramics are notably smaller. The record high ΔT_{EC} obtained in Pb-based bulk ceramics was 3.5 K in PMN-10PT at an electric field of 160 kV/cm [51]. Some reported values of EC temperature changes obtained in PMN-PT bulk ceramics are collected in Table 1.1.

Peräntie et al. [52] studied the EC effect in PMN-PT ceramics with $0 \leq x \leq 0.3$. The direct EC measurements were performed upon increasing the electric field up to 50 kV/cm, while only the PMN was investigated up to 90 kV/cm, see Figure 1.5a. They observed that the maximum ΔT_{EC} increased with increasing PT fraction. The maximum ΔT_{EC} at 50 kV/cm were 0.77 K and 1.55 K for PMN and PMN-30PT, respectively. They concluded that for PMN-rich materials the maximum ΔT_{EC} at low electric fields was obtained near the depolarization temperature. At higher electric fields, an additional maximum appeared. The shift of the ΔT_{EC} maximum was observed in all the compositions. Moreover, the trend of increasing the shift with decreasing PT fraction was noticed, see Figure 1.5b.

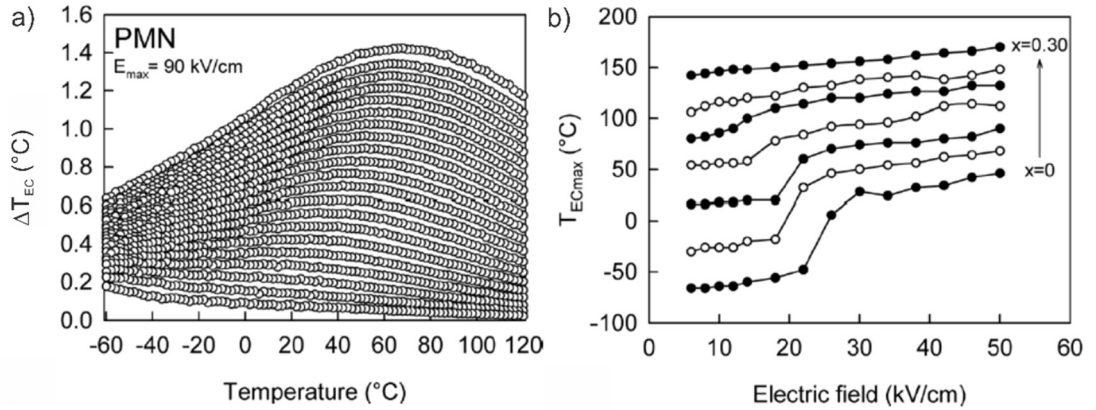


Figure 1.5: (a) EC effect (ΔT_{EC}) measured in PMN at different temperatures and electric fields up to 90 kV/cm. (b) Temperature of maximum ΔT_{EC} vs electric field (4–50 kV/cm) for PMN-PT solid solutions ($x=0-0.30$) [52].

Rožič et al. also observed the existence and up-shifting of the ΔT_{EC} peak at electric fields of up to 90 kV/cm in PMN [20], [53]. In addition, they associated the ΔT_{EC} maximum with the middle of the low-temperature slope of the dielectric permittivity peak. This relation was also confirmed by Vrabelj et al. [51] in PMN-10PT bulk ceramics.

Only in a few EC studies did the electric fields exceed 50 kV/cm. In those rare studies [51], [53] the peak, i.e., the shift of the maximum ΔT_{EC} , could not be determined due to not enough measured ΔT_{EC} at different temperatures. Therefore, the ΔT_{EC} measurements at fields up to ~100 kV/cm are needed in a wider temperature range.

Table 1.1: EC temperature change, electric field and measurement temperature in PMN-rich and PMN-PT bulk ceramics (selected results)

Material	ΔT_{EC} (K)	Temperature (°C)	Electric field (kV/cm)	Ref.
PMN	2.5	67	90	[53]
PMN	1.4	70	90	[52]
PMN-5PT	1.0	70	50	[52]
PMN-10PT	1.2	90	50	[52]
PMN-10PT	3.5	127	160	[51]

1.3.1 Influence of the DC bias-field on the dielectric permittivity and the relation to the EC effect

In ferroelectrics, the temperature of the permittivity peak (T_m) increases, while the peak permittivity value decreases (ϵ'_{max}) with applied DC bias (E_{DC}) [54]. In relaxor PMN-PT with $0 \leq x \leq 0.25$, the up-shifting of T_m was confirmed in several studies [54]–[58]. However, in some of these studies [54], [58], a slight down-shift of T_m at E_{DC} of about 2–3 kV/cm was first noticed, followed by a significant up-shift of T_m . The E_{DC} where T_m reaches the minimum is denoted as the threshold field (E_t). In Figure 1.6a, such a dependence of T_m versus E_{DC} is presented for different PMN-PT solid solutions, where the down-shift of T_m in PMN-13PT can be clearly observed. Note that these studies were performed on single crystals. Raevski et al. [54] explained this down-shift phenomenon by analysing different models of relaxors. They showed that the E_t depends on the PMN-PT composition, i.e., with increasing PT content the E_t is decreasing, see Figure 1.6b. Thus, the E_t of PMN-10PT is 3.6 kV/cm, while in case of PMN-40PT, the T_m immediately starts to increase linearly with increasing DC bias field (i.e., $E_t = 0$).

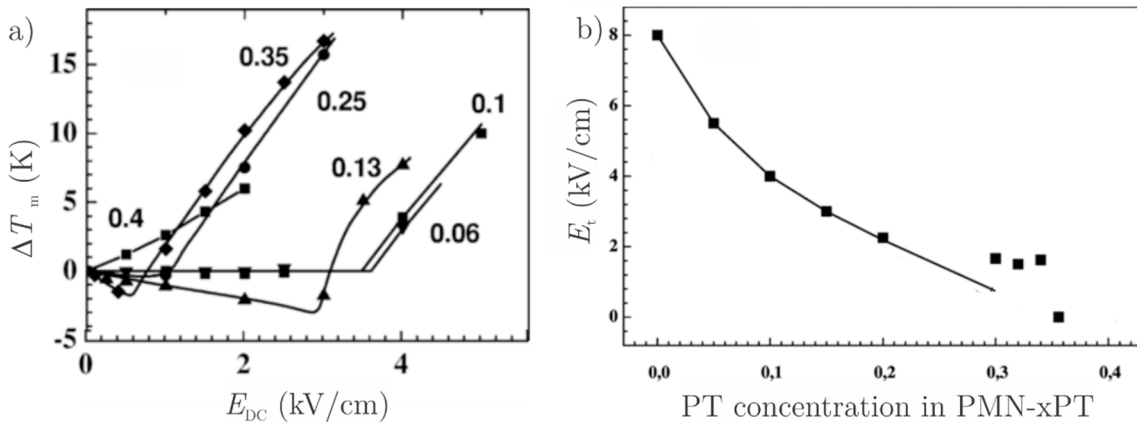


Figure 1.6: (a) Shifting of T_m with increasing DC bias field (E_{DC}) for PMN-PT single crystals, where $\Delta T_m = T_m(E_{\text{DC}}) - T_m(0 \text{ kV/cm})$ of PMN-PT solid solution with $x = 0.06, 0.1, 0.13, 0.25, 0.35$, and 0.4 are shown. In (b) the threshold field (E_t) versus PT concentration in PMN-xPT is presented for PMN-PT single crystals, after [54].

As was discussed in Section 1.3, the temperature of the maximum ΔT_{EC} ($T_{\text{EC max}}$) also increases with increasing electric field. In the literature T_m is frequently reported as the characteristic temperature where the $T_{\text{EC max}}$ is expected [52], [59], [60]. Although such an approach can give a rough estimate, a better understanding of the relation between T_m and $T_{\text{EC max}}$ is needed.

The correspondence between the dielectric permittivity and ΔT_{EC} as a function of temperature was described for PMN-30PT. After analysing the dielectric and EC data it was concluded that the $T_{\text{EC max}}$ can be expected at the temperature of the induced ferroelectric transition, which is typically in the middle of the low-temperature slope of the dielectric peak [53]. However, in this study the ΔT_{EC} values at high temperatures were not measured, and thus the $T_{\text{EC max}}$ could not be clearly determined under electric fields up to 90 kV/cm. Vrabelj et al. [51] reported the measurements of the PMN-10PT dielectric permittivity with and without DC bias fields of 10 and 25 kV/cm, and they showed that the maximum dielectric permittivity decreases and T_m is up-shifted with increasing electric field, see Figure 1.7a. However, the T_m up-shift seems to be almost linear and thus different from the observations of Raevski et al. [54], which could be due to missing measurements at DC fields between 0 and 10 kV/cm. Furthermore, they compared the T_m with $T_{\text{EC max}}$, both measured at ~ 25 kV/cm, and concluded that the $T_{\text{EC max}}$ coincides with the middle of the low-temperature slope of the dielectric permittivity peak, see Figure 1.7b.

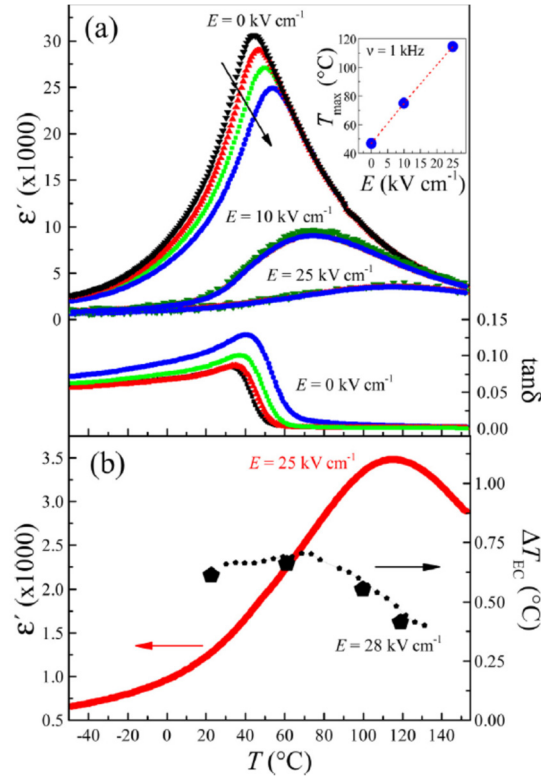


Figure 1.7: a) Dielectric permittivity versus temperature measured without electric field and with DC-bias of 10 kV/cm and 25 kV/cm in PMN-10PT ceramics. b) Comparison of the dielectric permittivity upon a DC bias of 25 kV/cm and the EC effect at 28 kV/cm versus temperature [51].

1.3.2 Electrocaloric stability upon electric field cycling

Only a few EC demo-devices have been realized until now [14], [15], [61], and they were all operating for only up to a few hours. However, in order for an EC device to operate for a few years, a large number of EC cycles has to be applied. Therefore, it is crucial to know if a material can withstand $\sim 10^8$ – 10^9 applied electric fields without any significant degradation of the EC properties. Fatigue in ferroelectric ceramics upon electric field cycling has been studied often in relation to electromechanical applications [62]–[66]. Only a few studies have been made on relaxors [67]–[70], which are more appropriate for EC applications due to their diffuse ΔT_{EC} peak and lower energy losses [13].

In the stability study of PMN, bulk samples were subjected to electric field cycling while monitoring P - E loops, which revealed a high fatigue resistivity up to 10^8 cycles [69]. In particular, the saturated and remanent polarizations slightly decreased. Furthermore, modifying the PMN with La resulted in denser ceramics, while the fatigue was even more suppressed, i.e., saturated and remanent polarizations and the coercive field remained unchanged after 10^9 applied cycles. In the literature some studies on the stability of lead-free relaxors upon cycling can be found, exhibiting similarly minimal or no degradation of the ferroelectric properties. For instance, fatigue in relaxor $0.91\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3$ - 0.06BaTiO_3 - $0.03\text{K}_{1/2}\text{Na}_{1/2}\text{NbO}_3$ was investigated by Luo et al. [71] under bipolar and unipolar cycling. Under bipolar cycling the saturated polarization decreased by $\sim 15\%$ after 10^6 cycles and in the case of unipolar cycling, the material withstood 10^7 cycles with a final saturated polarization decrease of about 12%. Bobnar et al. [67] studied the polarization stability of relaxor $0.85\text{K}_{1/2}\text{Na}_{1/2}\text{NbO}_3$ - 0.15SrTiO_3 under electric field cycling. They showed that the P - E loop and remanent polarization remained unchanged after 10^6 cycles, see Figure 1.8.

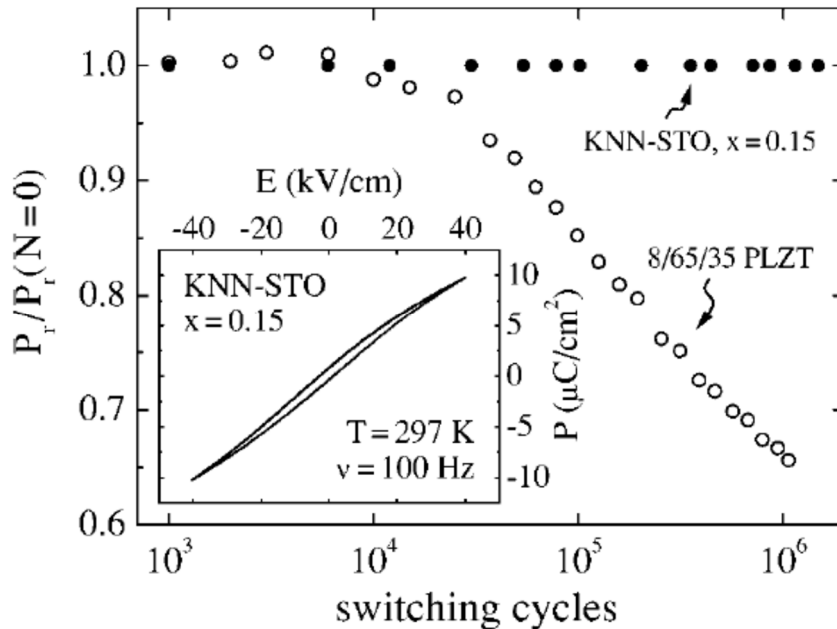


Figure 1.8: Normalized remanent polarization in a relaxor $0.85\text{K}_{1/2}\text{Na}_{1/2}\text{NbO}_3$ - 0.15SrTiO_3 ceramic as a function of applied electric field cycles, compared to a fatigue investigation on ferroelectric $(\text{Pb}_{0.88}\text{La}_{0.08})(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$ ceramics. A typical slim relaxor P - E hysteresis loop of $0.85\text{K}_{1/2}\text{Na}_{1/2}\text{NbO}_3$ - 0.15SrTiO_3 ceramic is shown in the inset [67].

On the basis of these studies it could be assumed that relaxors are suitable for EC cooling applications. We note that these studies were not conducted at high electric fields, close to dielectric breakdown fields, which are needed for inducing large ΔT_{EC} . Moreover, the shape and frequency of the applied electric fields can also influence the stability [66]. In EC studies the unipolar step signal is most commonly employed, while the frequencies range from 1 to 100 Hz [10], [61], [72]. The optimal cycling frequency ($v_{cycling}$) should be low enough to allow the heat transfer from and to the EC element, which can be calculated using the thermal time constant (τ) equation. Since the EC cycle has two heat exchanges, $v_{cycling}$ has exceed two τ at least, and thus the following equation can be used [73]

$$v_{cycling} = \frac{1}{2 \cdot \tau} = \frac{\kappa}{2 \cdot \rho \cdot c_p \cdot d^2}. \quad (1.9)$$

Here, κ and d are the thermal conductivity and thickness of the sample, respectively [74], [75]. Furthermore, when considering the material for EC cooling also the heating during cycling has to be taken into account. The latter is mainly caused by hysteresis losses, and thus relaxors are a more reasonable choice for implementation in EC cooling devices, due to the significantly lower hysteresis losses compared to ferroelectrics [76], [77].

In the first study of the EC effect's stability, a significant decrease of ΔT_{EC} upon 10 cycles in a BaTiO₃ single crystal was reported [78]. Only recently, in 2018, Weyland et al. studied the stability of the EC effect in lead-free Ba(Zr_{0.2}Ti_{0.8})O₃ bulk ceramics [75]. The cycling was performed at a moderate electric field of 20 kV/cm, which yields a ΔT_{EC} of about 0.15 K at RT. They showed that by periodically changing the polarity of the electric field, ΔT_{EC} remained constant up to 10⁶ cycles. Thus, further investigations are needed, especially at high electric fields where the induced ΔT_{EC} are large enough for potential cooling devices.

1.4 Multilayer Elements; a Viable Solution for EC Cooling

According to numerical studies [61], [72] EC refrigeration could be possible at a ΔT_{EC} of at least 2 K. However, to reach such temperature changes electric fields of about 100 kV/cm are required, which is in the range of the dielectric breakdown strength of bulk ferroelectric or relaxor ceramics. Therefore, in order to increase the dielectric breakdown strength and to enable the application of even higher electric fields, the thickness of the samples should be reduced [79], [80]. A proposed solution is to use multilayer (ML) elements [81], [82], which consist of alternating ceramic layers, separated by internal electrodes (see Figure 1.9a and b).

In such ML elements, the thickness of individual ceramic layers can be reduced to the micron range, typically a few 10 μ m, which enables the application of electric fields significantly higher than 100 kV/cm. Furthermore, the applied voltage is a few times lower than for bulk ceramics. Due to the arbitrary number of layers the overall dimensions and the mass of a ML element can be equal or even larger than bulk samples [81], [82]. Finally, the higher surface-to-volume ratio in ML leads to a faster heat transfer compared to the bulk, which in combination with the high thermal conductivity of internal electrodes pushes ML closer to real EC cooling applications [83].

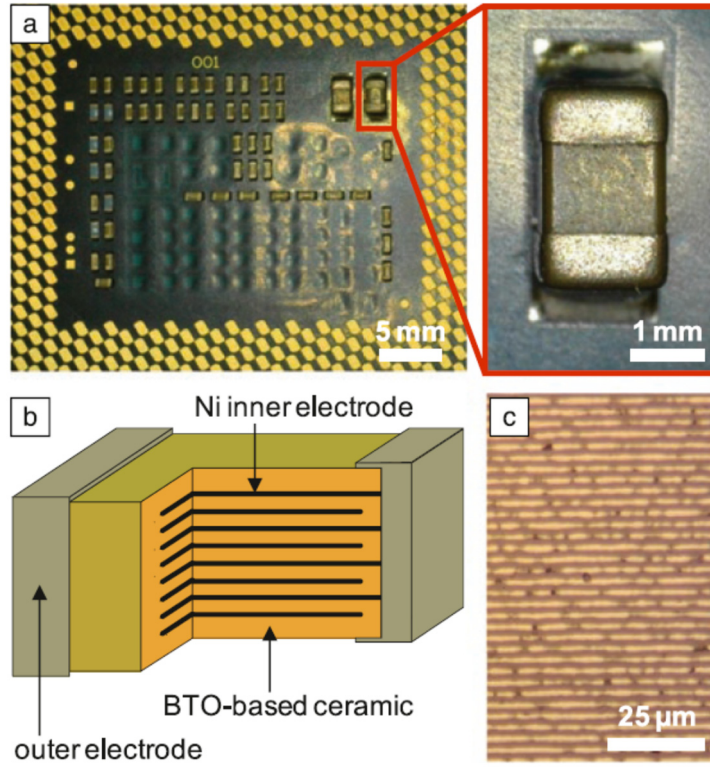


Figure 1.9: a) Multilayer (ML) capacitor as an existing electronic component, which can be found on an Intel Xenon E3 processor. (b) Schematic of a ML element based on BaTiO_3 (BTO). (c) Optical microscope image of a ML cross-section obtained after sawing and polishing [16].

The fabrication of ML elements of ferroelectric or relaxor ceramics has been widely employed in the commercial production of ML capacitors [84] and ML actuators [85]. The description of ML fabrication can be found in Appendix B. However, the materials of these MLs are not optimized for achieving large ΔT_{EC} , at least not in the vicinity of the RT.

The EC studies including ML elements are summarized in Table 1.2. The EC effect in ML elements was measured already in 1987 by Lawless and Clark [86]. However, ΔT_{EC} was determined at a temperature of -180°C , and for that reason it could not be considered for EC cooling applications. Following the revival of the EC effect in 2006, Kar-Narayan and Mathur [82], [87] experimented with commercially available capacitors, based on BaTiO_3 (Y5V). The obtained ΔT_{EC} values were about 0.5 K, in spite of very high electric fields of 300 kV/cm. Nevertheless, they showed that MLs exhibit a high potential for cooling applications due to their geometry. The expected EC effect should be higher if materials with better EC properties were used for the ML elements. Therefore, more recently, studies of PMN-PT ML elements were published in papers by Hirose et al.[88], Molin et al.[23], [89], and Usui et al.[90]. They verified that higher electric fields are achievable in ML elements compared to those obtained in bulk. Accordingly, in PMN-8PT a maximum ΔT_{EC} of 2.7 K at an electric field of 160 kV/cm was obtained [23]. In PMN-10PT an even higher electric field of 288 kV/cm resulted in a ΔT_{EC} of 2.7 K. Note that these ΔT_{EC} values cannot be directly compared, due to the fact that they are expressed without any correction factor.

Table 1.2: Reported values of the EC effect measured in ML elements

Composition	ΔT_{EC} (K)	Temperature (°C)	Electric field (kV/cm)	Layer thickness (μm)	Ref.
BaTiO ₃ -based	0.5	75	300	6.6	[82]
PMN-8PT	2.7	80	160	86	[23]
PMN-8PT	0.2	25	21	95	[89]
PMN-10PT	1.2	100	103	38	[88]
PMN-10PT	2.7	107	288	35–39	[90]

In Figure 1.10, from a review paper published in April 2018 [16], all the significant EC results obtained with ML elements are collected in a three-dimensional graph, in which the axes represent temperature, electric field and ΔT_{EC} . Two conclusions can be drawn from the graph. The first one is that the majority of the investigations have been only recently published, namely in 2016 and 2017, meaning that investigations of EC in ML are still at early stage. The second conclusion is that the material of choice used to be BaTiO₃, but more recently it became PMN and PMN-PT. The explanation is that the first studies were performed on commercial BTO-based ML capacitors. However, due to the excellent EC properties, PMN and PMN-PT ML have been recently fabricated just for EC applications.

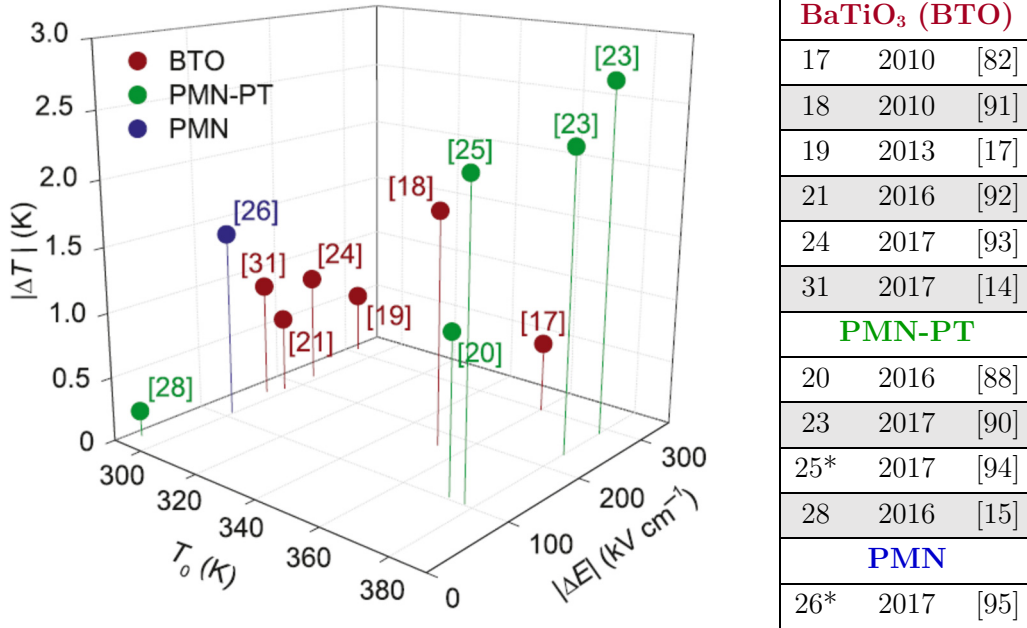


Figure 1.10: The EC effect of ML elements found in the literature, presented in a three-dimensional graph. The three axes represent, temperature (T_0), electric field ($|\Delta E|$), and ΔT_{EC} ($|\Delta T|$) [16]. * These results are also included in this thesis.

Chapter 2

Aims and Hypothesis

Relaxor $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) and $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $x\text{PbTiO}_3$ (PMN-100xPT) with $x=0.05$ and 0.10 exhibit a large electrocaloric (EC) effect near room temperature. The EC temperature change depends on the chemical composition, the temperature and the applied electric field. For a given material the temperature of the maximum EC temperature change ($T_{\text{EC max}}$) increases with increasing electric field. Such behaviour is similar to the upshifting of the temperature of the dielectric permittivity peak (T_m) under increasing DC bias field. Our hypothesis for the first part of the thesis is that $T_{\text{EC max}}$ and T_m are correlated when subjected to an electric field.

The aims of the first part are:

- To prepare single-phase perovskite PMN, PMN-5PT and PMN-10PT bulk ceramics from mechanochemically synthesized powders.
- To measure the EC effect of respective materials in wide temperature and electric field ranges, which will allow a precise determination of $T_{\text{EC max}}$.
- To resolve the $T_{\text{EC max}}$ and T_m correlation based on the temperature-dependent dielectric permittivity measurements under DC bias.

The lead-based perovskites have been largely investigated in bulk and thin-film forms, while the idea of multilayer (ML) elements has been appealing, yet almost without realization. This has been mostly due to the challenging fabrication associated with MLs.

The main hypothesis for this part is that the EC properties of PMN and PMN-10PT materials are independent of the sample geometry, i.e., the EC responsivities of the ML and bulk samples should be comparable. Additionally, a considerably reduced thickness of an individual layer compared to the thickness of a bulk ceramic sample should make it possible to reach high electric field amplitudes in MLs at much lower voltages than in bulk samples. The electric field cycling should not impair the stability of the EC effect.

Therefore, the aims of second part of this thesis are:

- To fabricate PMN and PMN-10PT ML elements by tape-casting, lamination and sintering.
- To study the EC effect of ML elements by direct and indirect measurements.
- To compare the dielectric, ferroelectric and EC properties of ML elements with their bulk counterparts.
- To investigate the stability of the EC effect of ML elements under electric field cycling.

Chapter 3

Materials and Methods

3.1 Sample Preparation

3.1.1 Mechanochemical synthesis of the (1-x)Pb(Mg_{1/3}Nb_{2/3})O₃-xPbTiO₃ powders

The PMN-PT ceramic powders were prepared by mechanochemical synthesis. The lists of the chemicals and equipment that were used in the processing procedures within this thesis are collected in Table 3.1 and Table 3.2.

In the mechanochemical synthesis of Pb(Mg_{1/3}Nb_{2/3})O₃ (PMN) metal oxides PbO, MgO and Nb₂O₅ were homogenised in the molar ratio corresponding to the PMN stoichiometry in a planetary mill at 200 rpm for 2 h in isopropanol (IPA), using 10-mm yttria-stabilized zirconia (YSZ) balls and an YSZ vial (250 ml). Next, the powder mixture was dried at 105 °C and sieved (note that all further powder drying was also performed at 105 °C). The high-energy milling of the homogenised powder mixture (200 g) was performed in a planetary mill at 300 rpm for 90 h and the ratio of the rotational speeds of the tungsten carbide (WC) vial (250 ml) and the supporting disk was -3. The mass ratio of the powder and the WC balls with a diameter of 20 mm was 1:5. In the final step the powder was additionally milled in an attritor mill with YSZ balls (dia. 3 mm) at 800 rpm for 4 h in IPA, dried and sieved.

In the synthesis of PMN-5PT and PMN-10PT powders, first the PbTiO₃ (PT) powder was prepared by solid-state synthesis from a homogenized mixture of PbO and TiO₂ by calcination in a closed alumina crucible, placed in a chamber furnace at 750 °C for 2 h with heating and cooling rates of 5 °C/min. In the next step, PbO, MgO and Nb₂O₅ were added to the PT powder in accordance with the respective molar ratios of the PMN-5PT and PMN-10PT. The next processing steps included homogenisation, high-energy milling and attrition milling, as in the case of PMN described above. The milling times for the PMN-5PT and PMN-10PT were 72 and 48 h, respectively. The processing of the PMN and PMN-PT powders is schematically depicted in Figure 3.1.

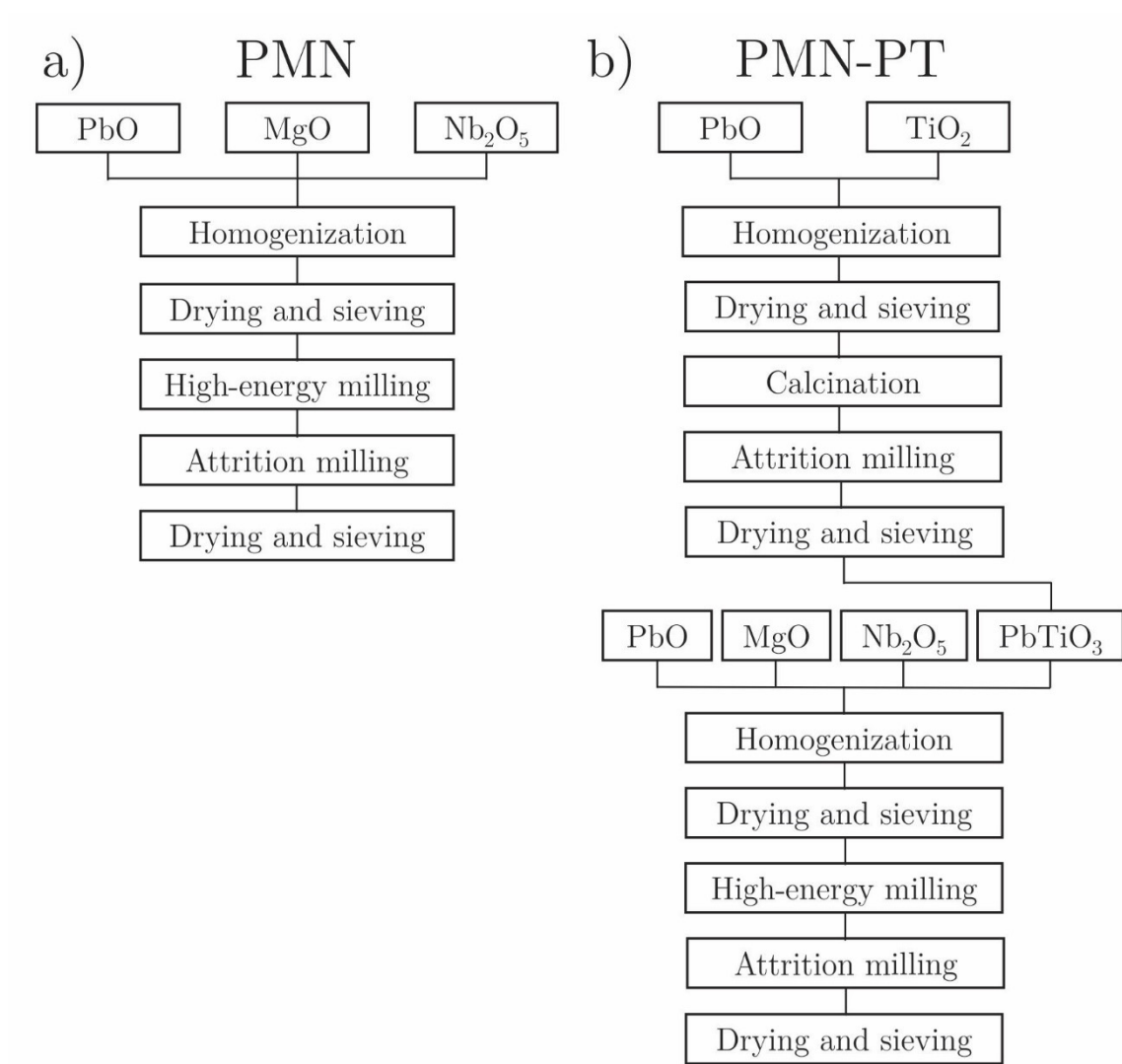


Figure 3.1: Schematic presentation of the (a) PMN and (b) PMN-PT mechanochemical synthesis.

Table 3.1: List of chemicals used in the preparation of PMN and PMN-PT powders and green tapes.

Chemical formula	Name	Specification and producer	Role
PbO	Lead oxide	99.9 %, Sigma-Aldrich, St. Louis, Missouri, USA	Reagent
MgO	Magnesium oxide	99.95 %, Alfa Aesar, Ward Mill, Massachusetts, USA	Reagent
Nb ₂ O ₅	Niobium oxide	99.9 %, Sigma-Aldrich, St. Louis, Missouri, USA	Reagent
TiO ₂	Titanium oxide	99.8 %, Alfa Aesar, Ward Mill, Massachusetts, USA	Reagent
CH ₃ CH ₂ CH ₂ OH	Isopropanol	Analytical Grade, Carlo Erba, Milano, Italy	Solvent
CH ₃ C(O)CH ₂ CH ₃	Methyl ethyl ketone	99.8 %, Carlo Erba reagents, Milano, Italy	Slurry additive - solvent
CH ₃ CH ₂ OH	Ethanol	Analytical Grade, Carlo Erba reagents, Milano, Italy	Slurry additive - solvent
CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇ COOH	Oleic acid		Slurry additive - dispersant
H-(O-CH ₂ -CH ₂) _n -OH.	Polyethylene glycol	Polyethylene glycol 400, Alfa Aesar, Ward Mill, Massachusetts, USA	Slurry additive - binder
(C ₈ H ₁₄ O ₂) _n	Polyvinyl butyral	Mowital B 45 H, Kuraray, Tokyo, Japan	Slurry additive - plasticizer

Table 3.2: List of equipment used in the preparation of PMN and PMN-PT powders, bulk and ML samples.

Item	Specification and manufacturer
Attritor mill	Netzsch, PE 075/PR 01, Selb, Germany
Planetary mill	PM400, Retsch, Haan, Germany
	PM100, Retsch, Haan, Germany)
Grinding jar	Tungsten-carbide (WC), 250 mL, Retsch, Haan, Germany
	Yttria-stabilized-zirconia (YSZ), 250 ml, Retsch, Haan, German
	Yttria-stabilized-zirconia (YSZ), 500 ml, Retsch, Haan, German
Milling medium	WC 20 mm, Retsch, Haan, Germany
	Yttria-stabilized-zirconia (YSZ) 3 mm, Tosoh Corporation, Tokyo, Japan
	Yttria-stabilized-zirconia (YSZ) 10 mm, Tosoh Corporation, Tokyo, Japan
Chamber furnace	Custom-made, Terna, Ljubljana, Slovenia
Uniaxial press	PW 40, P/O/Weber, Ramshalden, Germany
Isostatic press	401C-0063, Flow Autoclave systems, Columbus, Ohio, USA
Laser	ProtoLaser S, LPKF Laser & Electronics AG, Garbsen, Germany
Tape caster	CAM-L252, KEKO Equipment, Žužemberk, Slovenia
Screen printing machine	C1010, Aurel Automation S.P.A., Modigliana, Italy

3.1.2 Sintering of bulk ceramics

The PMN, PMN-5PT and PMN-10PT powders were pressed into pellets with a diameter of 8 mm by applying 50 MPa of uniaxial pressure and additionally with an isostatic pressure of 300 MPa. Afterwards, the pellets were placed in double alumina crucibles and sintered in a chamber furnace in the presence of inherent packing powder at 1200 °C for 2 h with heating and cooling rates of 2 K/min. The sintered pellets were cut with a diamond-wire saw and ground on both sides using SiC grinding paper (gradations 1200 and 2400) to a thickness ranging from 100 to 250 μm . Afterwards, the samples were annealed at 600 °C for 1 h and cooled with a rate of 1 K/min to relieve the stresses. A radio-frequency magnetron-sputtering device (5 Pascal, Milano, Italy) was used to deposit the Cr/Au electrodes on the faces of the pellets.

3.1.3 Fabrication of multilayer elements

PMN and PMN-10PT multilayer (ML) elements were prepared by tape casting. In both cases the formulation of the slurry was optimised, as described in the following text.

3.1.3.1 Slurry preparation

The formulations of PMN and PMN-10PT slurries are collected in Table 3.3. In both cases the slurry was prepared with a three-step mixing process. In the first step the powder was mixed with a solvent and a dispersant. The solvent was a mixture of methyl ethyl ketone and ethanol in the volume ratio 60:40, and the dispersant was oleic acid. The mixture of the powder (70 g), solvent and dispersant was homogenized in a planetary mill for 2 hours at 100 rpm. 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 μm sieve, which also acted as a de-airing step. About 50 ml of the slurry was then used for a tape-casting experiment. We note that the formulations of the PMN and PMN-10PT slurries were slightly different, as evident from Table 3.3. In the case of PMN the amounts of plasticizer and binder were decreased by a few % compared to the amounts in the PMN-10PT, in order to reduce the problem of tape twisting.

Table 3.3: The amount of slurry additives for the PMN and PMN-10PT compositions.

Additives	PMN (wt%)	PMN-10PT (wt%)
Powder	66.55	62.96
Solvent	27.57	26.08
Dispersant	0.17	0.16
Plasticizer	2.85	5.40
Binder	2.85	5.40

3.1.3.2 Tape casting and the fabrication of ML elements

The temperatures of the drying segments of the tape caster were set at 25 °C for both heating zones and the temperature of the air was 25 °C, see Figure 3.2. The tape speed was set at 0.8 m/min. The tape casting of 50-ml batches resulted in about 0.15-m-wide green tape of ~2 m in length. The dry green tape was afterwards cut into 100 mm $\times$ 100 mm sheets, onto which the platinum paste (Ferro 6482 0002, Mayfield Heights, Ohio, USA) was screen printed. Two holes were perforated with a laser, which allowed the precision stacking of 5 green tape sheets. The lamination was performed in an isostatic press with 20 MPa and at 50 °C. Finally, the sheets were cut into (green) ML elements with dimensions of about 5 mm $\times$ 5 mm $\times$ 0.35 mm.



Figure 3.2: Tape caster with the heating zones 1 and 2 marked with a red line.

3.1.3.3 Sintering of ML elements

The ML elements were sintered with a two-step heating process in a chamber furnace. First, the ML elements were placed in an alumina crucible (28 ml) containing 3 g of PbZrO_3 packing powder, as shown in Figure 3.3. A not completely covered alumina crucible was heated to 450 °C, held for 5 h and cooled to 25 °C, with heating and cooling rates of 1 K/min. In the second step, the alumina crucible was completely closed and heated to the sintering temperature, 1000 °C for 2h or 988 °C for 8h, respectively, for PMN and PMN-10PT. The heating and cooling rates were 5 K/min.

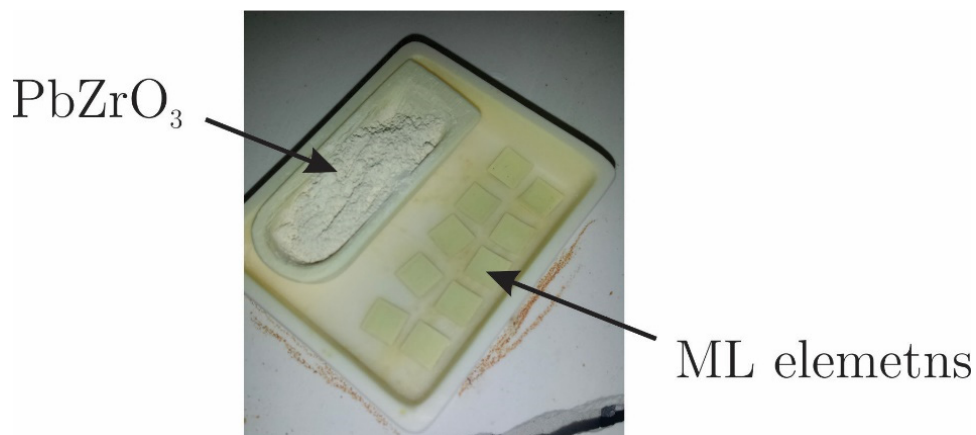


Figure 3.3: ML elements placed in an alumina crucible with the PbZrO_3 packing powder alongside.

The dimension of the ML elements after sintering were approximately $4.5 \text{ mm} \times 4.5 \text{ mm} \times 0.25 \text{ mm}$. The faces where the inner electrodes end were ground with SiC grinding paper (gradations 1200, 2400 and 4000) to provide better contacts and coated with a silver paint (Flash-Dry Silver Conductive Paint SPI, West Chester, Pennsylvania, USA).

3.2 Characterization Methods

3.2.1 Particle size and size distribution

The particle size and size distribution of the powders were determined using a static light-scattering granulometer (Microtrac S3500 Particle Size Analyzer, Montgomeryville, Pennsylvania, USA). Before the measurement the powder samples were dispersed in IPA and placed in an ultrasound bath (Iskra Sonis 4, Šentjernej, Slovenia) for a few minutes in order to break up the agglomerates. The results are presented as the particle size distribution and the cumulative curve, with the particle size limit of 90 % (d_{90}), 50 % (d_{50}), and 10 % (d_{10}).

3.2.2 X-Ray diffraction

The X-ray powder diffraction (XRD) data were collected at RT by a diffractometer (X'Pert PRO MPD, PANalytical, Almelo, Netherlands) using Cu-K α_1 radiation (1.54060 Å). The XRD patterns were recorded in the 2θ range 10° to 70° using the 1D detector (X'Celerator, PANalytical, Almelo, Netherlands) with a 0.034° step and an integration time of 100 s. The phases were analysed with the X'Pert High Score software package using the PDF-2 database. Prior to the measurement the bulk ceramic samples were crushed in an agate mortar, while the XRD patterns of the ML elements were collected from the surfaces.

3.2.3 Density

The density of the sintered bulk ceramic samples was determined by a gas-displacement density analyser (Micromeritics, AccuPyc III 1340 Pycnometer, Georgia, USA). Each sample was subjected to ten consecutive measurements and the average was calculated. Theoretical densities (TDs) of the PMN-PT were calculated using the unit-cell parameters, and the values are collected in Table 3.4.

Table 3.4: Theoretical densities (TD) of PMN and PMN-PT.

Composition	Unit cell parameter (Å)		TD (g/cm ³)
PMN	4.046	[96], [97]	8.15
PMN-5PT	4.041	[97]	8.15
PMN-10PT	4.036	[97]	8.16

3.2.4 Inductively coupled plasma spectroscopy

Quantitative elemental analyses of the powders were performed with inductively coupled plasma (ICP) mass spectroscopy using a quadrupole-based 7500 CE spectrometer. The measurements were made without a reference. Instead, an additional technique was used to verify the results, i.e., ICP atom emission spectroscopy using a Thermo Jarrel Ash Atomscan 25 spectrometer.

3.2.5 Viscosity of ceramic slurries

The viscosity of the slurry was measured with the rheometer (Physica MCR 301, Anton Paar, Graz, Austria) using a CP50-1 cone/plate measuring system at 25 °C. The viscosity was acquired in the shear-rate range $10 \text{ 1/s} \rightarrow 500 \text{ 1/s} \rightarrow 10 \text{ 1/s}$.

3.2.6 Thermogravimetric analysis

The thermal decompositions of the green tapes were analysed by simultaneous thermogravimetry and differential thermal analyses (TG/DTA, Netzsch STA 409 PC/PG, Selb, Germany) upon heating from RT to 700 °C with a heating rate of 5 °C/min in a dynamic synthetic air atmosphere. The samples of about 70 mg were characterized in Pt-Rh crucibles.

3.2.7 Microstructural analysis

Microstructural analyses of the powders and sintered samples were performed with a field-emission scanning electron microscope (FE SEM, JSM 7600, JEOL, Tokyo, Japan) equipped with a wavelength-dispersive X-ray spectrometer (WDXS). The surfaces of the bulk ceramic samples and cross-sections of the ML samples were ground and polished with standard metallographic techniques. The bulk ceramic and ML samples were thermally etched at 900 °C and 850 °C, respectively.

Prior to analysis in the FE-SEM, the samples were coated with a few-nm-thick carbon layer (Balzers SCD 005, BAL-TEC GmbH, Witten, Germany), to provide electrical conductivity and avoid charging effects. The average grain size (GS) and GS distributions were determined by applying a stereological analysis of the micrographs. More than 200 grains per sample were measured using the Image Tool Software [98]. The GS values are expressed as the Feret's diameter [99].

The chemical composition of the bulk ceramic and multilayer samples was analysed with WDXS. As a reference a PMN-32PT single crystal with $\langle 111 \rangle$ orientation (APC International, Ltd. Mackeyville, PA, USA) was used for the quantification of the Pb, Mg, Nb, and Ti contents. The accelerating voltage of 30 kV was employed. The X-ray intensities for the Pb- $L\alpha$ spectral line were measured with a LiF (lithium fluoride) crystal; the Ti- $K\alpha$, Nb- $L\alpha$ and Zr- $L\alpha$ spectral lines were measured with a PET (pentaerythritol) crystal; and the Mg- $K\alpha$ spectral line with a TAP (thallium acid phthalate) crystal. The oxygen was calculated from the stoichiometry.

3.2.8 Dielectric spectroscopy

The complex dielectric permittivity $\epsilon^* = \epsilon' - i\epsilon''$ was measured with LCR meters 4980A and 4284A (Hewlett Packard, Palo Alto, California, USA) using a 1 V amplitude for the probing AC electric signal. The data were obtained during cooling with a cooling rate of 1 K/min. For the measurements at temperatures of up to 150 °C, the temperature of the samples was stabilized to within 0.1 K by using a lock-in bridge technique with a platinum resistor Pt100 as the thermometer. For the measurements at temperatures higher than 150 °C, a commercially available high-temperature cell (Novocontrol Technologies, Montabaur, Germany) was used.

For the dielectric measurements with a DC bias, a blocking circuit was used for protection between the LCR meter and the DC source (see Figure 3.4). It consists of two 1- μF capacitors C1 and C2 and a 100-kOhm resistor R1. A high-voltage amplifier (Trek 610E, Lockport, New York, USA) was used as the source of the DC voltage.

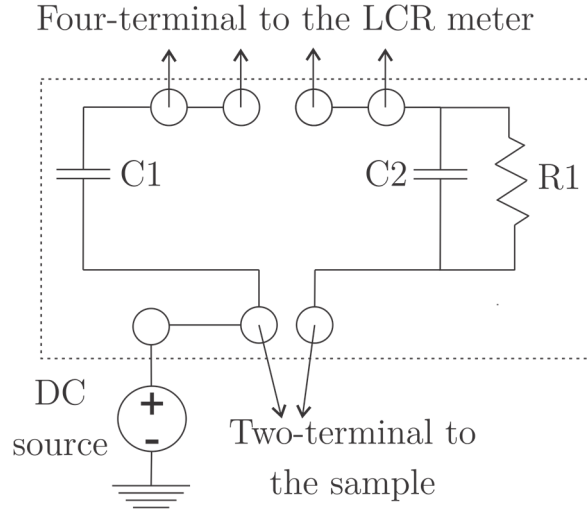


Figure 3.4: The DC bias blocking circuit for the LCR meter, where C1 and C2 are 1- μ F capacitors and R1 is a 100-kOhm resistor.

3.2.9 Polarization electric-field hysteresis measurements

The polarization-electric field (P - E) hysteresis loops were measured with a TF analyser 2000 (Aixacct, Aachen, Germany) at RT with a sinusoidal signal and with a frequency of 1 Hz. Only in the case when electrocaloric stability of the PMN was investigated were the P - E loops measured at RT with a Sawyer-Tower Bridge, for which a 10-mHz triangular signal was employed.

3.2.10 Piezoelectric measurements

The piezoelectric measurements were performed on multilayer samples with Au-sputtered outer electrodes, which were not previously poled. The piezoelectric d_{33} coefficient was measured using a Berlincourt piezometer (Take Control PM10, Birmingham, UK) at 100 Hz.

3.2.11 Electrocaloric measurements

3.2.11.1 Indirect electrocaloric measurements

The P - E hysteresis loops measured in the temperature range from 25 to 140 °C with a 5 °C step were used for calculating ΔT_{EC} via Equation (1.8). The temperature-dependent c_E was found in [100]. We note that its electric-field dependence was neglected.

3.2.11.2 Direct electrocaloric measurements via modified differential scanning calorimeter

The differential scanning calorimeter DSC 204 F1 (Netzsch, Selb, Germany) was modified for the purposes of the direct electrocaloric measurements. The basic principle of the measurement was adopted from high-resolution calorimetry [7], [21]. A new lid for the DSC was constructed so it could both carry the sample and connect it to a Digital multimeter (DMM) and a voltage source, see Figure 3.5.

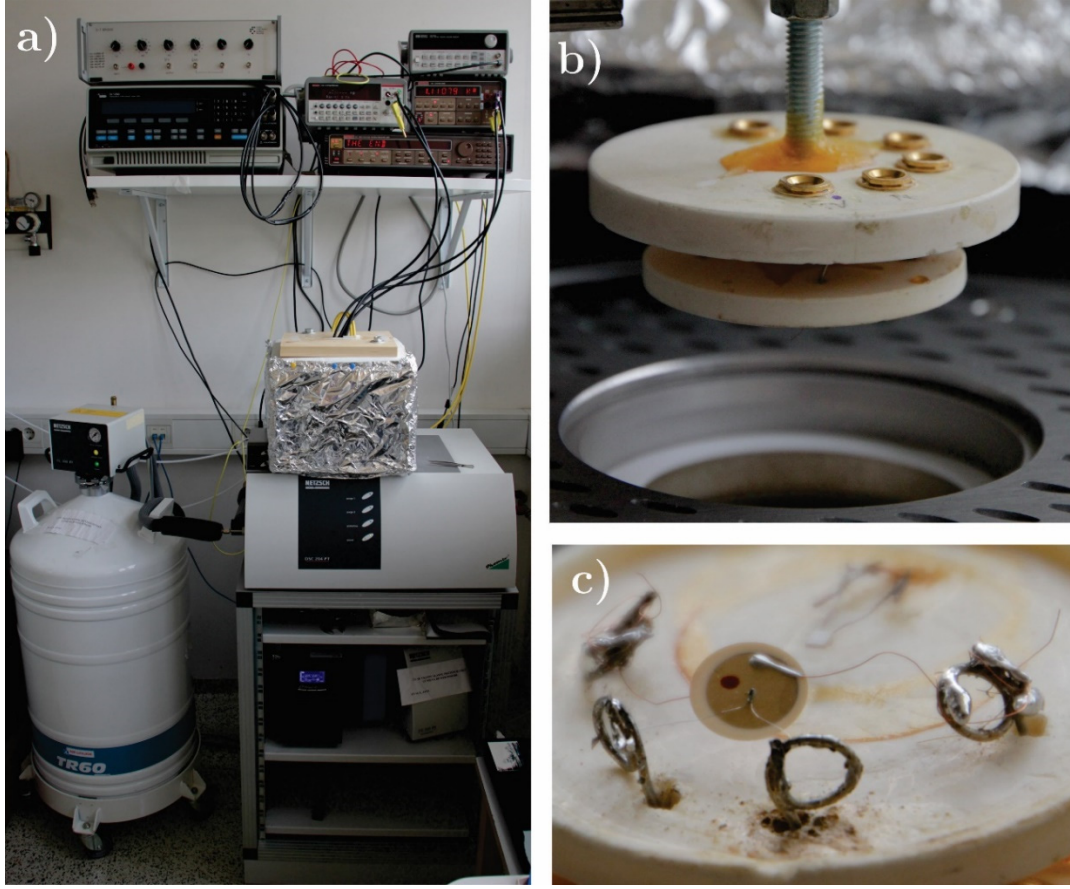


Figure 3.5: (a) Photograph of the DSC 204 F1 modified for EC measurements. (b) Custom made lid which serves as the sample holder. (c) Bulk ceramic sample mounted onto the lid with a miniature thermistor glued in the middle of the sample.

DMM (Keithley 2100, Keithley Instruments, Cleveland, Ohio, USA) was used to measure the resistivity change of a small thermistor, which was glued on the surface of the sample. Thus, fast and accurate temperature changes could be obtained. As the voltage source a Source Measure Unit 237 (Keithley Instruments, Cleveland, Ohio, USA) with a maximum voltage amplitude of 1100 V was used. In order to control the temperature of the sample cell, a PT 1000 was placed in the cell near the sample. The temperature of PT 1000 was acquired via a DMM (Keithley 196, Keithley Instruments, Cleveland, Ohio, USA). With additional insulation positioned on top of the new lid, the temperature in the DSC chamber was stabilized to within 5 mK.

The EC temperature change was induced by a pulse signal of 100 sec, allowing enough time for the temperature to relax after the application/removal of the electric field. As explained in Section 1.1.2, the (raw) measured EC temperature changes ($\Delta T_{EC\ raw}$) were multiplied by a correction factor in order to compensate for the thermal losses due to the passive parts of the sample, thus

$$\Delta T_{EC} = \Delta T_{EC\ raw} \frac{\sum_i m^i c_E^i}{m^a c_E^a}. \quad (3.1)$$

Here m^i and c_E^i are the mass and specific heat capacity of every component, including the active and passive parts. The active part is the ceramic under the electrodes, the mass and specific heat capacity of which are m^a and c_E^a . The passive parts include the parts of the ceramic sample that are not covered by electrodes, a thermistor, gold wire for establishing the electric field and glues used for attaching the thermistor and the wires.

3.2.12 Stability of the electrocaloric effect

To evaluate the stability of the EC effect PMN and PMN-10PT ML elements were placed in a thermally insulated box and suspended on two wires, which were used for connecting the sample with the high-voltage source and the ground (see Figure 3.6a).

Electric-field cycling of the PMN and PMN-PT ML elements was performed at room temperature by applying and removing the voltage controlled by a data-acquisition card (National Instruments, USA) coupled with a high-voltage amplifier (Trek 20/20C, Lockport, New York, USA). A unipolar step signal with a frequency of 2 Hz was applied (see Figure 3.6b). The EC stability was monitored after 10^N (for $N=0, 1, 2, \dots, 6$) cycles, while the ΔT_{EC} was measured with the unipolar step signal and a frequency of 5 mHz. This slow cycle is also denoted as the test EC cycles in Figure 3.6b. The EC response was measured by a thermistor glued onto the sample and a DMM (Hewlett Packard 34401A, Palo Alto, California, USA).

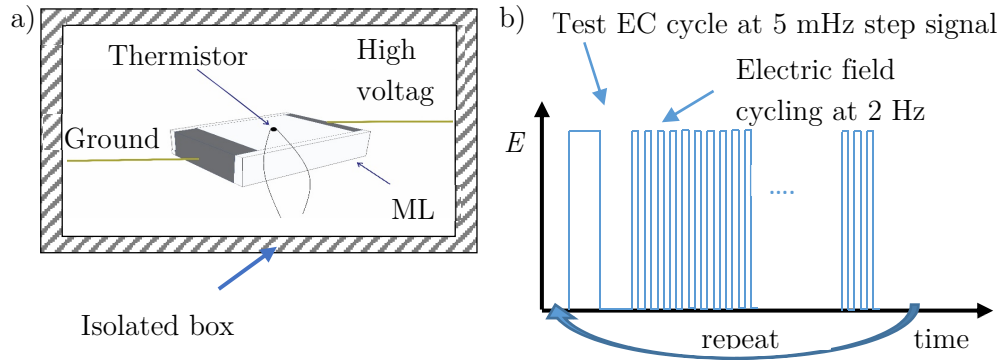


Figure 3.6: (a) The scheme of the sample holder for EC stability testing. (b) Monitoring the EC stability: test cycle (@5 mHz), electric field cycling (@2 Hz) with a unipolar step signal.

Chapter 4

Results and Discussion

4.1 PMN and PMN-PT Bulk Ceramics

In this section the structure and microstructure of the PMN, PMN-5PT and PMN-10PT powders and the bulk ceramics are described. In addition, the results of the dielectric, ferroelectric and electrocaloric measurements of the bulk samples are given and compared. A particular emphasis is placed on the impact of the DC bias electric field on the temperature-dependent peaks of the dielectric permittivity and the temperatures of the largest electrocaloric temperature changes.

4.1.1 Synthesis of PMN and PMN-PT powders

The PMN, PMN-5PT and PMN-10PT powders were prepared by mechanochemical synthesis. The synthesis of the PMN was performed on the basis of the procedure described by Kuščer et al. [42]. The authors found that after initial partial amorphisation (~60 weight %) of the oxide mixture, the amount of perovskite phase was progressively increasing, while the amount of pyrochlore phase reached a peak after 16 hours, after which it gradually decreased. After 60 hours of high-energy milling the sample consisted of ~46 weight % of perovskite PMN, ~46 % of amorphous phase, 1.4 % of pyrochlore $\text{Pb}_{1.86}\text{Mg}_{0.24}\text{Nb}_{1.76}\text{O}_{6.5}$ and trace amounts of non-reacted oxides. In our case, the mixture of initial oxides was high-energy milled for 90 h, i.e., until the perovskite phase was the predominant phase according to the XRD, see Figure 4.1. The high background indicates the presence of an amorphous phase in agreement with [40]. The broadening of the peaks indicates a fine crystallite size. The left shoulder of the asymmetric (101) perovskite peak at $2\theta = 31^\circ$ suggests the possible presence of traces of the pyrochlore phase [42].

Note that later we use the term PMN-PT when discussing both the PMN-5PT and PMN-10PT materials. Earlier work [51] on the mechanochemical synthesis of PMN-10PT revealed that extended times of high-energy milling of the oxide mixture, typically about 100 hours, were needed to obtain single-phase ceramics. In our preliminary experiments times exceeding 140 hours were needed to obtain pyrochlore-free ceramics from the oxide mixture. Therefore, we introduced another approach to reduce the milling time and thus reduce the possibility of contamination due to the wear of the milling bodies. Namely, we used the pre-synthesized PT particles in the mixture of remaining oxides as seeds for the nucleation of the perovskite phase and thus almost halved the milling time. The mechanism of this synthesis is described in Dragomir et al. [101]. In our work, the milling times for PMN-5PT and PMN-10PT were 72 and 48 h, respectively. In Figure 4.1 the XRD patterns of both powders are collected.

Similarly to the case of PMN, we observe broadening of the perovskite peaks, a high background and an asymmetric (101) peak, respectively, indicative of the fine crystallite size, the presence of an amorphous phase and traces of pyrochlore. A slight shift towards higher 2θ values from PMN towards PMN-10PT is a consequence of a progressively smaller perovskite unit cell with increasing PT content.

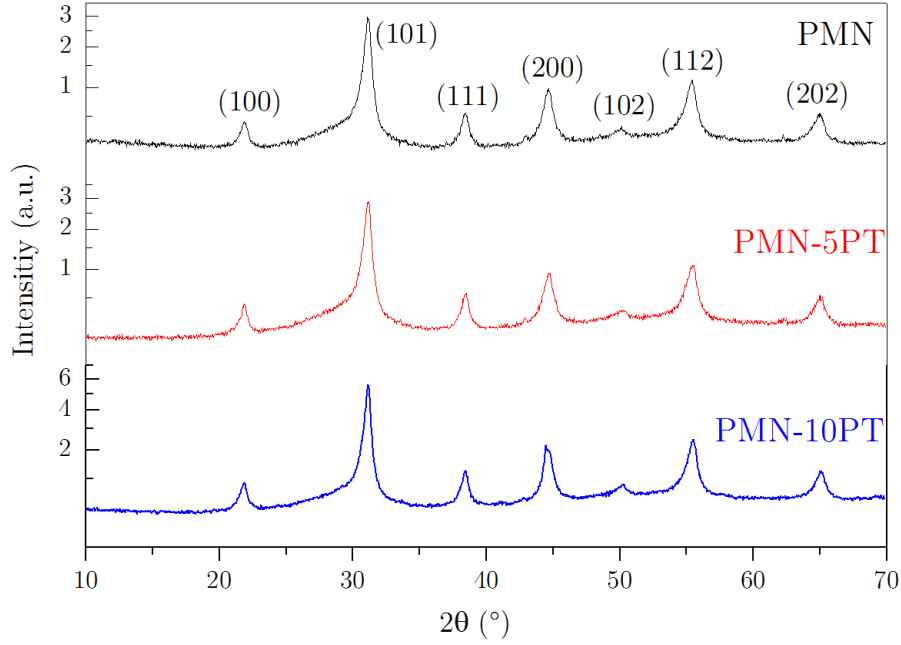


Figure 4.1: XRD patterns of the PMN and PMN-PT powders after high-energy milling. The peaks corresponded to the perovskite phase (ICDD 88-1867) and they are denoted with the Miller indices.

The particle size distributions (PSDs) of the mechanochemically synthesized PMN and PMN-PT powders are shown in Figure 4.2. All the samples have quite narrow PSDs with a d_{50} of about 0.4 μm , see Table 4.1. We note that the PMN-10PT has a slightly larger population of large particles, which is also reflected in a larger d_{90} compared to other two samples, i.e., 1.2 μm versus 0.9 μm (Table 4.1).

Table 4.1: The PMN-PT particle size limit of 10 % (d_{10}), 50 % (d_{50}), and 90 % (d_{90}).

Composition	d_{10} (μm)	d_{50} (μm)	d_{90} (μm)
PMN	0.20	0.42	0.92
PMN-5PT	0.23	0.42	0.91
PMN-10PT	0.22	0.46	1.19

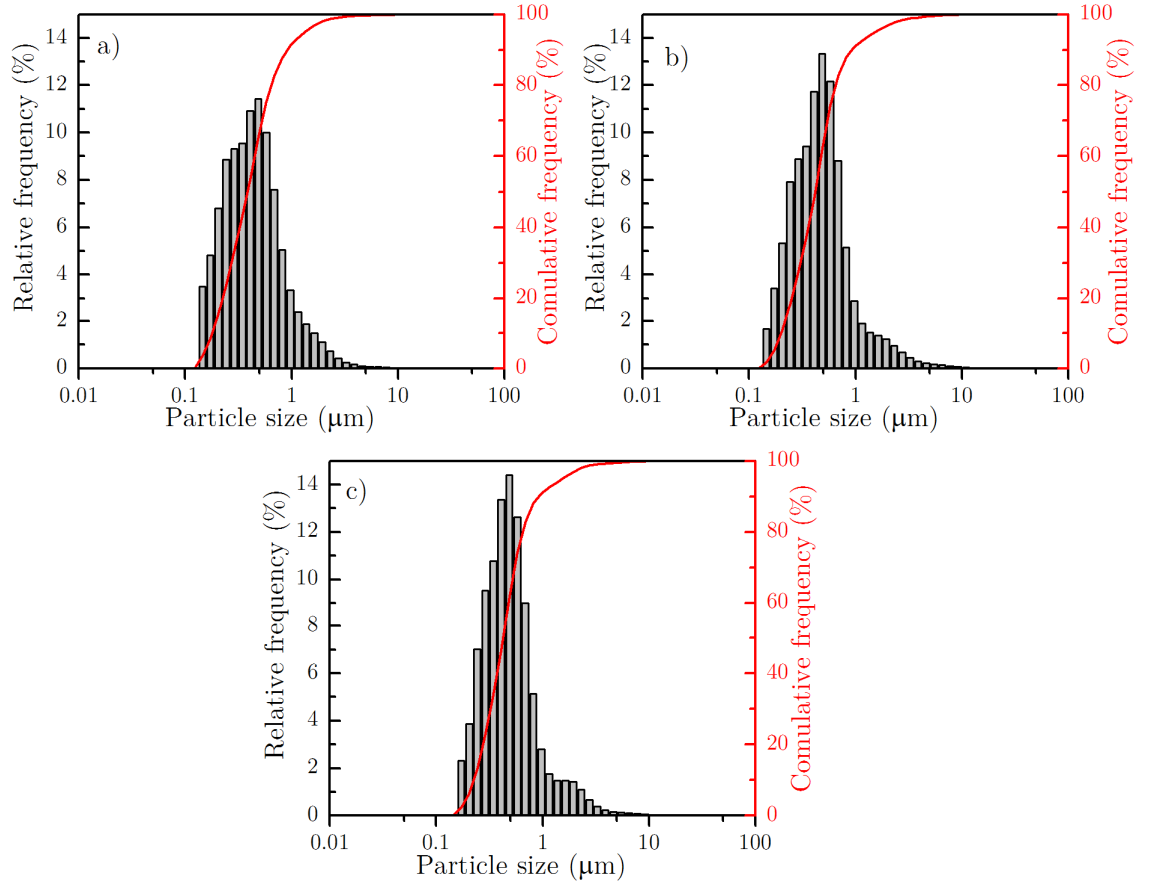


Figure 4.2: Particle size distributions of (a) PMN, (b) PMN-5PT and (c) PMN-10PT.

ICP spectrometry of the PMN and PMN-PT powders was performed in order to check for the possible presence of contaminants. These could be either W and Co stemming from the high-energy milling in a WC vial and milling bodies or the Zr from the attrition milling with YSZ milling bodies. The results of the analysis are collected in Table 4.2. The molar concentrations of W and Zr were calculated based on the assumption that they are incorporated on the B-sites of the perovskite unit cell. The values of Co were below the detection limit of the ICP method. The contamination with W in the PMN and PMN-10PT powders is about 0.1 mol% and much lower in the PMN-5PT, about 0.03 mol%. No correlation between the contamination with W and the time of the high-energy milling could be found. The contaminations with Zr are similar in all the samples, between 0.12 and 0.18 mol%, which is expected as the conditions of the attrition milling were the same in all the powders.

Table 4.2: Concentrations of contaminants (Co, W and Zr) in the PMN and PMN-PT powders due to the wear of the milling bodies, determined by the ICP spectrometry. The values in the brackets represent the percentage of mole of contaminant per mole of PMN or PMN-PT.

Composition	Co (mg/kg)	W (mg/kg)	W molar concentration	Zr (mg/kg)	Zr molar concentration
PMN	<50*	431	(0.08 %)	498	(0.18 %)
PMN-5PT	<50*	132	(0.03 %)	492	(0.18 %)
PMN-10PT	<50*	507	(0.09 %)	319	(0.12 %)

* below the detection limit

4.1.2 Microstructure and phase composition

The XRD patterns of the PMN and PMN-PT ceramics sintered at 1200 °C are shown in Figure 4.3. According to the XRD analysis all the samples crystallize in a pure perovskite phase. The PMN and PMN-PT samples reach about 95 % relative density (RD), see Table 4.3.

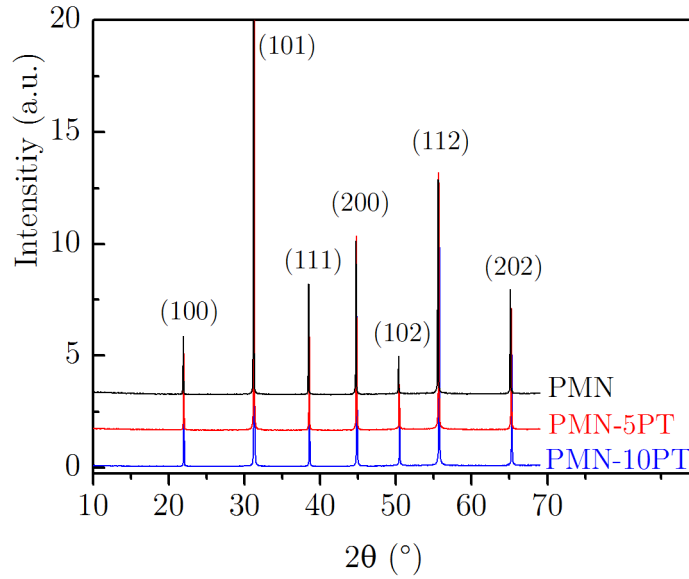


Figure 4.3: XRD patterns of the PMN, PMN-5PT and PMN-10PT sintered bulk ceramics. The Miller indices were assigned to the diffraction peaks, which correspond to the perovskite phase (ICDD 88-1867).

Table 4.3: Density and relative density (RD) of the PMN-PT bulk ceramics.

Material	Density (g/cm ³)	RD (%)
PMN	7.84	96.2
PMN-5PT	7.80	95.7
PMN-10PT	7.71	94.5

A FE SEM micrograph of the polished surface of PMN is shown in Figure 4.4a, while micrographs of the PMN-PT samples are collected in Figure 4.5. These micrographs confirm that no secondary phases are present in any of the three specimens. Furthermore, WDXS analyses were performed on all samples.

Figure 4.4b includes the concentrations of Pb, Mg and Nb in six randomly chosen areas of the PMN specimen. The concentration of Pb in all the analysed points is slightly higher, and conversely, the concentrations of Mg and Nb are slightly lower than the nominal values. The average concentrations of the individual elements and their standard deviations (STDEV) ranging from 0.17 to 0.15, confirm the almost stoichiometric composition with a high level of homogeneity, see Table 4.4. The A:B ion ratio is 1.05 ± 0.01 , meaning that there should be a slight excess of PbO in the matrix phase. However, the atmosphere powder was also PMN, so we expect that the PbO vapour-pressure gradient between the pellet and the atmosphere powder was small, if it existed at all, and thus the condensation of PbO in the pellet is not expected. Furthermore, the perovskite structure does not tolerate excess A-sites (or vacancies on B-sites) [31].

The concentrations of the Pb, Mg, Nb and Ti elements in the PMN-5PT and PMN-10PT samples are collected in Figure 4.5. The chemical compositions of all the analysed locations are close to the nominal values in both samples. The averages of six randomly selected areas are summarized in Table 4.5. The STDEV of both the PMN-PT samples are low, which indicates a high level of chemical homogeneity. The A:B ratios are 1.01 ± 0.02 and 0.99 ± 0.01 for the PMN-5PT and PMN-10PT, respectively.

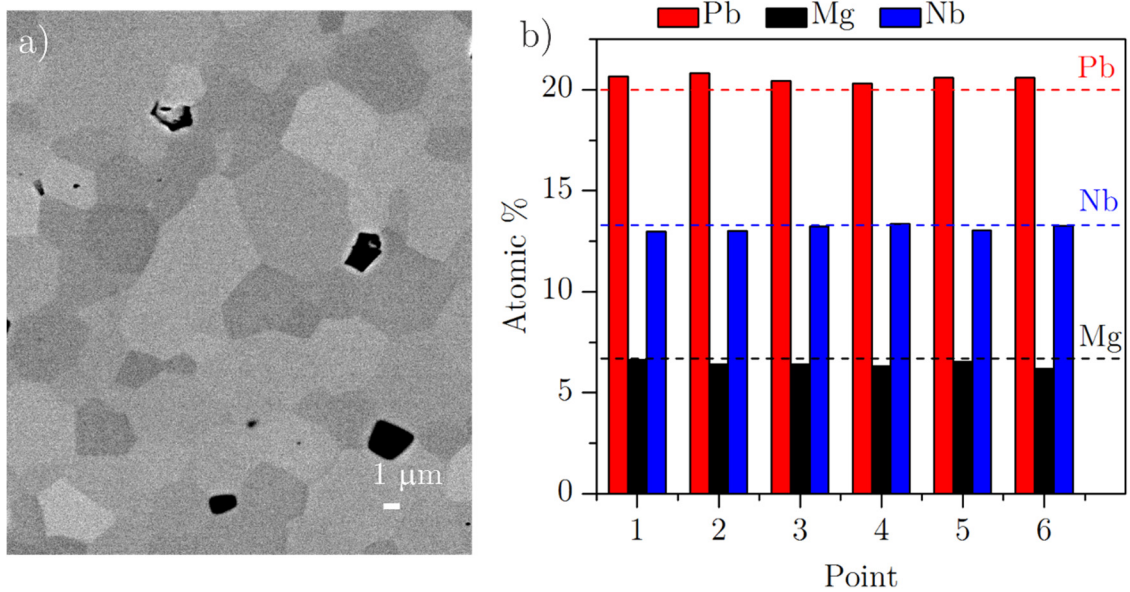


Figure 4.4: a) FE-SEM micrograph of a polished PMN surface. (b) WDXS analysis of six random points. The results are expressed as atomic %. The dashed horizontal lines mark the nominal concentrations of Pb, Mg and Nb.

We assume that there is a slightly higher STDEV of all elements in the PMN-5PT than in the PMN-10PT, which could be related to a larger fraction of PT in the reagent powder mixture and probably a better homogenization. Nevertheless, the absolute values of STDEV in both samples are low.

Table 4.4: Results of the WDXS analyses of the PMN expressed as the average of six measurements.

Element	Nominal composition (atomic %)	WDXS (atomic %)	STDEV
Pb	20.0	20.58	0.17
Mg	6.7	6.41	0.16
Nb	13.3	13.15	0.15
O	60.0	59.86	0.11

Table 4.5: Results of the WDXS analyses for PMN-PT expressed as the average of six measurements.

	PMN-5PT			PMN-10PT		
Element	Nom. comp. (atomic %)	WDXS (atomic %)	STDEV	Nom. comp. (atomic %)	WDXS (atomic %)	STDEV
Pb	20.0	20.18	0.24	20.0	19.93	0.16
Mg	6.3	6.34	0.18	6.0	6.15	0.09
Nb	12.7	12.57	0.14	12.0	11.99	0.07
Ti	1.0	1.00	0.01	2.0	1.96	0.04
O	60.0	59.92	0.10	60.0	59.97	0.06

FE-SEM micrographs of thermally etched PMN and PMN-PT bulk ceramics are collected in Figure 4.6. The micrographs reveal homogeneous and highly dense microstructures for all three samples, which is in agreement with the density measurements. The average grain size (GS) of the PMN is 3.12 μm , and it is slightly lower in the PMN-PT samples, i.e., 2.84 μm and 2.56 μm respectively in PMN-5PT and PMN-10PT. The grain size distributions in all the samples are unimodal, see Figure 4.6. The reported values [38], [51], [102] for the GS in PMN and PMN-rich PMN-PT solid solutions under similar sintering conditions are comparable with our results.

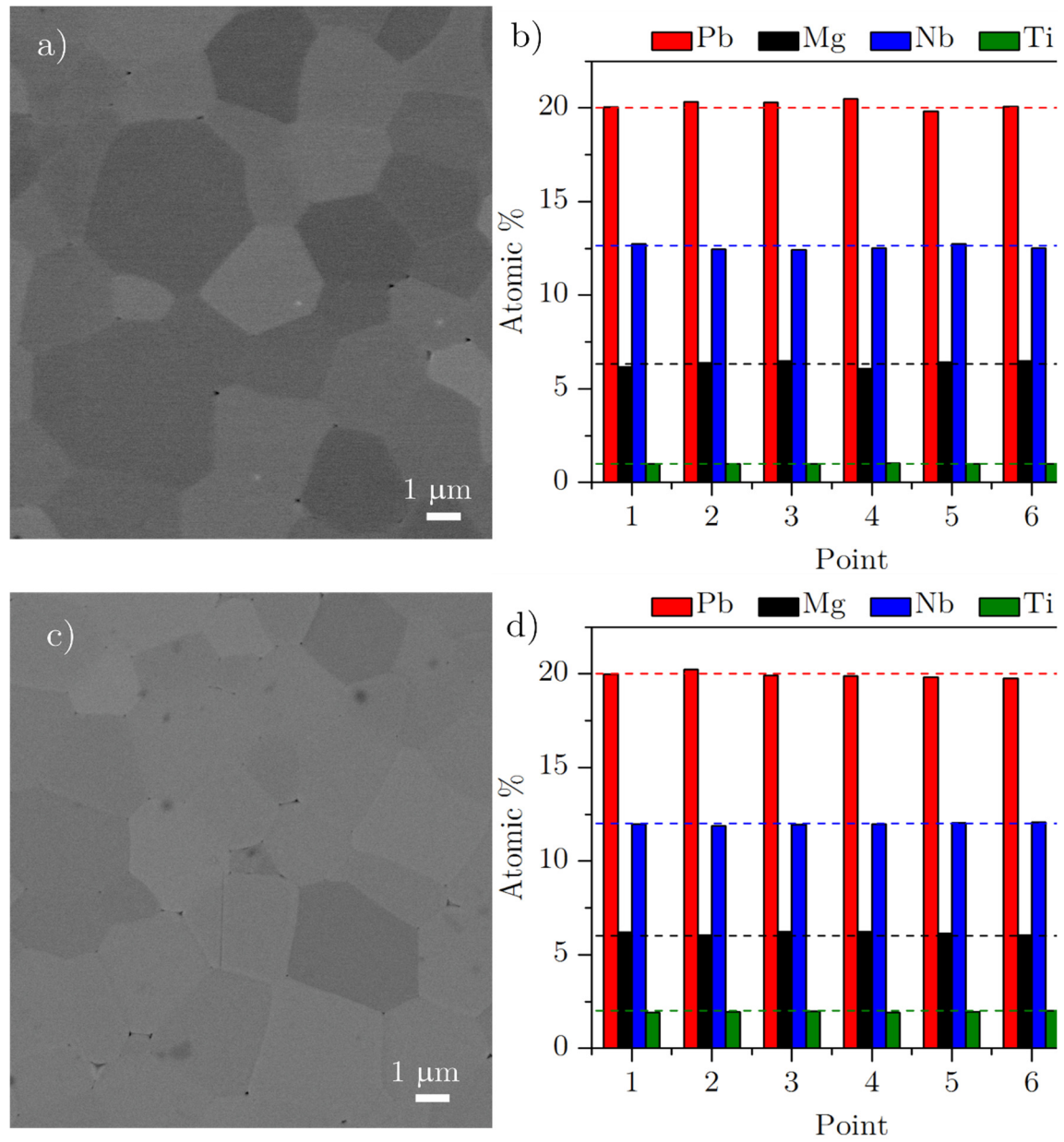


Figure 4.5: FE-SEM micrographs and WDXS analyses of the polished PMN-5PT (a, b) and PMN-10PT (c, d) surfaces. The results of the analyses of six random points in each sample are expressed as atomic %. The dashed horizontal lines mark the nominal concentrations of Pb, Mg, Nb and Ti.

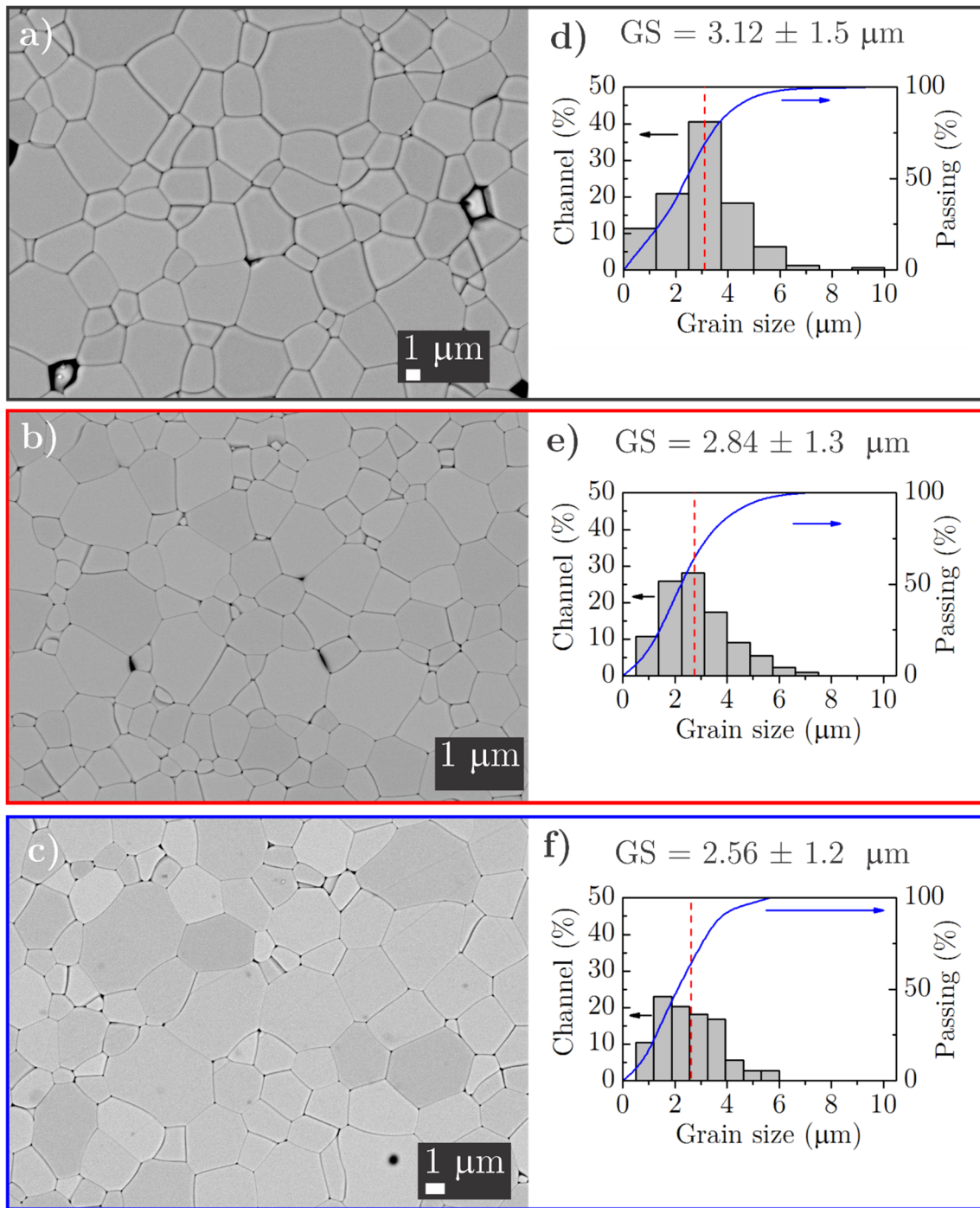


Figure 4.6: FE-SEM micrographs of thermally etched (a) PMN, (b) PMN-5PT and (c) PMN-10PT bulk ceramics. In (d), (e) and (f) the average grain size (GS) and grain size distribution plots are provided for PMN, PMN-5PT and PMN-10PT, respectively.

4.1.3 Dielectric and ferroelectric properties

The temperature-dependent complex dielectric permittivity, in particular its real (ϵ') and imaginary parts (ϵ''), as well as the dielectric losses ($\tan \delta = \epsilon''/\epsilon'$), are collected in Figure 4.7 for PMN, PMN-5PT and PMN-10PT. The measurements were performed during cooling runs in the frequency range 30 Hz to 30 kHz. Please note that the discussed values in the following paragraphs are for the data obtained at the frequency of 1 kHz.

The PMN exhibits a broad single peak of ϵ' , with a strong frequency dispersion, being characteristic for relaxors [30]. The maximum ϵ' value ($\epsilon'_{\max}$) of 23 200 is observed at a temperature (T_m) of -3 °C. At 25 °C the value of ϵ' is 16 770. The temperature-dependant ϵ'' also shows a frequency-dispersive peak with a maximum value of 2 200. The $\tan \delta$ value at -75 °C is 0.10, and with increasing temperature $\tan \delta$ increases up to a maximum value of 0.13 at -19 °C. With a further temperature increase, $\tan \delta$ drops significantly, and thus at 25 °C the $\tan \delta$ of PMN is 0.003.

The PMN-5PT and PMN-10PT exhibit similar relaxor, broad, dispersive, dielectric maxima to the PMN. The $\epsilon'_{\max}$ of PMN-5PT is 20 000 with a T_m of 16 °C. The PMN-10PT shows a $\epsilon'_{\max}$ value of 24 700 at 40 °C. The PMN-5PT has a maximum value ϵ'' of 1 700 at 7 °C, while the maximum ϵ'' of PMN-10PT is 2 000 at 29 °C. The $\tan \delta$ of PMN-5PT and PMN-10PT are similar to the $\tan \delta$ of PMN, and thus the maximum $\tan \delta$ of PMN-5PT and PMN-10PT are 0.100 and 0.095 at 2 °C and 24 °C, respectively.

The complex dielectric permittivity of PMN, PMN-5PT and PMN-10PT reveals that these compositions exhibit similar behaviour without any significant differences. The temperatures of the ϵ' , ϵ'' and $\tan \delta$ maxima are shifting to higher temperatures with increasing PT content, which is in good agreement with the literature [103], [104]. For example, the PMN has a 35 % higher maximum $\tan \delta$ value than PMN-10PT; however, due to the lower T_m , the $\tan \delta$ at 25 °C is significantly lower in PMN than in PMN-10PT. In addition, the correlation between the PT content and T_m is linear, which agrees well with the PMN-PT phase diagram in Figure 1.4.

In Table 4.6 the dielectric results of the PMN and PMN-PT materials are compared with selected values reported in the literature. The measured $\epsilon'_{\max}$ of PMN (23 300) is the highest value reported for bulk ceramics, being almost as high as the value obtained for the single crystal (23 500 [105]). The scattering of reported $\epsilon'_{\max}$ values for PMN ceramics is otherwise high. In fact, from Table 4.6 it is clear that different synthesis methods yield $\epsilon'_{\max}$ values from 10 000 to 19 000. Moreover, the span between T_m values is more than 10 K. Such scattering reveals that the method of synthesis has a profound influence on the dielectric properties.

The PMN-10PT composition, on the other hand, exhibits an $\epsilon'_{\max}$ value that is 20 % lower than the highest value in the literature, which is 29 000 [51]. Furthermore, the T_m value is 7 K lower than the T_m in reference [51].

A possible explanation for such a difference in the $\epsilon'_{\max}$ could, tentatively, be a different level of chemical homogeneity, as a result of the different synthesis methods. It was, for example, shown that with a mechanochemical synthesis of $\text{Pb}(\text{Sc}_{0.5}\text{Nb}_{0.5})\text{O}_3$ a higher ϵ' was obtained in comparison to the values obtained with a solid-state synthesis [106]. The difference in $\epsilon'_{\max}$ could also possibly be related to different levels of Zr contamination introduced by attrition milling [107], [108]. Namely, in our case the Zr contamination of 0.18 mol% is significantly higher than the 0.02 mol% reported in [51], and, as mentioned earlier, the T_m values of the two samples differ by 7 K. Moreover, the contamination with W can also lower the T_m value, as was shown for PMN-13PT doped with 1 % of W [109].

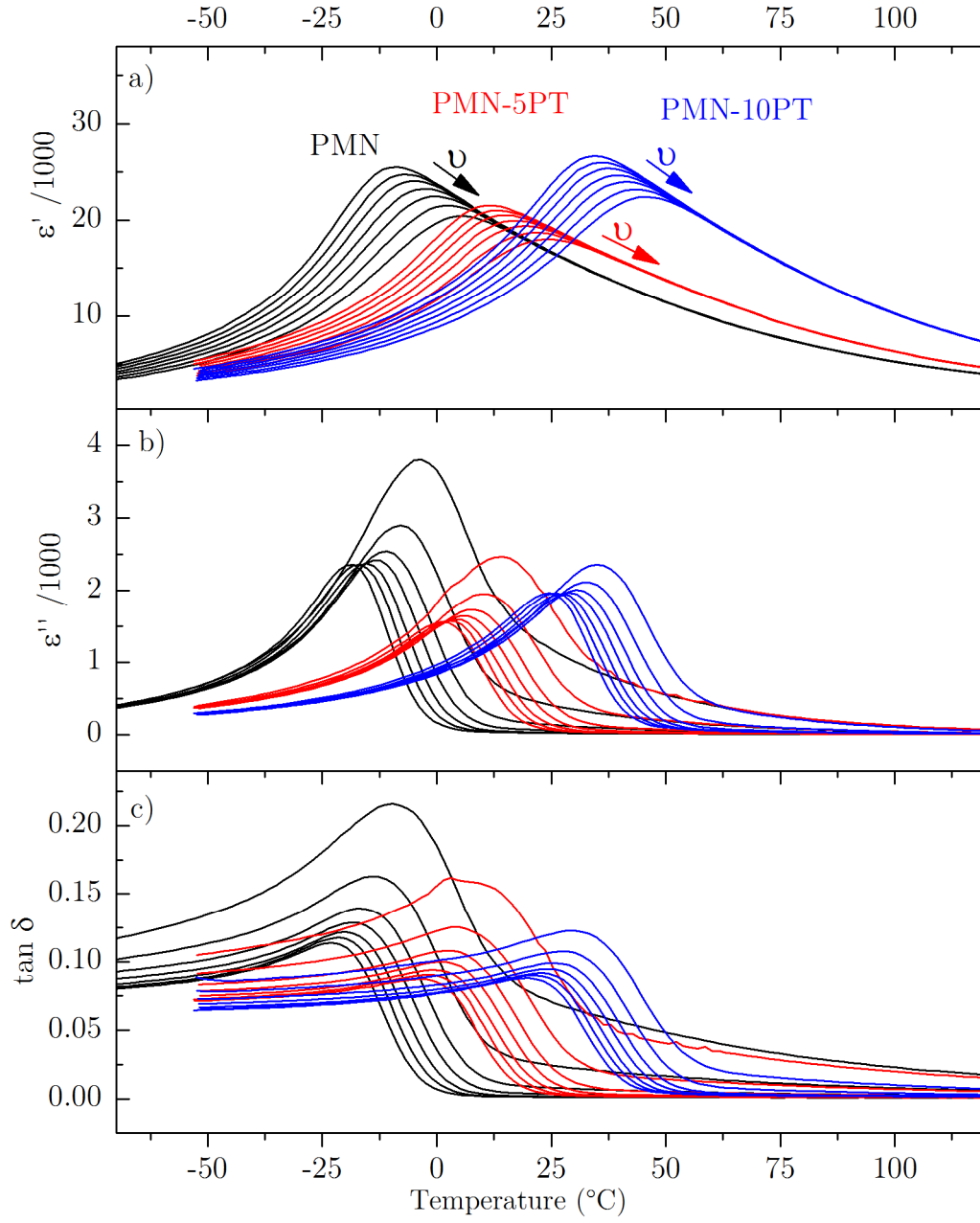


Figure 4.7: Temperature-dependent dielectric permittivity of PMN (black lines), PMN-5PT (red lines) and PMN-10PT (blue lines) bulk ceramics measured in the frequency range 30 Hz to 30 kHz. (a), (b) and (c) represent data for its real ϵ' , imaginary part ϵ'' , and losses $\tan \delta = \epsilon''/\epsilon'$, respectively.

Table 4.6: Values of $\epsilon'_{\max}$, maximum dielectric losses ($\tan \delta_{\max}$) and T_m obtained at 1 kHz in various bulk PMN and PMN-PT ceramics.

Composition	$\epsilon'_{\max}$	$\tan \delta_{\max}$	T_m	Synthesis method	Ref.
PMN	14 900*	/	-15*	Columbite	[38]
	17 500	/	-5	Mechanochemical	[40]
	19 100	0.11	-3	Aqueous suspension	[110]
	10 300		-5	Reactive sintering	[111]
	15 400		-5	Reactive sintering	[111]
	23 300	0.13	-3	Mechanochemical	This work
PMN-5PT	23 000	/	20	Columbite	[104]
	20 000	0.10	16	Mechanochemical	This work
PMN-10PT	29 000	0.08	47	Mechanochemical	[51]
	24 600	/	41	Soft mechanochemical	[112]
	25 500	/	45	Mechanochemical	[41]
	21 200*	/	40*	Columbite	[38]
	24 700	0.09	40	Mechanochemical	This work

* measured at 100 Hz

The polarization versus electric field (P - E) hysteresis loops of the PMN and PMN-PT bulk ceramics are presented in Figure 4.8. The loops measured at lower fields of 25 kV/cm are shown in order to more clearly reveal the difference between the investigated materials and also to allow easier comparisons with the values from the literature (these are determined at such moderate electric fields).

The PMN exhibits a slim hysteresis loop, typical for relaxors. The saturated polarization (P_s) at 25 kV/cm is 22 $\mu\text{C}/\text{cm}^2$, while at 90 kV/cm P_s increases to 32 $\mu\text{C}/\text{cm}^2$. Similarly, the P - E loops of PMN-5PT and PMN-10PT are slim, with a P_s of 22 and 27 $\mu\text{C}/\text{cm}^2$ at 25 kV/cm, respectively. With the increase of PT content a broadening of the P - E loops can be observed, with higher values of P_s , remanent polarization and coercive field. The P_s values are very similar to the reported values collected in Table 4.7. It should be emphasised that the spread of the P_s data is smaller than in the case of $\epsilon'_{\max}$ values. This is due to the fact that the external electric field induces a ferroelectric phase, i.e., long-range order is established in the system.

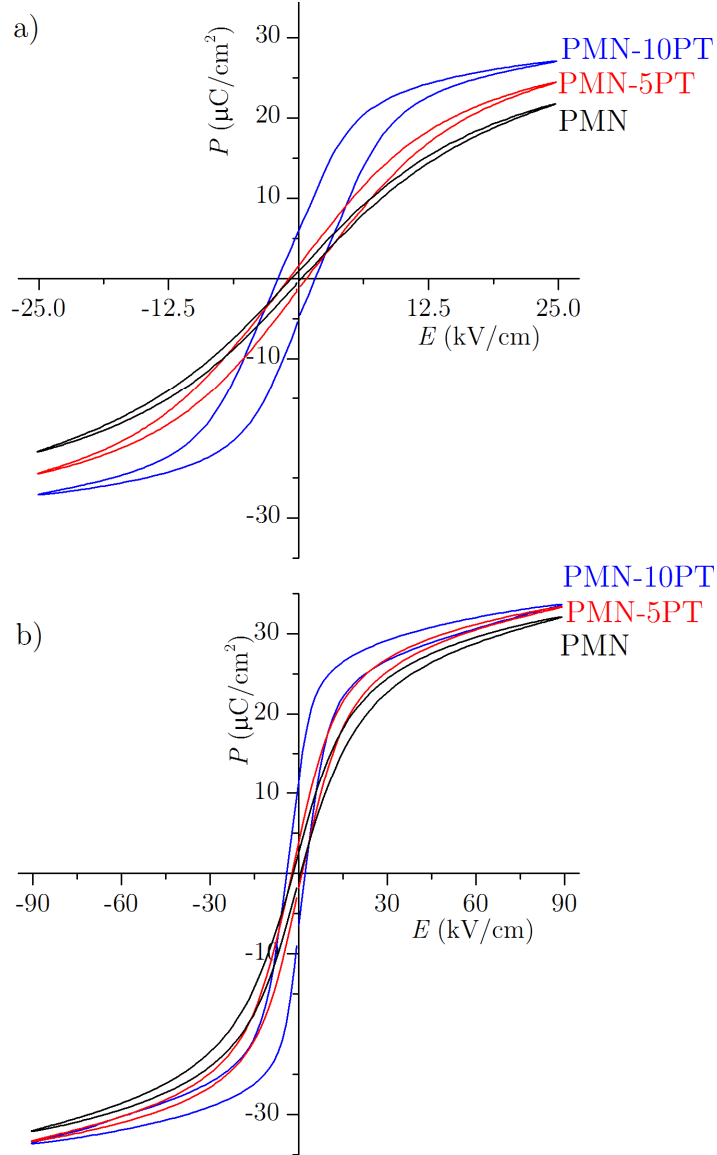


Figure 4.8: P - E hysteresis loops of PMN, PMN-5PT and PMN-10PT ceramics, measured at electric fields of (a) 25 kV/cm and (b) 90 kV/cm at RT and a frequency of 1 Hz.

Table 4.7: Saturated polarization (P_s) of various PMN and PMN-PT ceramics.

Composition	P_s ($\mu\text{C}/\text{cm}_2$)	E (kV/cm)	Ref.
PMN	21	40	[103]
	26	40	This work
PMN-5PT	26	40	[103]
	28	40	This work
PMN-10PT	30	40	[103]
	32	40	[51]
	29	40	This work

4.1.4 Dielectric permittivity under DC bias field

In this section the influence of the DC bias field on the dielectric permittivity is described, primarily the shifting of T_m when increasing the DC bias electric fields. The investigation was performed on the PMN, PMN-5PT and PMN-10PT bulk ceramics. The temperature-dependent ϵ' under DC bias fields of 0 to 50 kV/cm was measured at frequencies between 1 kHz and 30 kHz and the results are shown in Figure 4.9. Prior to each field-cooling measurement run, the samples were annealed at 142 °C for 15 min, in order to erase any history-dependent effects. Note that in the case of PMN-10PT the measurement at 50 kV/cm is omitted due to the temperature limitation of the measuring set-up (see Section 3.2.8).

The PMN exhibits the frequency dispersion of the ϵ' peak as discussed in the previous section; however, with increasing DC bias this dispersion is gradually diminishing, see Figure 4.9d and Figure 4.9e. At 10 kV/cm the frequency dispersion is still present, while at a higher DC field of 15 kV/cm it is not detectable any more. Furthermore, with increasing DC bias the ϵ' peak is broadening and the $\epsilon'_{\max}$ value is decreasing. This decrease is steep at DC bias fields of up to 15 kV/cm, while at higher fields $\epsilon'_{\max}$ decreases more gradually. On the other hand, the effect of the DC bias on T_m shifting is more pronounced at electric fields higher than 10 kV/cm. Thus, at 5 kV/cm T_m slightly down-shifts by 4.2 K, and with a further DC increase to 10 kV/cm, T_m up-shifts by 3.0 K, which is just below the temperature of T_m at 0 kV/cm. Afterwards, at larger DC bias fields T_m sharply increases, with the largest T_m shift of 97.3 K at 50 kV/cm.

The PMN-5PT exhibits a similar behaviour of the ϵ' peak and T_m shifting in DC bias fields as PMN, see Figure 4.9b. The frequency dispersion of the ϵ' peak can be detected at DC fields of up to 10 kV/cm (Figure 4.9f and Figure 4.9g). The $\epsilon'_{\max}$ decreases sharply at fields up to 15 kV/cm, while at higher DC fields this decrease saturates, just as in the PMN composition. The T_m down-shifts from 22.4 to 20.6 °C at 5 kV/cm, and later at 10 kV/cm the T_m up-shifts to 22.9 °C. At higher DC bias fields the T_m up-shift is significantly larger, which means that at 50 kV/cm the T_m is 123 °C, which is a 100.2 K up-shift from T_m at 0 kV/cm. In Figure 4.9c the results for the PMN-10PT are presented. The frequency dispersion of the ϵ' peak is visible at DC fields of 0 and 5 kV/cm (Figure 4.9h), and at such DC biases the decrease of $\epsilon'_{\max}$ is the steepest. On the other hand, the T_m down-shift at 5 kV/cm is quite low, i.e., 0.5 K. A large T_m shift to higher temperatures is noticeable at the DC bias of 10 kV/cm and at higher electric fields. Therefore, at the DC field of 25 kV/cm the T_m shift is 73.8 K from the T_m at 0 kV/cm.

The dependence of T_m on the DC bias field (E_{DC}) for all the bulk samples is shown in Figure 4.10a, while Figure 4.10b presents the dependence of the normalized values $\Delta T_m = T_m(E_{DC}) - T_m(E_{DC}=0)$. At low E_{DC} the T_m shift is gradual, while at high electric fields the T_m shift is steeper for all compositions. The field at which the T_m starts to abruptly increase is denoted as the threshold field (E_t). E_t is related to the critical point in the electric field versus temperature (E - T) diagram [54], [113], and is thus suitable for locating the position of the critical point.

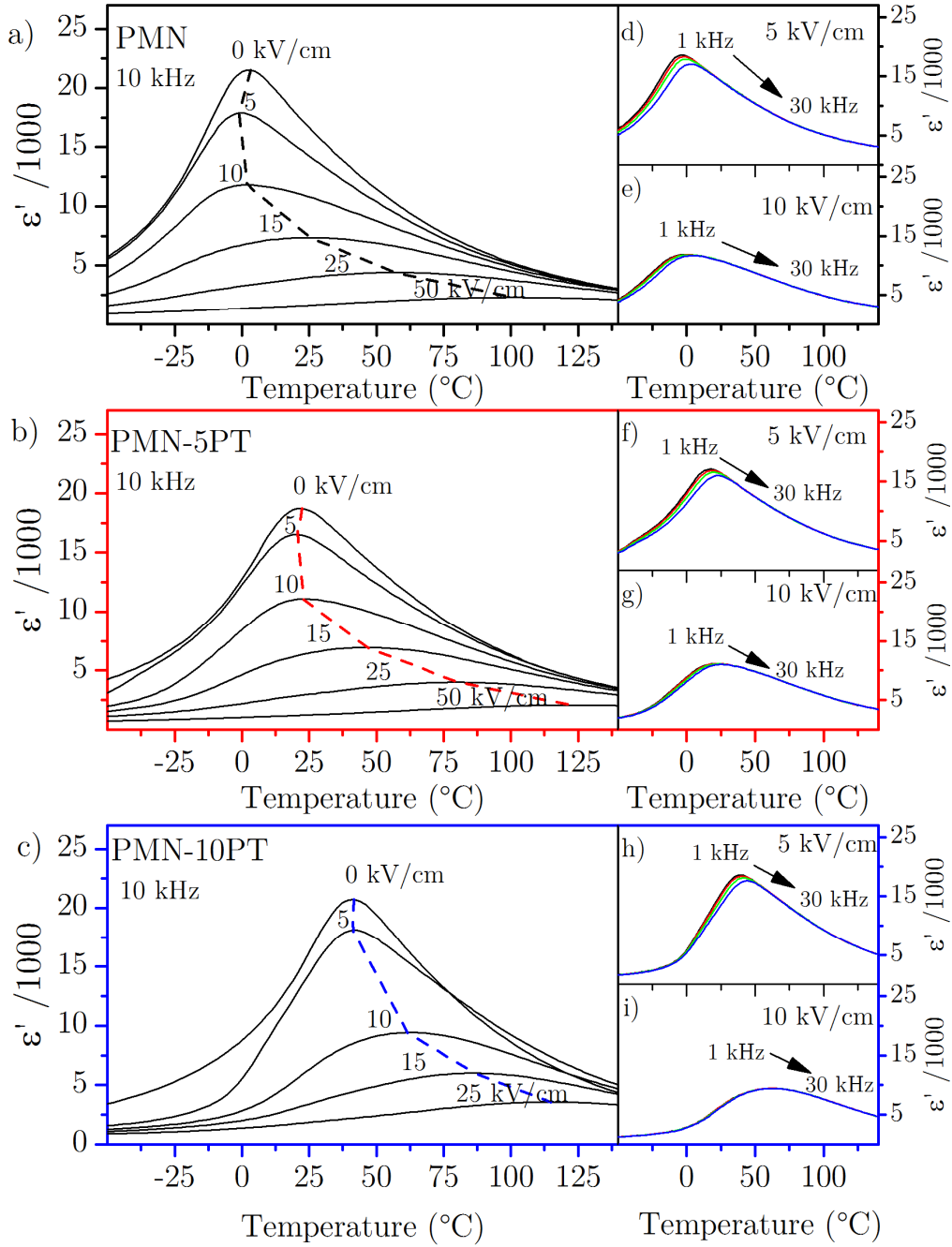


Figure 4.9: The real part of the complex dielectric permittivity (ϵ') versus temperature, measured at DC bias fields of 0 to 50 kV/cm, is shown in (a) PMN, in (b) PMN-5PT, and in (c) PMN-10PT bulk ceramics. Due to the clarity the ϵ' values are measured at a single frequency of 10 kHz. The maximum ϵ' values at each electric field are presented with dashed lines in (a, b and c). Note that these lines are a guide for the eyes. The insets (d, f and h) show the results obtained at 5 kV/cm for PMN, PMN-5PT and PMN-10PT ceramics, respectively, in the frequency range of 1 kHz to 30 kHz. The insets (e, g and i) present the temperature-dependent ϵ' at 10 kV/cm for PMN, PMN-5PT and PMN-10PT ceramics, respectively.

The E_t of PMN is approximately 10 kV/cm. With a higher PT content the E_t is decreasing, and for PMN-10PT the E_t is approximately 5 kV/cm. (Note that the measuring steps of 5 kV/cm do not allow a more precise determination of E_t .) At low E_{DC} a down-shift of T_m in all the samples is observed (inset in Figure 4.10b), which is the highest for PMN (4.2 K) and the lowest in PMN-10PT (0.5K). We can observe that the ΔT_m versus DC bias dependencies of PMN and PMN-5PT are very similar, compared to PMN-10PT. Such a trend is further noticed when comparing $\epsilon'_{\max}$ as a function of DC bias, i.e., for both PMN and PMN-5PT the $\epsilon'_{\max}$ strongly decreases at fields up to 10 kV/cm, which in the case of PMN-PT is a gradual decrease. Thus, it can be concluded that the electric field needed for inducing the relaxor-to-ferroelectric transition is higher in PMN-10PT than in PMN and PMN-5PT.

The behaviour when T_m first slightly down-shifts at low DC bias and abruptly increases at DC bias fields higher than E_t has been explained by Raevski et al. [54], and was discussed in detail in Section 1.3.1. However, Raevski et al. [54] showed that experimentally determined T_m at low fields was not down-shifting in PMN-6PT and PMN-10PT single crystals, only in the PMN-13PT. Their E_t values of 4 and 3 kV/cm for PMN-6PT and PMN-10PT, respectively, are also lower than our results. Nevertheless, the trend of decreasing E_t with increasing PT content is present in both cases.

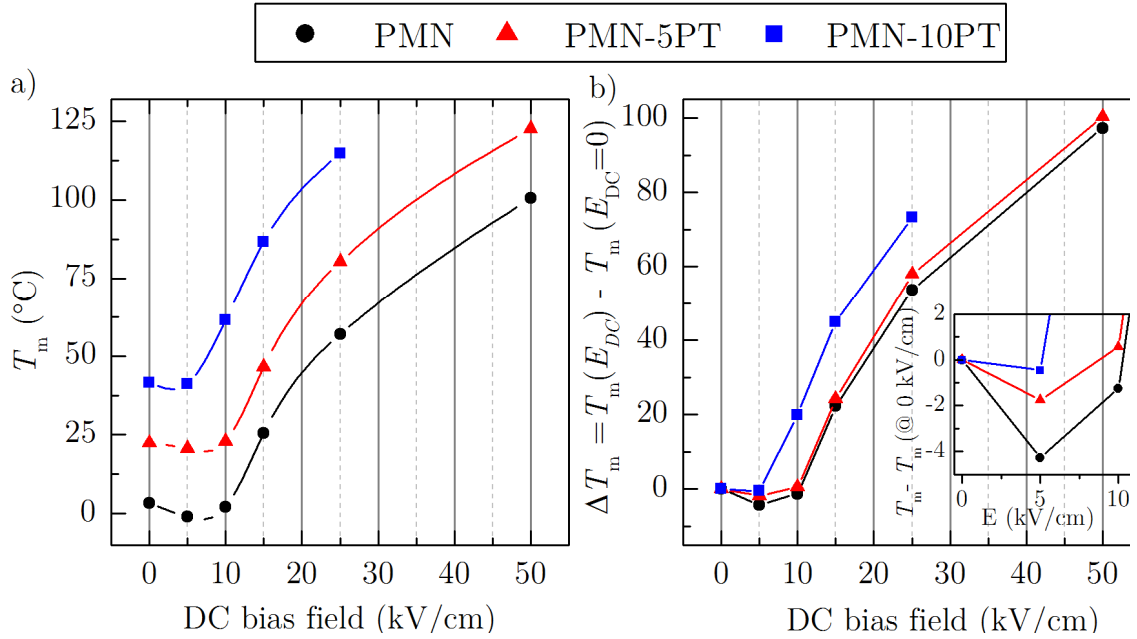


Figure 4.10: DC bias field dependence of (a) absolute values of T_m and (b) normalized values $\Delta T_m = T_m(E_{DC}) - T_m(E_{DC}=0)$ for PMN, PMN-5PT and PMN-10PT. The inset in (b) shows ΔT_m at low DC bias fields, up to 10 kV/cm. Note that the lines are a guide for the eyes. All the values are determined at a frequency of 10 kHz.

Viehland et al. [114] measured T_m versus DC bias field in PMN-10PT ceramics, showing that ΔT_m is indeed negative at low DC bias fields, with the minimum of T_m at 3 kV/cm. Moreover, they observed that at a frequency of 100 Hz the T_m down-shift is more pronounced than at higher frequencies. In fact, at 1 MHz, the T_m down-shift has not been observed. However, in our case, the ΔT_m at low DC bias fields is increasing with decreasing frequency.

4.1.5 Electrocaloric effect in bulk ceramics

Electrocaloric temperature changes (ΔT_{EC}) were measured at electric fields of 10 to 90 kV/cm and the results are collected in Figure 4.11 for PMN, PMN-5PT and PMN-10PT bulk ceramics. They were determined by a direct measuring method in a modified DSC (see Section 3.2.11.2) in the temperature range of 0 to 120 °C with a step of 10 K.

In PMN (Figure 4.11a) the ΔT_{EC} is increasing with the electric field at a constant temperature, while at a constant electric field the temperature-dependent ΔT_{EC} exhibits a broad peak. This peak can be observed at electric fields of 20 kV/cm and higher. Moreover, with increasing electric fields the peak is becoming more pronounced. In addition, the temperature of the peak maxima ($T_{\text{EC max}}$) is shifting to higher temperatures with an increasing electric field (note that the ΔT_{EC} peak for each electric field is fitted to the Gaussian function, in order to precisely determine the $T_{\text{EC max}}$). Thus, at 20 kV/cm the largest ΔT_{EC} is at 16 °C, while at 70 kV/cm the maximum ΔT_{EC} is at 61 °C. This ΔT_{EC} of 1.33 K is also the largest EC response obtained for our PMN. Nevertheless, due to the broadness of the peak, ΔT_{EC} at 25 °C is still comparably large, i.e., 1.16 K. These ΔT_{EC} results agree well with the values reported by Peräntie et al. [52]. They showed that PMN at 50 kV/cm has a ΔT_{EC} peak maximum at a temperature of 46 °C. However, their ΔT_{EC} values are lower, for example, the highest ΔT_{EC} is 0.77 K at 50 kV/cm, which is 28 % lower than in our case. The difference between the ΔT_{EC} values is smaller at electric fields of 10 or 20 kV/cm. In another study of PMN bulk ceramics by Rožič et al. [53], the maximum ΔT_{EC} of 1.4 K was determined under 52.5 kV/cm and at 47 °C. This confirms that the $T_{\text{EC max}}$ is very consistent among studies, which is not the case for the magnitude of ΔT_{EC} . A possible explanation for the differences in ΔT_{EC} magnitudes could be related to the different microstructures or phase compositions, which are not reported in these two EC studies of PMN bulk ceramics [52], [53].

The PMN-5PT (Figure 4.11b) also exhibits a broad peak of temperature-dependent ΔT_{EC} at electric fields of 20 kV/cm and higher. The maximum ΔT_{EC} of 2.2 K was measured at 91 °C and upon an electric field of 90 kV/cm. With decreasing temperature, the ΔT_{EC} is also decreasing, thus at 30 °C the ΔT_{EC} is about 25 % lower than the maximum value. The $T_{\text{EC max}}$ is shifting from 34 °C at 20 kV/cm to 89 °C at 90 kV/cm. In comparison, Peräntie et al. [52] measured the EC effect up to 50 kV/cm, where the maximum ΔT_{EC} is 1.04 K at about 65 °C. Again, our results coincide better with $T_{\text{EC max}}$ than with the maximum ΔT_{EC} values. The latter one in our case is about 25 % higher for the same electric field.

The PMN-10PT shows analogous EC behaviour with the PMN and PMN-5PT, just that with a higher PT content, the $T_{\text{EC max}}$ values are higher and also the ΔT_{EC} magnitudes are larger. At 20 kV/cm $T_{\text{EC max}}$ is at approximately 42 °C, while at 90 kV/cm the peak ΔT_{EC} is up-shifted to 93 °C, where the maximum ΔT_{EC} is 2.34 K. This value is higher than the ΔT_{EC} of 1.7 K obtained by Vrubelj et al. [51] at 87 kV/cm for ceramics of a similar average grain size. Moreover, the ΔT_{EC} results of Peräntie et al. [52] are also lower, i.e., at 50 kV/cm they obtained a maximum ΔT_{EC} of 1.2 K, which is 0.27 K lower than our result. Note that the ΔT_{EC} reaches the maximum value at the electric field of 10 kV/cm and at 10 °C. This anomaly is due to the release of latent heat [115], as a consequence of an induced relaxor-to-ferroelectric transition [52], [116], [117].

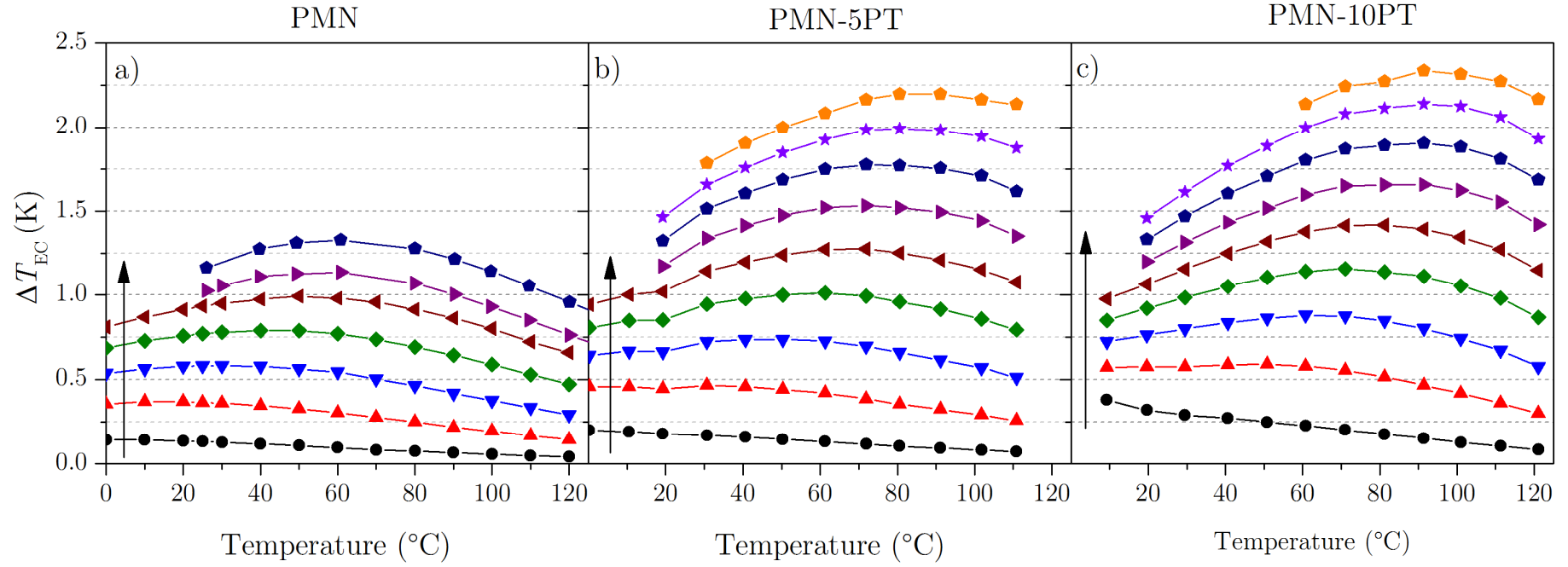


Figure 4.11: Electrocaloric temperature change (ΔT_{EC}) of (a) PMN, (b) PMN-5PT and (c) PMN-10PT bulk ceramics determined by a direct measuring method at electric fields of 10 to 70 kV/cm (a) and 90 kV/cm (b,c) with a 10 kV/cm interval. The direction of the increasing electric field is marked with arrows. Lines are a guide for the eyes.

4.1.6 Comparison of the electrocaloric properties between PMN and PMN-PT bulk ceramics

The comparison of ΔT_{EC} values determined for PMN, PMN-5PT and PMN-10PT is presented in Figure 4.12. The electric fields of 20, 50 and 80 kV/cm were selected to represent low, moderate and high electric fields, respectively. We note that at even lower electric field amplitudes the dielectric and electrocaloric properties of PMN-PT relaxor ceramics were investigated in [3], [52], [116], [117].

At a low electric field of 20 kV/cm all three materials exhibit similar trends; however, they differ in the $T_{EC\ max}$ values. These are increasing with increasing PT content, i.e., from 16 °C for PMN to 42 °C for PMN-10PT. Moreover, with a higher PT content the maximum ΔT_{EC} increases, and thus the PMN-10PT exhibits the largest ΔT_{EC} of 0.59 K, while for PMN it is 0.37 K. Similarly, at 30 °C, PMN-10PT has the largest ΔT_{EC} of 0.58 K.

The comparison at 50 kV/cm shows a distinct difference between the PMN and both PMN-PT samples. More precisely, the ΔT_{EC} maximum of PMN is 0.99 K, which is significantly lower than 1.28 and 1.42 K, for PMN-5PT and PMN-10PT, respectively. However, at 30 °C, this difference is smaller, as the ΔT_{EC} of the PMN is 0.95 K in contrast to 1.14 K for the PMN-5PT. Additionally, we can observe that at 30 °C, the ΔT_{EC} of PMN-5PT is practically the same as the ΔT_{EC} of PMN-10PT. The difference is just 0.01 K.

At a high electric field of 80 kV/cm, the ΔT_{EC} of PMN-5PT and PMN-10PT are still comparable at 30 °C. Although here the PMN-5PT has a higher ΔT_{EC} than the PMN-10PT, with a difference of 0.05 K. The ΔT_{EC} values of these two materials start to differ at temperatures higher than 50 °C. This is due to the 6 K difference in $T_{EC\ max}$, and thus at these higher temperatures PMN-10PT has larger ΔT_{EC} values than PMN-5PT. For instance, the maximum ΔT_{EC} of PMN-10PT is 0.16 K higher than the maximum ΔT_{EC} of PMN-5PT.

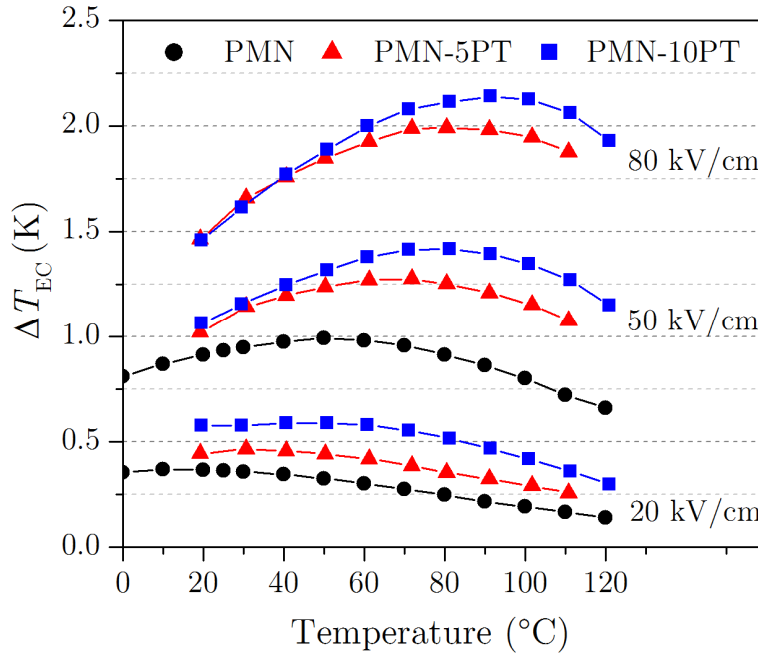


Figure 4.12: Electrocaloric temperature changes (ΔT_{EC}) in PMN, PMN-5PT and PMN-10PT bulk ceramics under electric fields of 20, 50 and 80 kV/cm.

Therefore, in terms of the maximum ΔT_{EC} values, PMN-10PT has the highest EC response of all three tested materials. However, at 30 °C the difference between PMN-5PT and PMN-10PT is almost negligible, and at 20 °C the ΔT_{EC} of PMN is almost the same as the values for PMN-PT. The difference in ΔT_{EC} between PMN and PMN-PT materials then noticeably increases with increasing temperature and increasing electric field.

The $T_{\text{EC max}}$ as a function of electric fields from 20 to 70 kV/cm or 90 kV/cm for PMN and PMN-PT materials, respectively, are collected in Figure 4.13. As already explained in the previous section, the $T_{\text{EC max}}$ values are determined via Gaussian fits of the ΔT_{EC} values. For all three samples, the behaviour can be described by a random asymptotic function, i.e., the values are saturating at higher electric fields. Peräntie et al. [52] described the dependence of $T_{\text{EC max}}$ on the electric field (> 30 kV/cm) as linear in the PMN-PT. However, in a theoretical study [118] of the EC effect in PMN-10PT, it was shown that with increasing electric fields up to 1 MV/cm, the shifting of $T_{\text{EC max}}$ is indeed saturating at higher electric fields, which is in agreement with our results. .

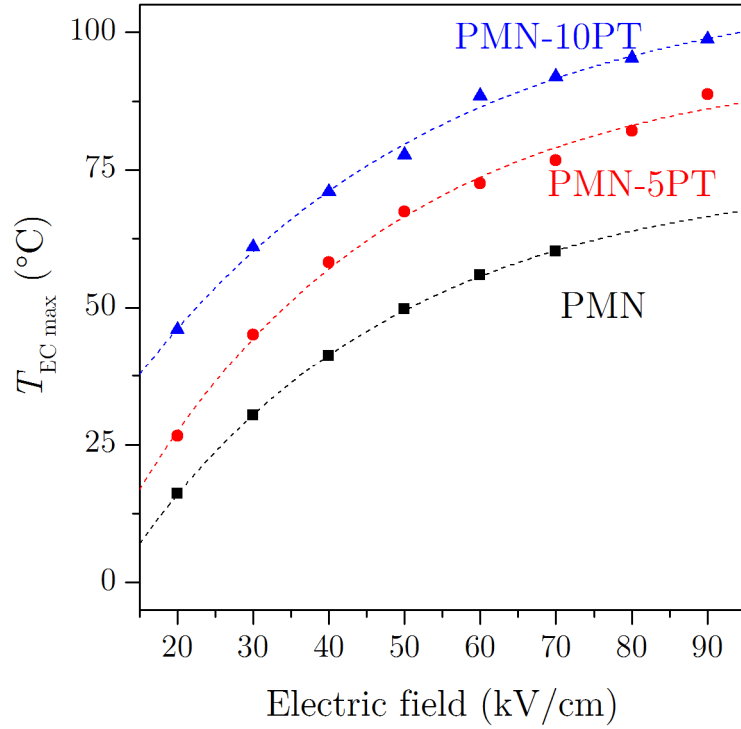


Figure 4.13: Temperature of the maximum ΔT_{EC} ($T_{\text{EC max}}$) versus electric field for PMN, PMN-5PT and PMN-10PT bulk ceramics. Dashed lines are fits with the random asymptotic function and are guides for the eyes.

The temperature-dependent ΔT_{EC} and ϵ' are compared at 50 kV/cm in Figure 4.14 for the PMN and PMN-5PT samples. As noted previously, the dielectric measurements at 50 kV/cm for PMN-10PT could not be performed due to the temperature limitation of the measuring set-up. In the case of PMN we see that the maximum of the temperature-dependent ΔT_{EC} peak, i.e., $T_{\text{EC max}}$ coincides with the temperature at which the slope of ϵ' is the steepest. This temperature is 49 °C, whereas T_m is 101 °C. In the case of PMN-5PT a $T_{\text{EC max}}$ of 67 °C is observed at the lower part of the ϵ' peak, where, again, the slope is the highest. Here, the T_m is at 123 °C, and thus the temperature difference of 56 K between $T_{\text{EC max}}$ and T_m is slightly larger than the temperature span of 52 K measured for PMN.

In the EC study of PMN-10PT [51], similar behaviour for the maximum ΔT_{EC} and ϵ' under a DC bias was observed at 25 kV/cm: $T_{\text{EC max}}$ coincides with the middle of the low-temperature slope of the ϵ' peak, where the slope is the steepest. These results for all three materials can be understood in terms of the E - T phase diagram of a relaxor system. As the EC effect is a maximum at or near the temperature of the ferroelectric phase transition [119], $T_{\text{EC max}}$ is a few 10 K below the broad dielectric maximum. The latter is a pure dynamic effect, while the ferroelectric state under DC bias field is induced at a significantly lower temperature [120].

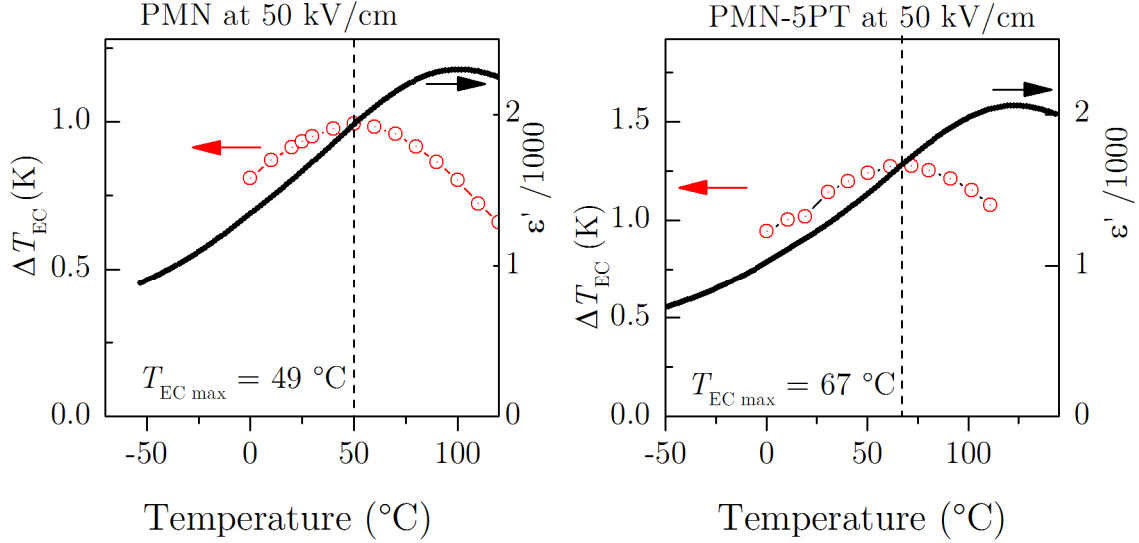


Figure 4.14: Comparison of ΔT_{EC} and ϵ' as a function of temperature at 50 kV/cm for PMN (on left) and PMN-5PT (on right). The vertical dashed lines mark the temperature of the maximum ΔT_{EC} ($T_{\text{EC max}}$).

In order to better present the relation between ΔT_{EC} and ϵ' , i.e., between $T_{\text{EC max}}$ and T_m , a two-dimensional contour graph of EC responsivity ($\Delta T_{\text{EC}}/\Delta E$) versus temperature and electric field is constructed and shown for PMN in Figure 4.15, and for PMN-5PT and PMN-10PT in Figure 4.16a and Figure 4.16b, respectively.* The EC responsivity is defined as ΔT_{EC} normalized to the electric field, and thus the data for EC responsivity were calculated from the measured ΔT_{EC} values. Furthermore, the electric-field-dependent T_m and $T_{\text{EC max}}$ values are added to these contour graphs.

In the contour graph of the PMN material (Figure 4.15), the area of the highest EC responsivity spans from 30 kV/cm and the temperatures between 20 and 40 °C, to 70 kV/cm and temperatures of 40 to 80 °C. Namely, the highest EC responsivity of 1.90×10^{-7} K m/V is progressively shifting to higher temperatures with an increasing electric field. The temperatures of the largest ΔT_{EC} values are following the middle of the highest EC responsivity area. In Figure 4.15 the largest ΔT_{EC} , i.e., $T_{\text{EC max}}$ values, are shown with blue symbols, and the T_m values measured under 5 to 50 kV/cm are presented with black symbols. After applying 10 kV/cm, which is approximately E_T , the T_m starts to abruptly increase with electric field, as discussed in Section 4.1.4. As can be observed in Figure 4.15 the T_m values follow the EC responsivity of approximately 1.50×10^{-7} K m/V,

*We note that the EC responsivity can be also shown in the frame of the E-T phase diagrams. The graphs with temperature and electric field as x- and y- axes, respectively, are collected in Appendix C.

which is $\sim 24\%$ lower than the maximum EC responsivity. This means that the T_m can be used to roughly estimate the upper boundary of the largest EC responsivity area. Furthermore, the T_m is saturating with an increasing electric field, as is the $T_{EC\ max}$. However, in case of $T_{EC\ max}$, the increase is more gradual than in case of T_m . The comparison of the T_m and $T_{EC\ max}$ at electric fields higher than 20 kV/cm, shows that the T_m is higher than $T_{EC\ max}$. Moreover, the temperature span between $T_{EC\ max}$ and T_m is increasing with the increasing electric field, i.e., from 27 K at 20 kV/cm to 52 K at 50 kV/cm. These results once again agree well with the E - T phase diagram of the relaxor system [120] – with increasing electric field the difference between the induced ferroelectric phase transition temperature and dielectric maximum is increasing.

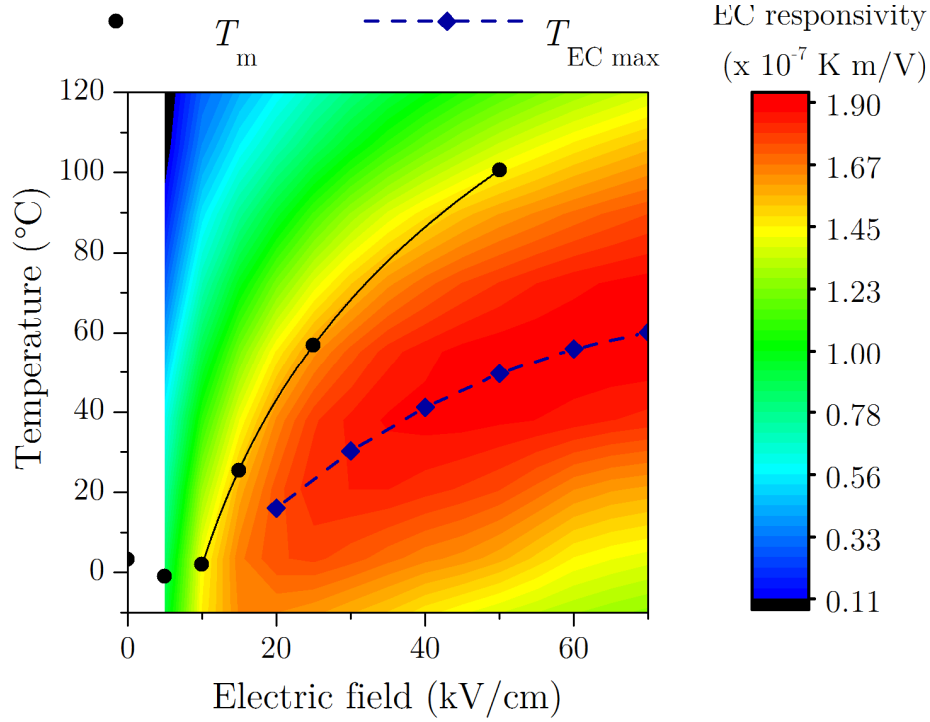


Figure 4.15: The EC responsivity as a function of temperature and electric field expressed for PMN. Black symbols denote T_m versus electric field, while blue symbols represent $T_{EC\ max}$ versus electric field. Lines are guides for the eyes.

Similar behaviour of the EC responsivity versus temperature and electric-field-dependent T_m and $T_{EC\ max}$ values is observed for the PMN-5PT sample, which is presented in Figure 4.16a. The $T_{EC\ max}$ values are in the middle of the area of the highest EC responsivity value, which gradually shifts to higher temperatures with increasing electric field. For the PMN-5PT material the area of the highest EC responsivity is bounded on the low-side at 30 kV/cm and between 37 °C and 66 °C, and on the upper-side at 70 kV/cm at the temperatures of 53 °C to 101 °C. Also, the T_m values are following the EC responsivity of 2.05×10^{-7} K m/V, which is 26 % lower than the maximum EC responsivity. The temperature span between $T_{EC\ max}$ and T_m is, like in PMN, increasing with an increasing electric field. However, in the case of PMN-5PT, this temperature span is slightly broader, i.e., at 20 kV/cm the span is 37 K, while at 50 kV/cm the span between $T_{EC\ max}$ and T_m is 56 K.

The EC responsivity as a function of temperature and electric field for PMN-10PT bulk ceramics is shown in Figure 4.16b. As in PMN and PMN-5PT, there exists an area of the

highest EC responsivity. The central part of that area is marked with $T_{\text{EC max}}$ values. However, in the case of PMN-10PT this area is broader, and thus at 30 kV/cm it is determined by temperatures of 33 to 86 °C. This temperature span of 53 K is almost two times that for PMN and PMN-5PT. The T_m at electric fields of 10 to 25 kV/cm are following the EC responsivity, which is approximately 27 % lower than the maximum EC responsivity of 2.90×10^{-7} K m/V .

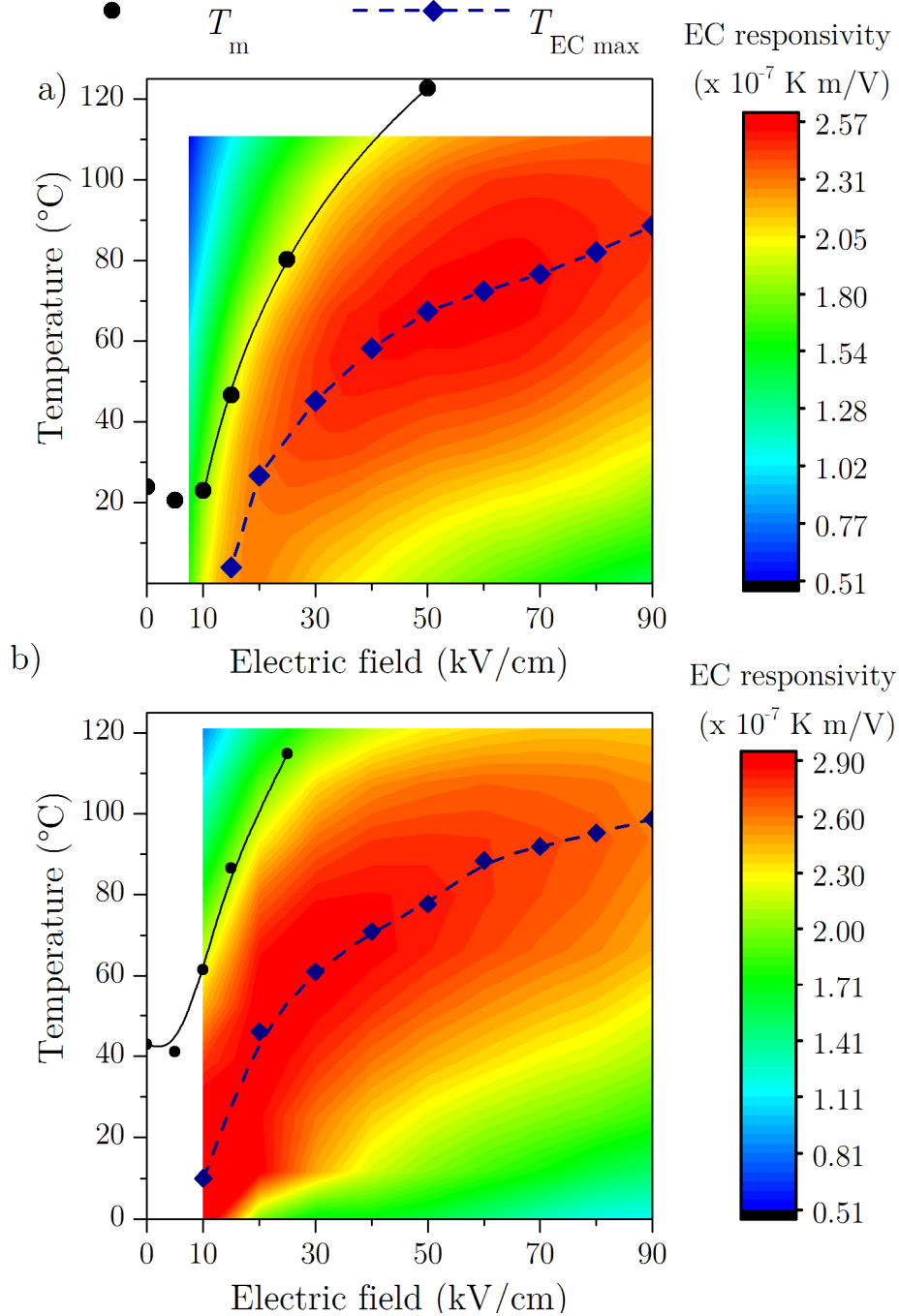


Figure 4.16: The EC responsivity as a function of temperature and electric field expressed for (a) PMN-5PT and (b) PMN-10PT. Black symbols denote T_m versus electric field, while blue symbols represent $T_{\text{EC max}}$ versus electric field. Lines are guides for the eyes.

4.2 PMN and PMN-10PT Multilayer Elements

In this section the fabrication of PMN and PMN-10PT multilayer (ML) elements is described and their phase composition and microstructure are analysed. Furthermore, the dielectric, ferroelectric and EC properties of the ML elements are measured and compared with their bulk ceramic counterparts. In addition, the stability of the EC effect upon electric field cycling is investigated for the ML elements.

4.2.1 Preparation of ML elements

PMN and PMN-10PT ML elements were prepared by tape-casting of the respective slurries, screen printing of the internal platinum electrodes, lamination, dicing and sintering. The details of the process are described in Appendix B. It was shown in the previous section that the electrocaloric (EC) properties of PMN-5PT and PMN-10PT bulk ceramics are nearly the same; therefore, we have selected only PMN-10PT for the processing of ML elements.

Note that we observed almost no differences between the PMN and PMN-10PT powders in the process of slurry preparation, which we relate to the similar particle size distributions of the powders, with the median values between 0.4 and 0.5 μm (Figure 4.2, Table 4.1).

In the following text we describe the preparation of the PMN-10PT slurry only. The formulation of the slurry was based on the reports by Ceylan et al.[121] and Setz et al.[122]. The solvent was a mixture of methyl ethyl ketone and ethanol with a nearly azeotropic ratio. The dispersant, plasticizer and binder were oleic acid, polyethylene glycol and polyvinyl butyral, respectively. The solid load was about 65 wt.%, and the amounts of all the additives are given in Table 3.3. After sequentially adding the organic additives over a period of 24.5 hours the viscosity of the slurry was measured. In the process of optimisation of the slurry formulation the fraction of the dispersant oleic acid was varied between 0 and 0.48 wt.%. In Figure 4.17a the dependence of the viscosity in the shear rate range from 113 1/s to 500 1/s on the oleic acid fraction shows that the viscosity of the slurry significantly decreases with the addition of 0.16 and 0.32 wt%, below 0.6 $\text{Pa} \cdot \text{s}$, while the values with or without 0.48 wt. % were much higher. Therefore, 0.16 wt% of dispersant was selected for further work. The value of the viscosity at the shear rate of 113 1/s, 0.56 $\text{Pa} \cdot \text{s}$, is within the suitable range for tape casting, in agreement with the reported values [121]. The viscosity of the PMN-10PT slurry as a function of the shear rate in the range from 0 to 500 1/s is shown in Figure 4.17b. The viscosity decreases with increasing shear rate, exhibiting a typical shear thinning behaviour, suitable for tape casting [123].

The formulations of the PMN and PMN-10PT slurries slightly differed in the amounts of binder and plasticizer, see Table 3.3. Namely, the PMN slurry contained fewer organic additives to reduce the problem of twisting and bloating of the ML during the burn-out step. Furthermore, the gap of the doctor blade was set at different heights for PMN and PMN-10PT, which resulted in different thicknesses of the respective tapes after drying, i.e., $\sim 60 \mu\text{m}$ and $\sim 100 \mu\text{m}$.

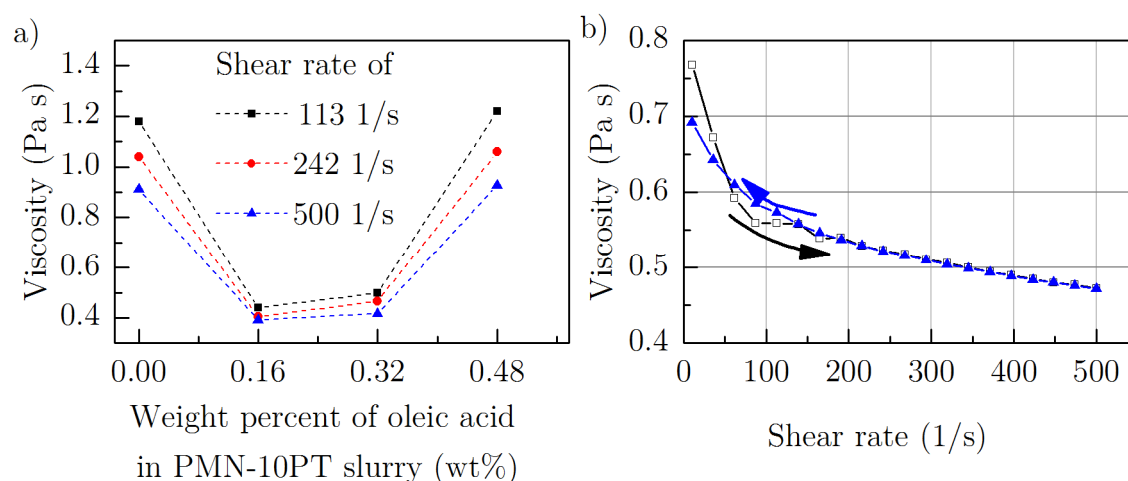


Figure 4.17: (a) Dependence of viscosity on the weight percent of the dispersant oleic acid in a PMN-10PT slurry, presented for shear rates of 113, 242 and 500 1/s. (b) Viscosity as a function of the shear rate for the PMN-10PT slurry. Black hollow and solid symbols, respectively, denote the values obtained for increasing and decreasing shear rates.

In order to determine the temperature profiles of the organic-phase burnout, the thermal decomposition of the green tapes was studied. The results of the thermogravimetric and differential thermal analyses of the PMN-10PT tape are presented in Figure 4.18. The mass loss of 1.2 % from RT to ~ 175 °C is accompanied by a broad endothermic effect and is attributed to the evaporation of residual solvents and possibly the adsorbed humidity. The major mass loss of 15.6 % occurs between ~ 175 and ~ 430 °C, and is accompanied by strong exothermic peaks at 232 °C, 317 °C and 420 °C. This mass loss is due to the thermal decomposition of the organic additives in the air. Since no mass loss was observed upon further heating to 700 °C, the temperature of 450 °C was selected for the organic-phase burn-out step.

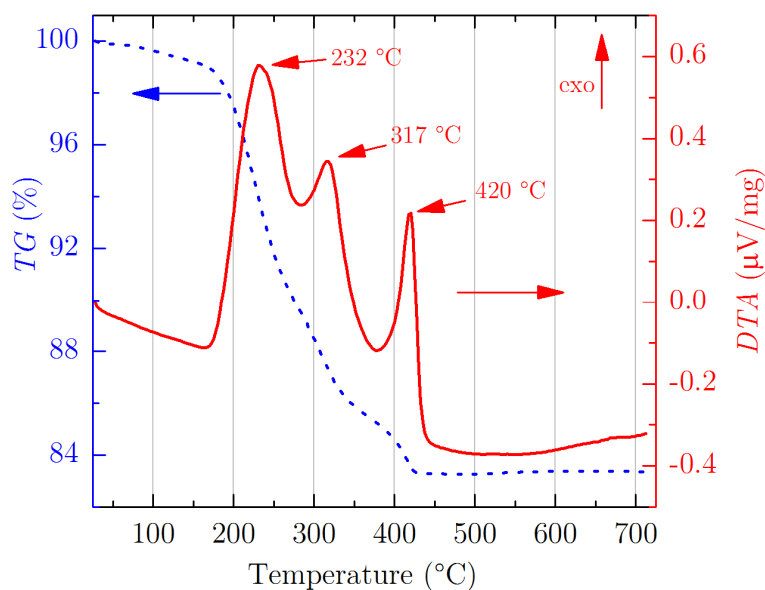


Figure 4.18: Thermogravimetry (TG) and differential thermal analysis (DTA) of the PMN-10PT green tape in the temperature range of 25 to 700 °C.

4.2.2 Microstructure and phase composition

The PMN and PMN-10PT ML elements consisted of five layers of ceramic tape with screen-printed platinum electrodes. After lamination the green sheets were diced into specimens with lateral dimensions of $5\text{ mm} \times 5\text{ mm}$. The annealing process consisted of two steps: in the first one the organic additives were burnt-out at $450\text{ }^{\circ}\text{C}$, according to the TG/DTA analysis, see Figure 4.18. The sintering took place at $1000\text{ }^{\circ}\text{C}$ for 2 h in the case of PMN and at $988\text{ }^{\circ}\text{C}$ for 8 h in the case of PMN-10PT. Further details related to processing can be found in Section 3.1.3.3.

The lateral dimensions of the sintered ML elements were approximately $4.6\text{ mm} \times 4.6\text{ mm}$, see Figure 4.19a. The thicknesses of the PMN and PMN-10PT elements were 0.18 mm and 0.32 mm , respectively. A photograph of a PMN-10PT ML element is shown in Figure 4.19b. The thicknesses of the individual ceramic layers were, respectively, approximately $32\text{ }\mu\text{m}$ and $60\text{ }\mu\text{m}$, while the thickness of the internal electrodes was about $5\text{ }\mu\text{m}$, as evident from the low-magnification cross-section FE-SEM micrographs (Figure 4.19c and Figure 4.19d).

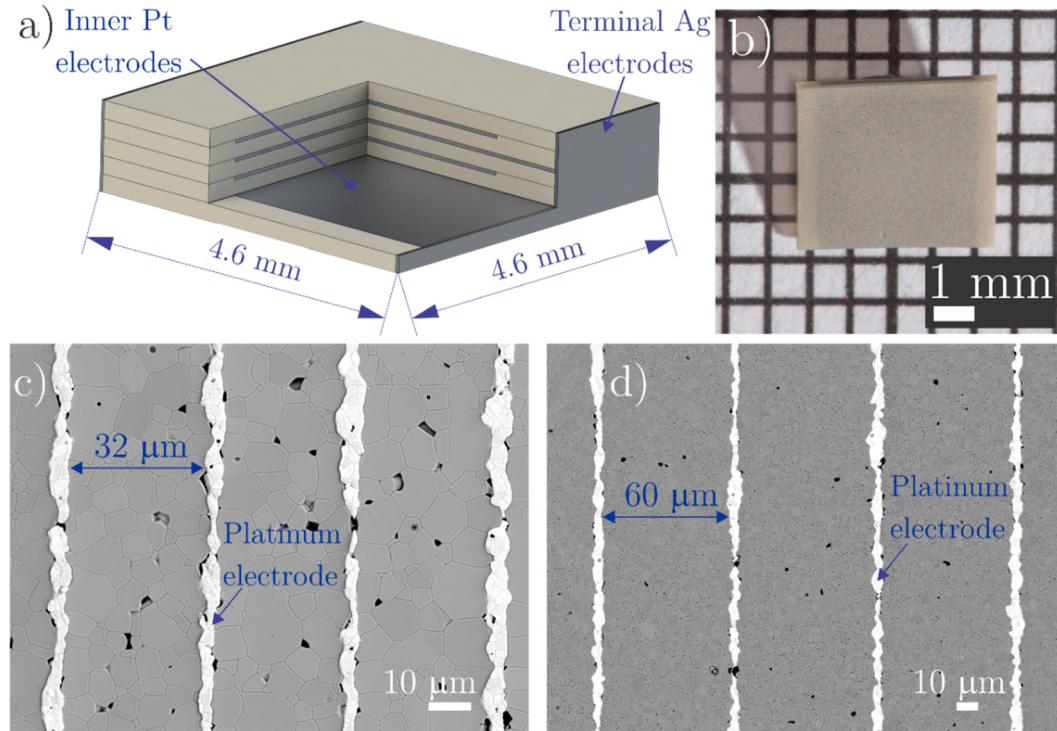


Figure 4.19: (a) Scheme of a ML layer with lateral dimensions. (b) Photo of a sintered ML element (PMN-10PT). The FE-SEM micrographs showing the cross-sections of (c) PMN and (d) PMN-10PT ML elements, with the layer thickness.

Both samples were analysed by XRD. As is evident from the respective patterns collected in Figure 4.20, a weak reflection at $\sim 29.1^{\circ}$ was discerned beside the major perovskite reflections. This peak could correspond to a pyrochlore phase, but also to lead oxide (ICDD 001-0797 or ICDD 01-0824). The presence of lead oxide could be a consequence of the condensation of the lead-oxide vapour upon sintering in a lead-oxide enriched atmosphere in the presence of the PbZrO_3 packing powder.

The FE-SEM micrograph of the outer surface of the PMN ML revealed some minute impurities at the grain boundaries or grain junctions (inset to Figure 4.21a), which could tentatively explain the weak reflection at $\sim 29.1^\circ$ in the XRD patterns. Their size was too small to allow a confident elemental analysis in the SEM. In the polished cross-section microstructure no secondary phases could be seen (see Figure 4.21b), which is in agreement with the XRD analysis.

Furthermore, the chemical composition was probed with WDXS and the results of nine randomly selected points are collected in Figure 4.22. The atomic % of Pb, Mg and Nb elements are close to the atomic % of the nominal composition for each of the measured. The results together with the low standard deviations suggest a high level of homogeneity (Table 4.8). The A:B ratio of 0.99 ± 0.01 could indicate a slight lead deficiency. Note that such a ratio is slightly smaller than the one determined for the bulk PMN, i.e., 1.05 ± 0.01 (compare Figure 4.4 and Table 4.4). No relation between the atomic % of elements and the layer position was observed, meaning that the perovskite stoichiometry was preserved within the whole element.

The micrograph of the thermally etched cross-section of a PMN ML element reveals a homogenous and dense microstructure with a GS of $5.13 \pm 2.3 \mu\text{m}$ (see Figure 4.21c). A relative density of about 99 % was determined with a stereological analysis.

Similar to the case of PMN, the micrograph of the outer surface of the PMN-10PT ML element exhibits trace impurities (Figure 4.23a). The micrograph of the polished cross-section in Figure 4.23b confirms that no secondary phases can be observed, which is consistent with the XRD analysis.

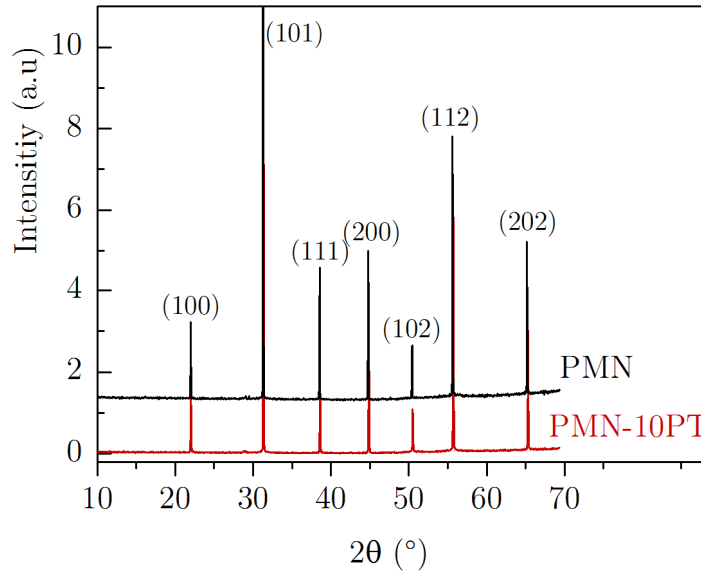


Figure 4.20: XRD patterns of the PMN and PMN-10PT sintered ML elements. The Miller indices were assigned to the diffraction peaks, which correspond to the perovskite phase (ICDD 88-1867).

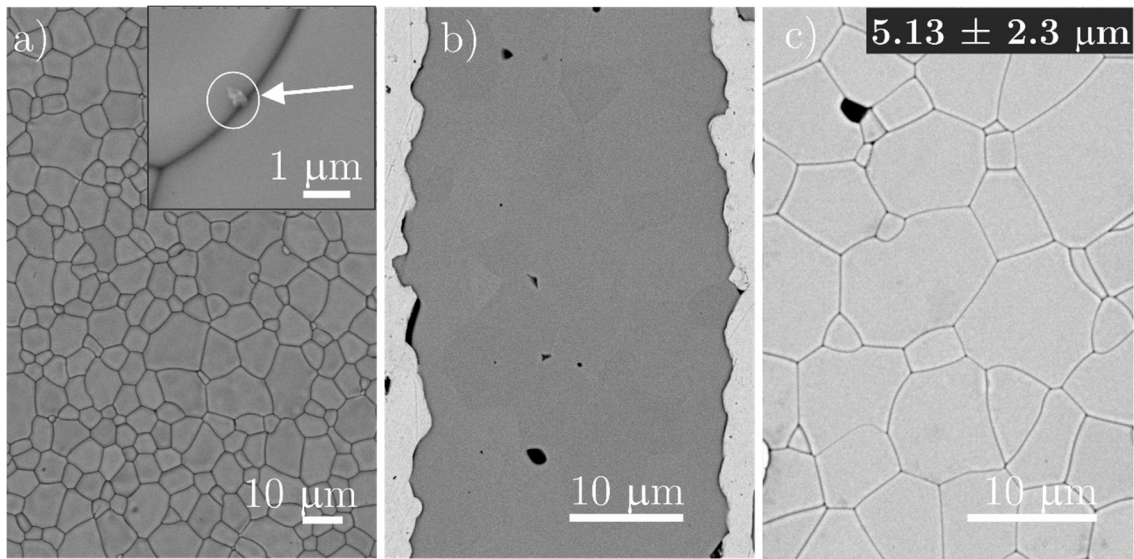


Figure 4.21: In (a) FE-SEM micrographs of the outer surface of the PMN ML element is presented, while the high-magnification inset reveals trace impurities at the grain-boundaries. Micrographs of the (b) polished and (c) thermally etched cross-section of the PMN ML element are shown. The average grain size is included in the right upper corner of the micrograph (c).

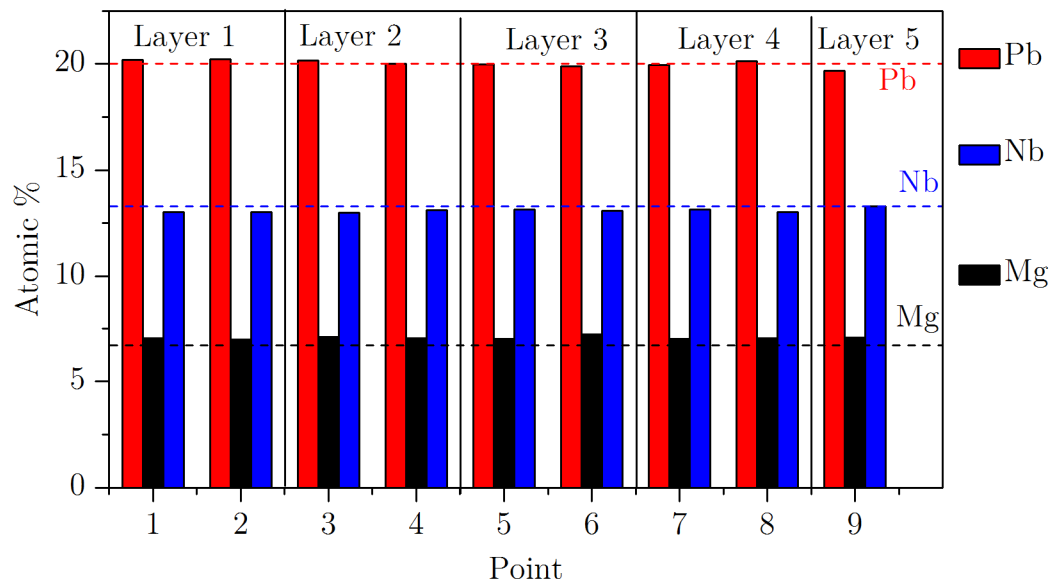


Figure 4.22: WDXS analyses of the PMN ML element, where for each layer two points were analysed, with the exception of layer 5, where only one data point could be reliably measured. The results are expressed as atomic %. The dashed horizontal lines mark the nominal concentrations of Pb, Mg and Nb.

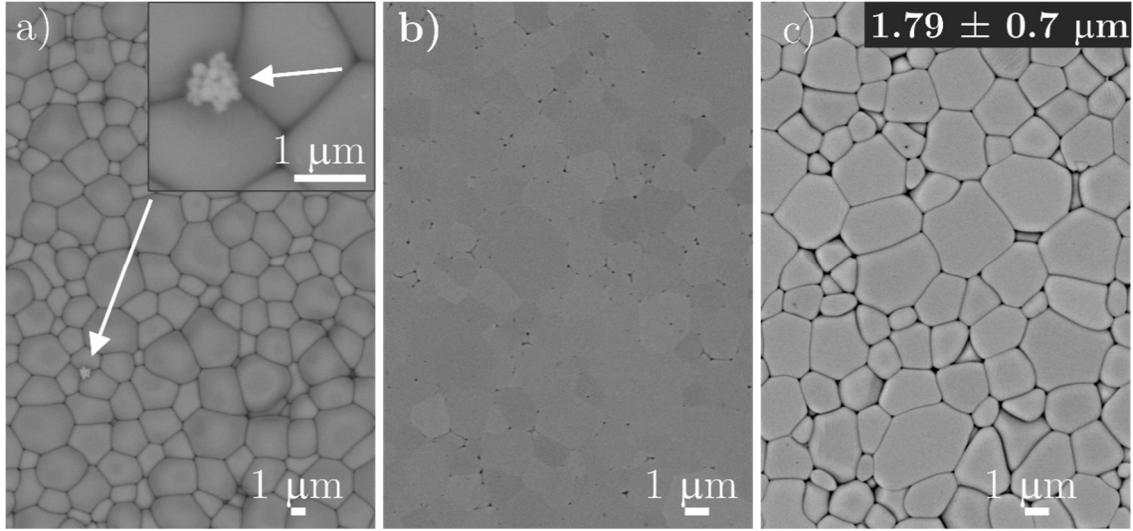


Figure 4.23: (a) PMN-10PT FE-SEM micrograph of the ML's outer surface, with high-magnification view of the impurity at the grain boundaries in the inset. Micrographs of the (b) polished and (c) thermally etched cross-section are shown. The average grain size is included in the right upper corner of the micrograph (c).

The results of the WDXS analyses of the PMN-10PT are shown in Figure 4.24. The ten randomly selected points exhibit values very close to the nominal composition of PMN-10PT. Here again, low standard deviations (Table 4.8) imply a high level of homogeneity, like in PMN ML. However, we observe that the atomic % of Pb slightly increases from layer 1 to layer 5, while the other elements do not show any correlation with the layer position. Consequently, the A:B ratio exhibits an increasing trend from 0.96 to 0.99 from layer 1 to layer 5, respectively. The average A:B ratio of 0.98 ± 0.01 is only slightly lower than the one in the bulk sample (0.99 ± 0.01), if we compare with Figure 4.5 and Table 4.5. In Figure 4.23c the thermally etched cross-section reveals a homogenous and highly dense microstructure with a GS of $1.71 \pm 0.7 \mu\text{m}$. The average A:B ratio is slightly below 1 in the PMN and PMN-10PT ML elements

Table 4.8: Results of the WDXS analyses for the PMN and PMN-10PT ML elements expressed as the average of the measurements performed on all five layers.

Element	PMN ML			PMN-10PT ML		
	Nom. comp. (atomic %)	WDXS (atomic %)	STDEV	Nom. comp. (atomic %)	WDXS (atomic %)	STDEV
Pb	20.0	20.02	0.17	20.0	19.75	0.13
Mg	6.7	7.06	0.07	6.0	6.29	0.16
Nb	13.3	13.10	0.09	12.0	12.02	0.13
Ti	/	/	/	2.0	1.95	0.05
O	60.0	59.97	0.07	60.0	59.97	0.06

The average A:B ratio is slightly below 1 in the PMN and PMN-10PT ML elements, respectively, 0.99 ± 0.01 and 0.98 ± 0.01 , and lower than in their bulk counterparts, which could also be related to the different sintering conditions. Namely, the packing powder used for the MLs was PbZrO_3 powder placed close to the samples (see Figure 3.3), while the bulk samples were immersed into the packing powder with the same composition as the pellets. Note that the choice of the packing powder for the MLs was based on the report of Lejeune and Boilot [124], as there are no data on PbO vapour pressures above the PMN-PT system. In addition, the surface-to-volume ratio is much higher in a ML than in bulk pellets, which could also be the reason for the lower A:B ratio in the ML than in the bulk samples.

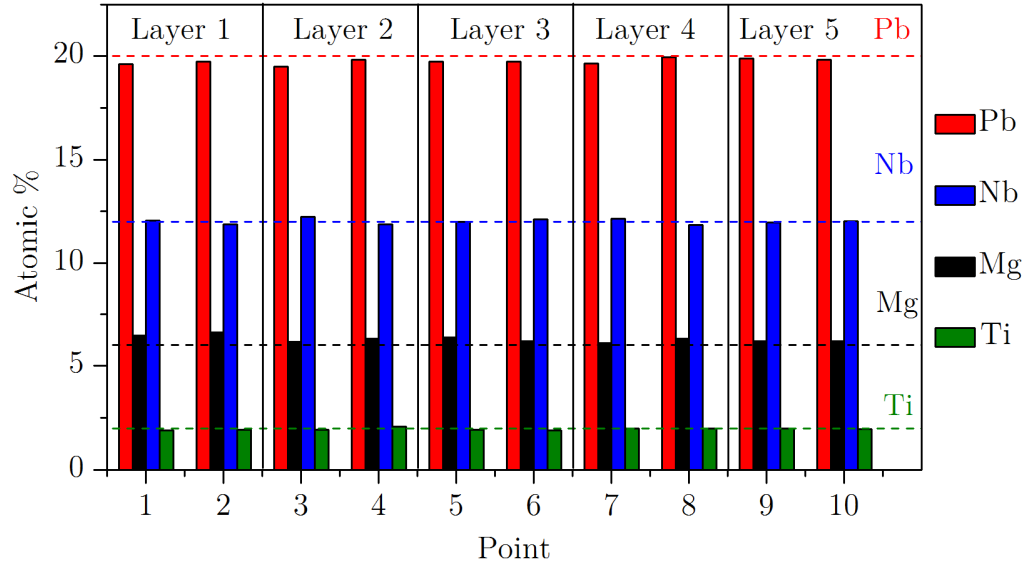


Figure 4.24: WDXS of PMN-10PT ML element, where for each layer two points were probed. The results are expressed as atomic %. The dashed horizontal lines mark the nominal concentrations of Pb, Mg, Nb and Ti.

4.2.3 Dielectric and ferroelectric properties

Temperature-dependent dielectric response for the PMN and PMN-10PT ML elements is presented in Figure 4.25 and Figure 4.26, respectively, as ϵ' , ϵ'' , and $\tan \delta$ in the frequency range 100 Hz to 50 kHz. The dielectric properties of the ML elements are compared to their bulk counterparts. Note, that later on the values of the dielectric properties are compared at a frequency of 10 kHz.

The ϵ' of the PMN ML exhibits a broad peak with an $\epsilon'_{\max}$ value of 20 960 at -3.4°C , see Figure 4.25a. The frequency dispersion of the ϵ' peak, which confirms the relaxor behaviour of the ML sample, is presented in the right inset of Figure 4.25a. The frequency dispersion is also observed in the ϵ'' peak, with its 10-kHz maximum value of 2 740 (Figure 4.25b). The $\tan \delta$ maximum at -21°C is 0.16, while at higher temperatures the dielectric losses are decreasing, reaching a value of 0.005 at 25°C .

The comparison of the dielectric properties of the ML and the bulk PMN sample reveals similar $\epsilon'_{\max}$ values and a down-shift of T_m by 6.6 K in the case of the ML (see the left inset in Figure 4.25a). This down-shifting of T_m could be related to the differences in the lead stoichiometry between the bulk and the ML samples [38]. As discussed in the previous section, the PMN ML elements are slightly lead deficient, i.e., the A:B molar ratio is 0.99 ± 0.01 (Table 4.4), while this ratio in the bulk is 1.05 ± 0.01 (Table 4.8).

We note that we only found one paper reporting PMN MLs. Lejeune and Boilot [124] in 1986 studied the relationship between the processing conditions and the dielectric properties of PMN ML elements. These optimum dielectric properties were obtained by sintering at 1000°C in the presence of a PbZrO_3 atmosphere powder, very much in agreement with our processing conditions. They reported a much lower $\epsilon'_{\max}$ value of 10 800 than our result (20 960), which could be tentatively related to the presence of a pyrochlore phase in their samples.

The PMN-10PT ML sample exhibits broad dispersive dielectric peaks, see Figure 4.26. The $\epsilon'_{\max}$ value of 22 000 is at 48°C , which is in good agreement with earlier dielectric spectroscopy studies of PMN-10PT [88], [90], [107] and PMN-8PT [23], [89] MLs. For example, an $\epsilon'_{\max}$ of 23 000 was measured at 47°C in PMN-10PT [90], which is similar to our result.

However, if we compare the temperature-dependent dielectric peaks of ML and bulk PMN-10PT, we observe that the $\epsilon'_{\max}$ value of ML is lower by 5.4 % than the value of the bulk and the T_m of the ML is 6.5 K higher than in the bulk. Similar deviations are observed in the ϵ'' and $\tan \delta$ peaks. The upshift of T_m in the PMN-10PT ML element could tentatively be related to a stress-induced ferroelectric phase [125], [126]. In addition, a slight kink in ϵ' appears at 2°C , the origin of which is discussed in detail in the following Section 4.2.3.1.

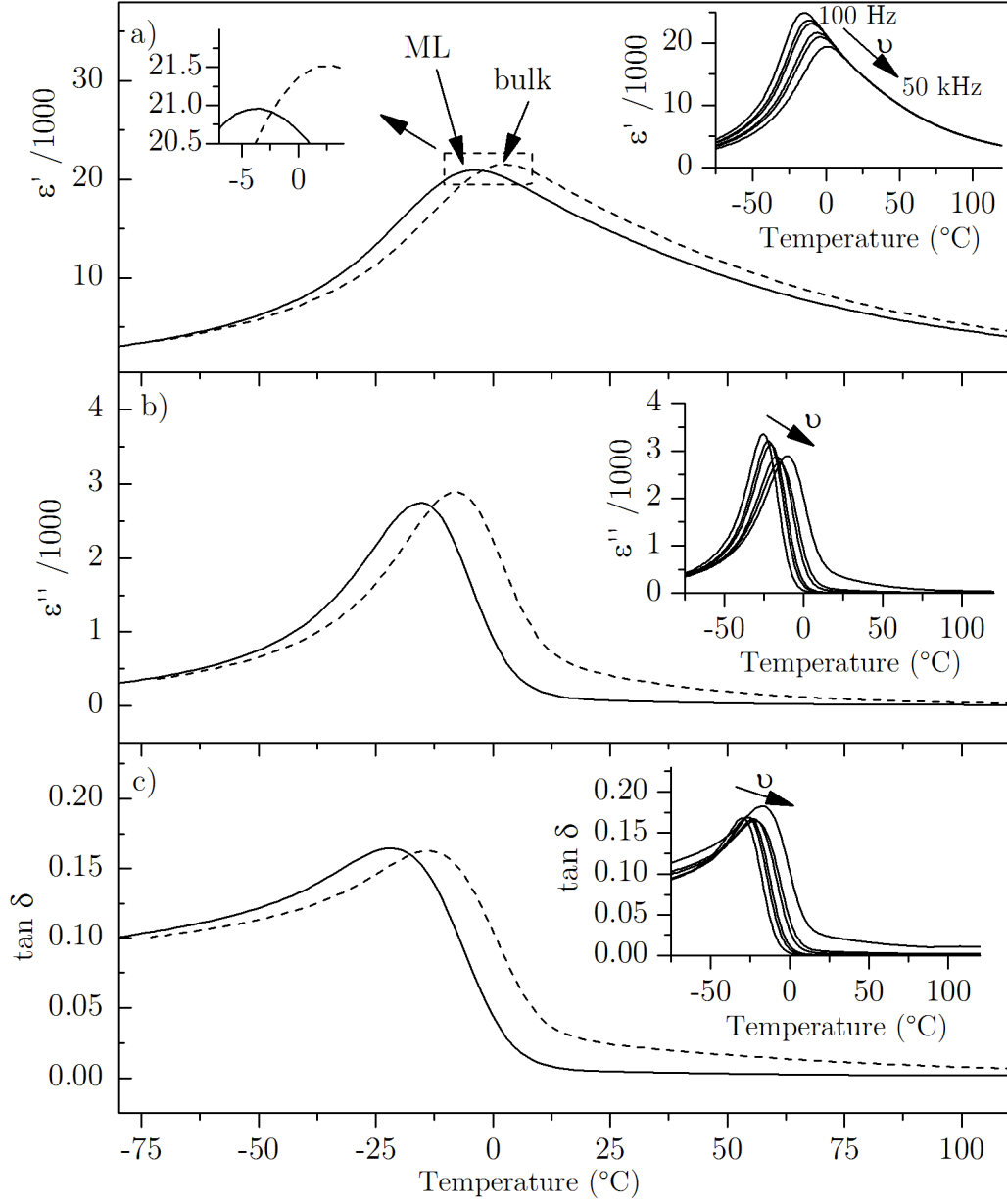


Figure 4.25: Temperature-dependent dielectric response of PMN ML element (solid line) and bulk ceramics (dashed line) measured at a frequency of 10 kHz. a, b and c present its real part ϵ' , imaginary part ϵ'' and the losses $\tan \delta$, respectively. The insets present the frequency dispersion of ϵ' , ϵ'' and $\tan \delta$, respectively, of a ML element in the frequency range 100 Hz to 50 kHz.

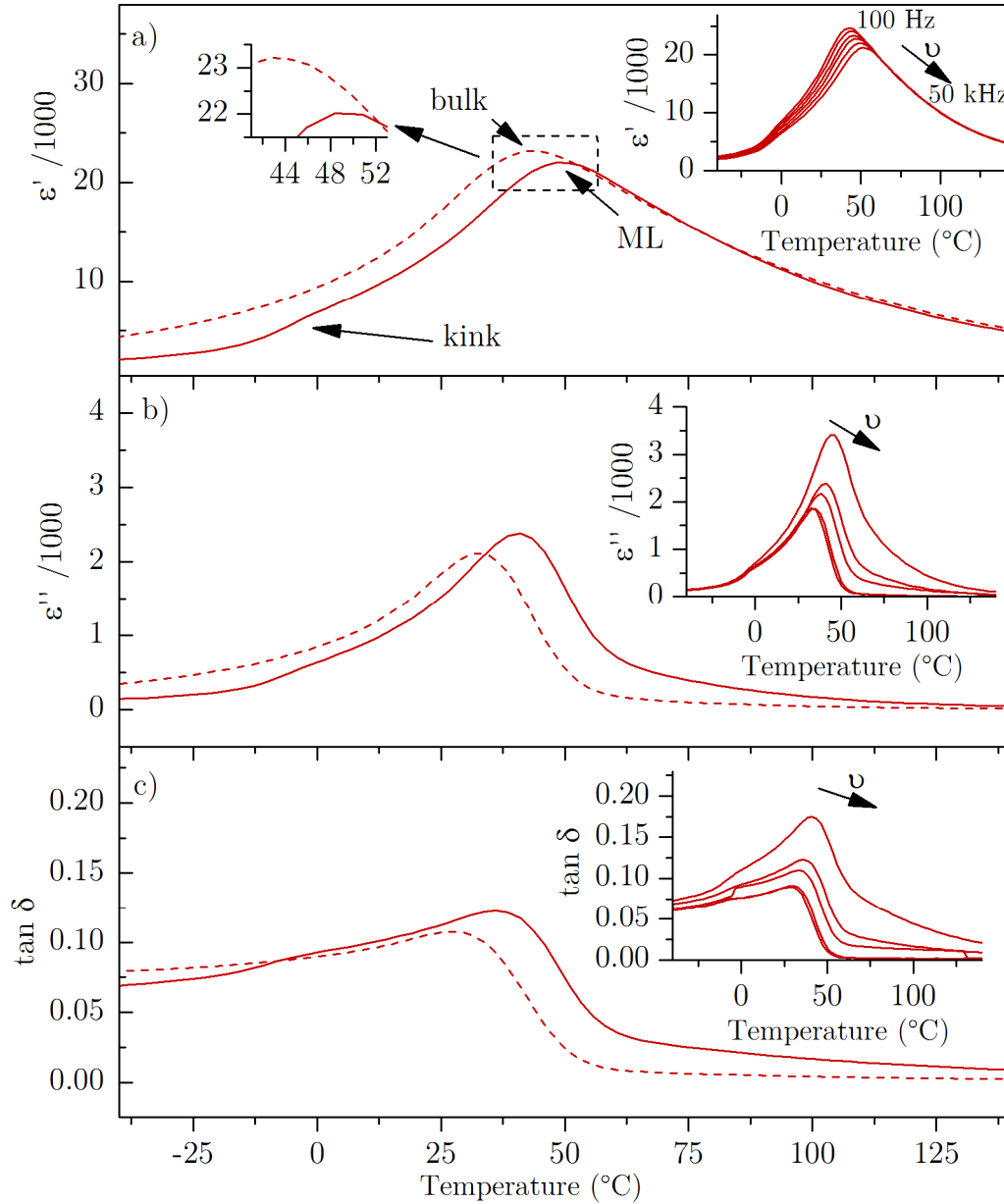


Figure 4.26: Temperature-dependent dielectric response of PMN-10PT ML element (solid line) and bulk ceramic (dashed line) measured at a frequency of 10 kHz. a, b and c present its real part ϵ' , imaginary part ϵ'' and the losses $\tan \delta$, respectively. The insets present the frequency dispersion of ϵ' , ϵ'' and $\tan \delta$, respectively, of a ML element in the frequency range 100 Hz to 50 kHz.

The P - E hysteresis loops of the PMN and PMN-10PT ML elements measured at RT and at 90 kV/cm are presented in Figure 4.27. The PMN exhibits a slim loop and a P_s of 29 $\mu\text{C}/\text{cm}^2$. The comparison of the ML and the bulk reveals similarly slim loops, with a slightly lower P_s value for the ML. The P - E loop of PMN-10PT is also slim and exhibits a P_s value of 35 $\mu\text{C}/\text{cm}^2$, which is similar to the value of 33 $\mu\text{C}/\text{cm}^2$ reported for PMN-10PT ML by Usui et al.[90]. The P - E loop of the ML element is similar to that of bulk ceramics, but the P_s of ML is slightly higher, the opposite to the PMN. It should be stressed that from the perspective of EC cooling a slim P - E loop implies lower hysteretic losses, i.e., a higher energy efficiency [13].

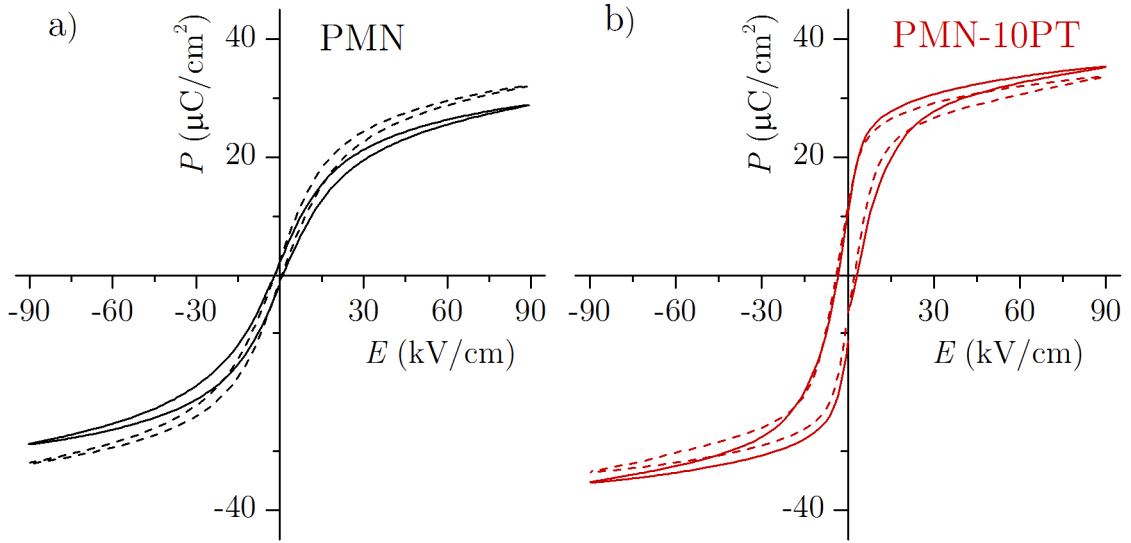


Figure 4.27: P - E hysteresis loops of (a) PMN and (b) PMN-10PT ML elements (solid line) and bulk ceramics (dashed line) measured in electric fields of 90 kV/cm at RT with a frequency of 1 Hz.

4.2.3.1 Stress-induced ferroelectric phase in PMN-10PT ML elements

The observed kink at 2 °C in the ϵ' versus temperature dependence of PMN-10PT (see Figure 4.26) could be explained by the stress-induced transition from the relaxor to the ferroelectric phase. Namely, the first derivative of ϵ' versus temperature results in a peak, the temperature of which is frequency independent, being characteristic for ferroelectrics, see Figure 4.28. In a study of relaxor $\text{Pb}_{0.865}\text{La}_{0.09}(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$ the ferroelectric phase was induced by a DC bias [120], exhibiting such a frequency-independent peak. Schader et al.[127] showed that a compressive stress induces a relaxor-to-ferroelectric transition in $0.4(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3\text{-}0.6\text{BaTiO}_3$ (NBT-BT) in a similar way to an electric field. The phase-transition temperature, often referred to as the depolarization temperature, was slightly different if the samples were electrically or mechanically stressed. Interestingly, the electrically poled NBT-BT sample exhibited a non-zero piezoelectric coefficient above the depolarization temperature. The authors explained this effect by explaining that some remanent macroscopic polarization persists to higher temperatures, until the frequency dispersion in the permittivity versus temperature could be observed.

The piezoelectric d_{33} coefficient of our PMN-10PT ML at RT is indeed non-zero, i.e., d_{33} equals 8 pm/V. Thus, the piezoelectric activity was confirmed above the stress-induced depolarization temperature (2 °C), similar to the case of NBT-BT. In the electrocaloric study of PMN-10PT bulk ceramics Peräntie et al. [52] observed that the (electric-field induced) depolarization temperature was at about 0 °C, which is in good agreement with our value. We should point out that our ML sample was not electrically poled before the piezoelectric measurement. So, the macroscopic piezoelectric response could be explained by the self-poling effect. Such self-poling has been previously reported in ferroelectric thin films [128]–[131], thick BiFeO_3 films [132] and piezoelectric ML actuators [133].

The residual stress that develops in our ML elements is a consequence of the different thermal expansion coefficients of the ceramic layers and the platinum electrodes [134]. Namely, upon cooling from the sintering temperature, the shrinkage of the platinum

electrodes is significantly higher than the shrinkage of the PMN-10PT, see Table 4.9. Therefore, after sintering the ceramic layers are under a residual compressive stress, while the platinum electrodes are under a residual tensile stress. In Figure 4.29 a simplified scheme of the shrinkage of the ML element is presented.

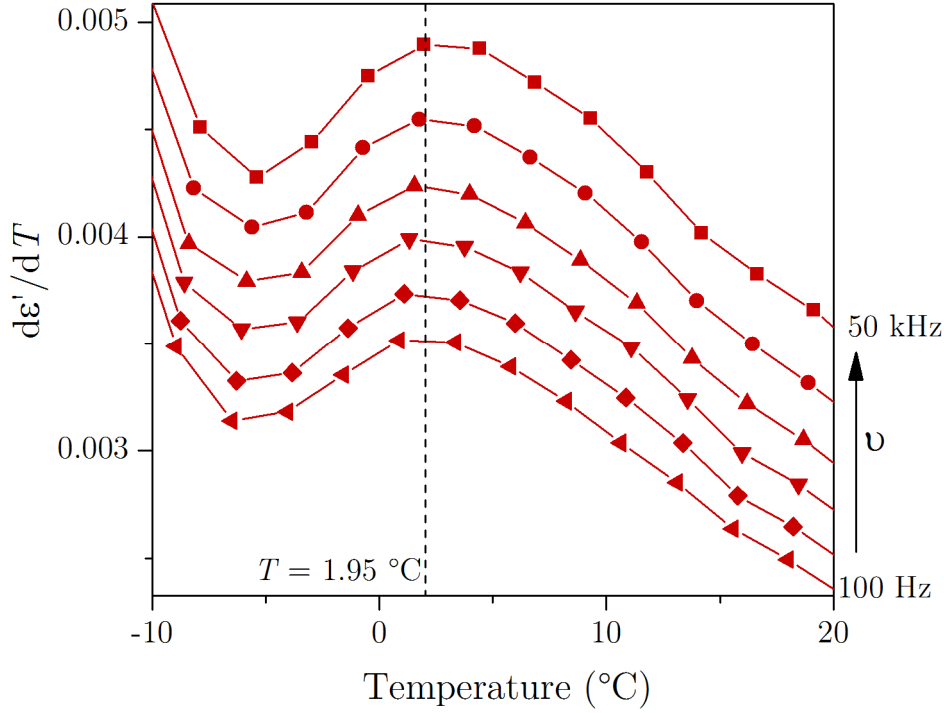


Figure 4.28: First derivative of ε' as a function of temperature for the PMN-10PT ML element in the frequency range from 100 Hz to 50 kHz. The temperature of the peak is frequency independent, in contrast to its magnitude, being characteristic for ferroelectrics [120].

Table 4.9: Material properties used for estimating the residual stresses in ML elements.

	PMN-10PT	Platinum
Elastic modulus (GPa)	75	170
Thermal expansion coefficient (1/K)	$6.3 \cdot 10^{-6}$ [134]	$8.8 \cdot 10^{-6}$ [135]
Poisson ratio	0.3	0.38
Thickness	60	5

In order to estimate the magnitude of the compressive stress in the ceramic layers, first the tensile stress in the electrodes (σ_{Pt}) is calculated using the following equation

$$\sigma_{Pt} = E_{Pt} \Delta x. \quad (4.1)$$

Here, E_{Pt} is the elastic modulus of the platinum and Δx is the difference between the thermal expansions of the platinum electrode and the ceramic layer. The Δx is defined as

$$\Delta x = \Delta T (\alpha_{Pt} - \alpha_{cer}), \quad (4.2)$$

where ΔT is temperature difference between the sintering temperature (988 °C) and 25 °C, while α_{Pt} and α_{cer} are the thermal expansion coefficients of the platinum and the PMN-10PT ceramics, respectively. The equation of the residual compressive stress in the

ceramic layer (σ_{cer}) is obtained from Equations (4.1), (4.2) and under the assumption that the force equilibrium in the multilayer is equal to 0

$$\sigma_{cer} = \frac{d_{Pt}}{d_{cer}} E_{Pt} \Delta T (\alpha_{Pt} - \alpha_{cer}). \quad (4.3)$$

The d_{Pt} and d_{cer} are the thicknesses of the platinum electrode and the ceramic layer, respectively. Using the values from Table 4.9, the compressive stress of PMN-10PT and the tensile stress of Pt are -34 MPa and 409 MPa, respectively.

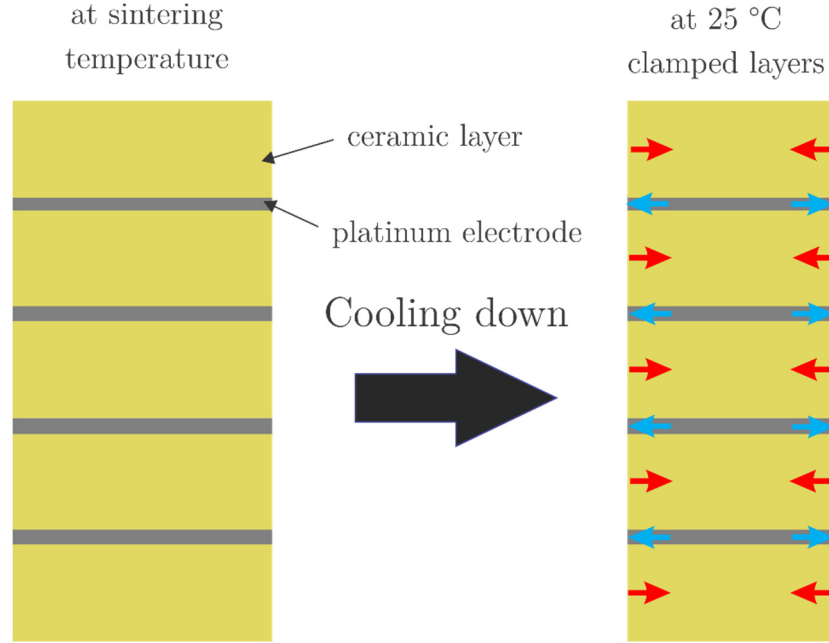


Figure 4.29: A simplified scheme of the thermal shrinkage of a ML element upon cooling from the sintering temperature. The residual compressive and tensile stresses are marked with red and blue arrows, respectively.

In addition, the stresses in the PMN-10PT ML element were calculated using the finite-element method with COMSOL software and the coefficients from Table 4.9. The 2D geometry and the calculated stresses are shown in Figure 4.30. Note that here only the values in the active part of the ML (marked with the dashed lines in Figure 4.30) are discussed, as they are crucial for the functional properties.

The calculated compressive stress in PMN-10PT is -31 MPa, while the tensile stress in the platinum electrodes is 466 MPa. Note that these stress values were extrapolated from the middle part of the ML for a length equal to 2.3 mm. The results obtained using the finite-element method are in good agreement with the estimated values obtained using Equation (4.3). Therefore, it can be concluded that the compressive stress is present in the PMN-10PT ML elements and it is large enough to induce the ferroelectric phase, which is in accordance with the dielectric and piezoelectric results. The compressive stress in the PMN-10PT ML elements is most probably also responsible for a slightly higher T_m (6.5 K) than in the bulk, see Figure 4.26. For example, Bobnar et al. observed that a tensile deformation of relaxor polymer foils resulted in a slight down-shift of T_m [126].

A similar compressive stress to that in PMN-10PT could also be expected in PMN ML. By following the same approach, the stress calculated using Equation (4.3) and with the finite-element method is -65 MPa and -52 MPa, respectively. However, we did not observe any kink in the dielectric measurements above -75 °C and any macroscopic piezoelectric

activity at room temperature. Thus, we conclude that there is no stress-induced ferroelectric phase in the PMN ML. A possible explanation for the absence of such a transition could be related to the insufficiently high compressive stress to induce the ferroelectric phase and the lower temperatures of the dielectric anomalies in PMN. In Section 4.1.4 it was shown that the electric field needed for inducing a ferroelectric state in PMN is twice as high as the one in PMN-10PT (Figure 4.10). Furthermore, PMN has a much lower electric-field-induced depolarization temperature than PMN-10PT, i.e., $-48\text{ }^{\circ}\text{C}$ [136] versus $0\text{ }^{\circ}\text{C}$ [52].

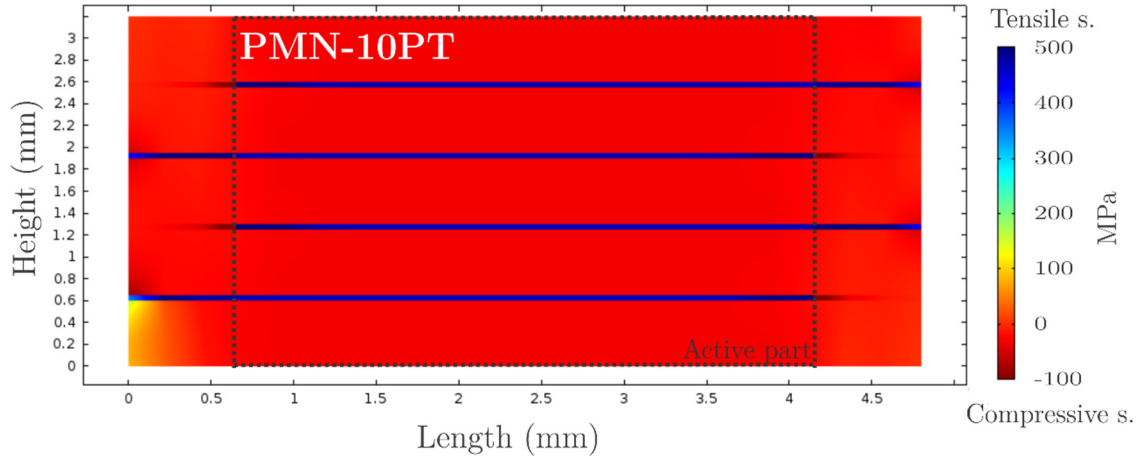


Figure 4.30: Calculated residual stresses with the finite-element method in PMN-10PT ML elements. The active parts of the ML are marked with dotted lines.

4.2.4 EC effect in multilayer elements

The results of the EC measurements using the direct method under electric fields of 20-120 kV/cm for PMN and PMN-10PT ML elements are summarized in Figure 4.31. In addition, the indirectly measured EC responses under electric field amplitudes of 20-100 kV/cm are included. The indirect method is used in order to verify the ΔT_{EC} values obtained via the direct method. The correction factors (see Sections 1.1.2 and 3.2.11.2) are 3.48 and 3.23 for the PMN and PMN-10PT ML elements, respectively.

The EC response of the PMN ML obtained by direct measurements is shown in the temperature range -10 to $105\text{ }^{\circ}\text{C}$, see Figure 4.31a. As expected, the ΔT_{EC} values increase with an increasing electric field and the peak values exhibit an upward temperature shift. The ΔT_{EC} of 1.99 K at 120 kV/cm and at $61.6\text{ }^{\circ}\text{C}$ is the largest measured value for PMN ML elements. Even at $30\text{ }^{\circ}\text{C}$, the ΔT_{EC} value is only slightly lower, i.e., 1.79 K, see Table 4.10.

The indirectly measured EC temperature changes ($\Delta T_{\text{EC IND}}$) of the PMN ML elements are almost equal to the values obtained by the direct method at electric fields up to 60 kV/cm. At higher fields the $\Delta T_{\text{EC IND}}$ are slightly lower than ΔT_{EC} , and the largest difference of 6 % is obtained at 100 kV/cm and $61.5\text{ }^{\circ}\text{C}$. The overall good agreement of the temperature changes obtained via the two methods verifies that the ΔT_{EC} of the PMN ML elements are trustworthy, see Table 4.10. To the best of our knowledge there are no other reports on EC studies of PMN ML elements.

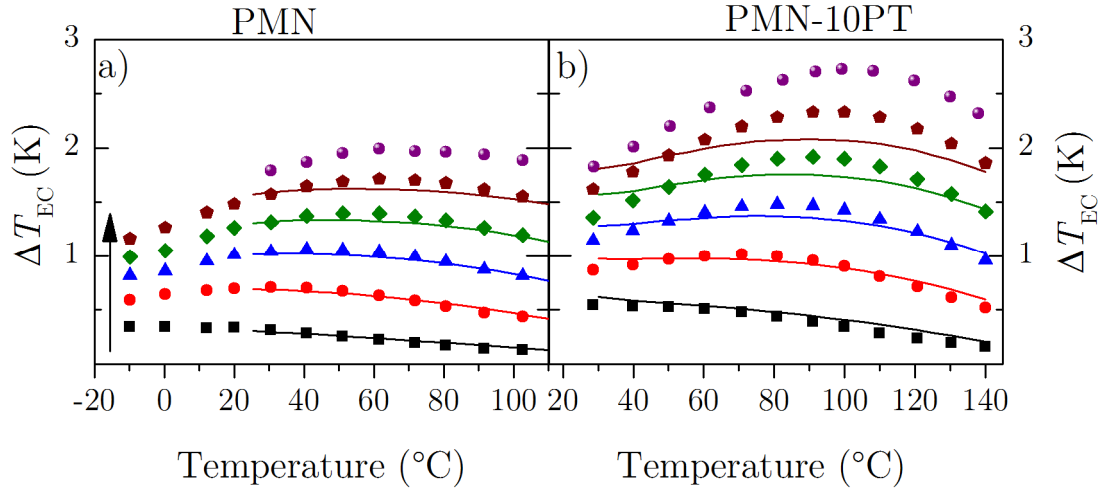


Figure 4.31: ΔT_{EC} versus temperature of (a) PMN and (b) PMN-10PT ML elements measured at electric fields of 20 to 120 kV/cm with a 20 kV/cm step. The direction of the increasing electric field is marked with an arrow. The symbols represent ΔT_{EC} values determined by the direct method in the DSC, while the lines represent the calculated ΔT_{EC} from the P - E hysteresis loops, i.e., ΔT_{EC} obtained by the indirect measurement method. Note that the temperature scales are different in (a) and (b).

The EC results of the PMN-10PT ML elements in the temperature range from 30 to 140 °C are collected in Figure 4.31b. The ΔT_{EC} increases with the electric field and the temperature, following a similar trend to the PMN MLs. The largest ΔT_{EC} of 2.72 K is obtained at 99.3 °C and at 120 kV/cm. The ΔT_{EC} at 30 °C is noticeably smaller, i.e., 1.83 K.

The indirect measurements agree with direct measurements at low fields, but with increasing field the indirectly obtained values are progressively lower, which is especially pronounced around 30 °C and at $T_{\text{EC max}}$, see Table 4.11.

Table 4.10: The EC effect of PMN determined via the direct (ΔT_{EC}) and indirect ($\Delta T_{\text{EC IND}}$) methods. Note that the ΔT_{EC} values are compared at temperatures in the vicinity of $T_{\text{EC max}}$, marked with an asterisk.

	ΔT_{EC} (K)	E (kV/cm)	T (°C)
direct method	1.57	100	30.6
	1.71	100	61.6 *
	1.79	120	30.6
	1.99	120	61.6 *
	$\Delta T_{\text{EC IND}}$	E (kV/cm)	T (°C)
indirect method	1.59	100	30.2
	1.62	100	55.3*

Table 4.11: The EC effect of PMN-10PT determined via the direct (ΔT_{EC}) and indirect ($\Delta T_{\text{EC IND}}$) methods. Note that the ΔT_{EC} are compared at temperatures in the vicinity of $T_{\text{EC max}}$, marked with an asterisk.

	ΔT_{EC} (K)	E (kV/cm)	T (°C)
direct method	1.62	100	28.6
	2.33	100	100.0 *
	1.83	120	28.8
	2.72	120	99.3 *
	$\Delta T_{\text{EC IND}}$	E (kV/cm)	T (°C)
indirect method	1.81	100	30.1
	2.08	100	90.0*

Recently, two articles were published on PMN-10PT [88], [90] and two on PMN-8PT MLs [23], [89], reporting the EC properties determined by the direct method. Note that in these studies the values are reported without the correction factor, making them difficult to compare with our results. Still, the trend of ΔT_{EC} with the electric field and temperature is in agreement with our results.

Usui et al.[90] studied PMN-10PT samples with 19 layers and 40 % ratio of the active-to-total ML volume, so that we could estimate that the correction factor (Eq. (3.1)) is about 2.5. Their highest ΔT_{EC} at an electric field of 288 kV/cm and 107 °C was 2.7 K, and at 102 kV/cm and at 103 °C the ΔT_{EC} is 2.5 K. This result is comparable with the data obtained on our PMN-10PT ML elements, with a similar ratio of active-to-total volume, i.e., 33 %. Nevertheless, at 100 kV/cm their $T_{\text{EC max}}$ is 10 K higher, but the ΔT_{EC} is just 0.2 K (7 %) higher than our results. Similar differences are also observed at lower electric fields. Such a slight ΔT_{EC} difference could tentatively be related to the measuring technique. As shown in reference [23], that EC measurements performed with a thermocouple as in [90] and with a thermistor as in our case, exhibit a 15 % variation of ΔT_{EC} . Such a difference could be due to the glass insulating layer on the thermistor, which decreases the heat transfer.

The comparison of the EC response in our PMN and PMN-10PT ML elements reveals that the latter has a significantly larger maximum ΔT_{EC} at the same electric field, see Figure 4.32. At 80 kV/cm and especially at 120 kV/cm the ΔT_{EC} of PMN-10PT is very strongly temperature dependent. However, as PMN has a lower $T_{\text{EC max}}$ than PMN-10PT, the ΔT_{EC} values at 30 °C of both samples are comparable, but with increasing temperature the ΔT_{EC} gap between PMN and PMN-10PT increases.

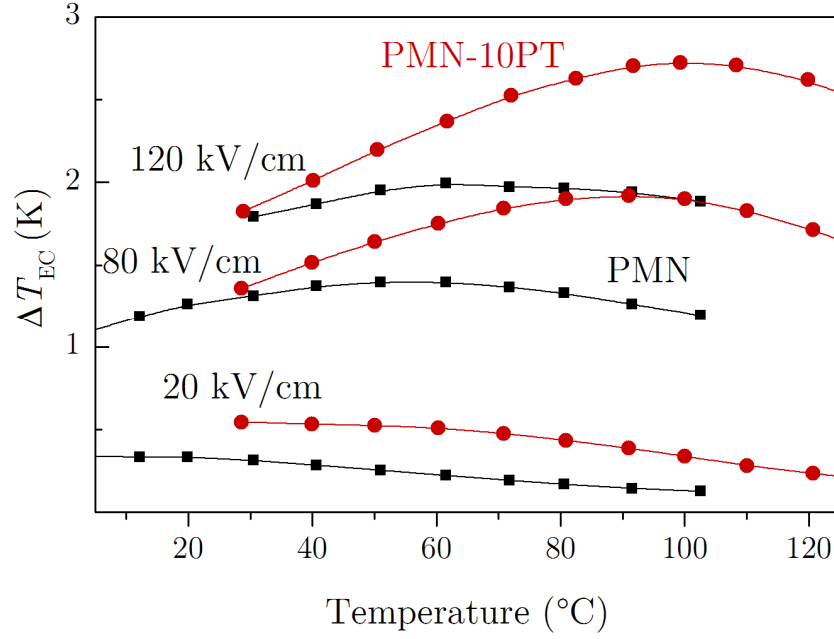


Figure 4.32: ΔT_{EC} comparison between PMN (black square symbols) and PMN-10PT (red circle symbols) ML elements measured at 20, 80 and 120 kV/cm. The lines are a guide for the eyes

4.2.5 Comparison of the EC properties between the ML elements and bulk ceramics

In Figure 4.33 the ΔT_{EC} of the ML elements are compared to their bulk counterparts. The values for PMN are compared under electric fields of 20, 40 and 60 kV/cm, see Figure 4.33a. The ΔT_{EC} of the ML and bulk ceramics exhibit similar trends. The $T_{EC \max}$ and the ΔT_{EC} values are higher for the bulk than for the ML; moreover, the ΔT_{EC} difference is more pronounced at temperatures above $T_{EC \max}$. The comparison of the EC measurements between the PMN-10PT ML elements and the bulk ceramic is shown in Figure 4.33b. Similar to PMN, the ΔT_{EC} and the $T_{EC \max}$ of the ML are lower than the values of the bulk ceramics. The ΔT_{EC} difference slightly increases with the increasing electric field, and it is almost constant with temperature. Thus, at 80 kV/cm and at 40 °C, the largest ΔT_{EC} difference is 16 % (0.15 K).

The significant difference between the ML and the bulk is in the highest possible electric field that will not cause a dielectric breakdown. From Figure 4.11 and Figure 4.31 it is clear that the ML elements can withstand much higher electric fields, which is even more pronounced for the PMN MLs that consist of layers that are half the thickness of the PMN-10PT. The bulk PMN and PMN-10PT bulk survived electric fields up to 70 kV/cm and 90 kV/cm, while the ML elements even endured fields of up to 120 kV/cm.

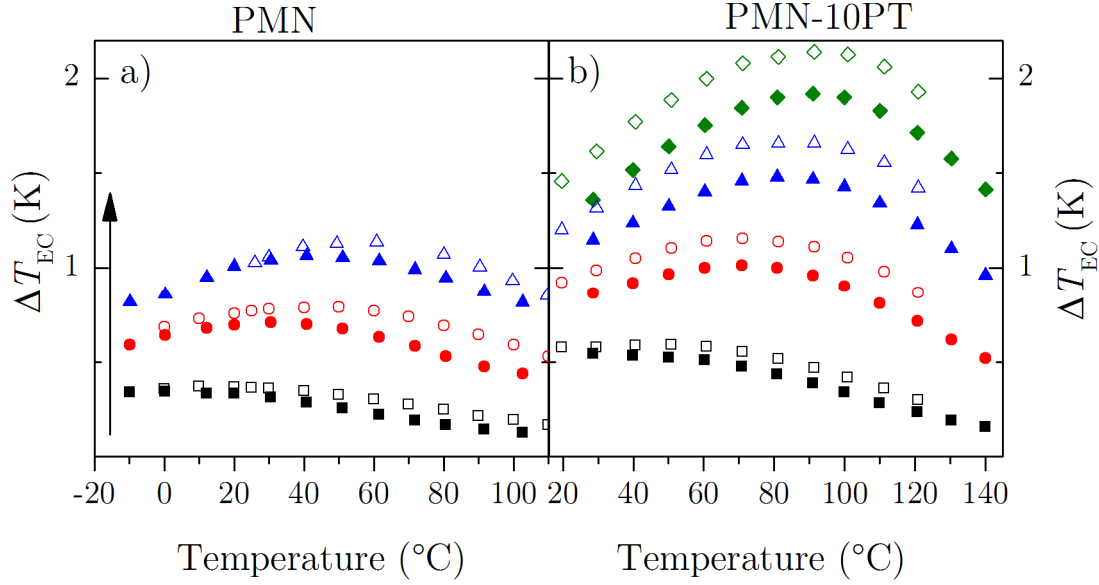


Figure 4.33: The ΔT_{EC} comparison between the ML elements and the bulk ceramics for (a) PMN and (b) PMN-10PT. The results for the ML elements are presented with solid symbols at electric fields of 20 to 60 kV/cm for the PMN and to 80 kV/cm for the PMN-10PT with a 20-kV/cm step. The ΔT_{EC} values of the bulk ceramics are shown with hollow symbols. Note that the temperature scales are different in (a) and (b). The direction of the increasing electric field is marked with an arrow.

In Table 4.12 the EC responsivities of our ML samples are compared to selected values of the PMN and PMN-PT MLs and the bulk ceramic samples reported in the literature. The EC responsivities of our PMN and PMN-10PT MLs are 1.65 and 2.26×10^7 K m/V, respectively. Only slightly higher values are obtained for our bulk ceramics. The bulk ceramics in other studies [51], [52], [59] have comparably high EC responsivities. On the other hand, it is difficult to compare the EC responsivities of MLs reported in literature, since the ΔT_{EC} are mostly expressed without the correction factor [23], [88], [90] and are thus significantly lower than the values of the bulk ceramics or our ML elements.

In Table 4.13 we collected the EC temperature changes of PMN-PT MLs without the correction factor ($\Delta T_{EC \text{ raw}}$) at similar electric field amplitudes and temperatures [91]. First, we notice that the $\Delta T_{EC \text{ raw}}$ and consequently also the ΔT_{EC} values are only comparable at similar ratios of the active-to-total volume of the ML elements. For example, at the volume ratio of about 30–40% the $\Delta T_{EC \text{ raw}}$ and ΔT_{EC} are, respectively, ~ 0.6 K and ~ 2 K. By increasing this ratio the $\Delta T_{EC \text{ raw}}$ significantly increases with respect to ΔT_{EC} [90]. Next, a comparison between the ML samples is not possible, when the ratio of the active-to-total volume is not given, which is usually the case. For example, in PMN-8PT MLs the $\Delta T_{EC \text{ raw}}$ is 1.6 K, but no details about the sample geometry are reported [23].

*: The values were extracted from graphs.

Table 4.12: Comparison of the EC properties of selected PMN and PMN-PT ML elements and bulk ceramics, measured at similar electric fields.

Sample, composition	Thickness (μm)	ΔT_{EC} (K)	ΔE (kV/cm)	EC responsivity (10^{-7} K m/V)	Measurement method	Ref.
ML PMN	32	1.99	120	1.65	Thermistor	This work
ML PMN	32	1.62	100	1.62	Indirect	This work
ML PMN-10PT	60	2.72	120	2.26	Thermistor	This work
ML PMN-10PT	60	2.08	100	2.08	Indirect	This work
ML PMN-10PT	38	1.2*	103	1.17	Thermocouple	[88]
ML PMN-10PT	38	2.7*	288	0.94	Thermocouple	[90]
ML PMN-8PT	86	2.7*	160	1.69	DSC	[23]
Bulk PMN	103	1.33	70	1.9	Thermistor	This work
Bulk PMN-10PT	106	2.33	90	2.58	Thermistor	This work
Bulk PMN	100–130	1.4	90	1.50	Thermocouple	[52]
Bulk PMN-10PT	100–130	1.2	50	2.40	Thermocouple	[52]
Bulk PMN-8PT	1000	0.6*	20	2.9	DSC	[59]
Bulk PMN-10PT	80	3.5	160	2.16	Thermistor	[51]

* Results for which the correction factor was not used

Table 4.13: The EC temperature changes of ML elements expressed with and without the correction factor.

Material	Ratio of active to total ML volume (%)	$\Delta T_{\text{EC raw}}$ (K)	ΔT_{EC} (K)	E (kV/cm)	T (°C)	Layer thickness (μm)	Ref
PMN-10PT	33	0.58	1.87	80	99	60	This work
PMN-10PT	28	0.6*	2.0	76	100	38	[90]
PMN-10PT	40	0.8*	2.0	76	100	38	[90]
PMN-10PT	52	0.9*	1.7	76	100	38	[90]
PMN-8PT	/	1.6*		92	96	39	[23]

In Figure 4.34 the shifting of $T_{\text{EC max}}$ with increasing electric field is compared for PMN, PMN-10PT ML and bulk ceramics. The $T_{\text{EC max}}$ values are deduced from the Gaussian function, which were fitted to the ΔT_{EC} values. The $T_{\text{EC max}}$ of the ML elements are slowly saturating with increasing electric field in the same manner as for the bulk samples. The $T_{\text{EC max}}$ temperatures of the ML are lower than the $T_{\text{EC max}}$ of bulk, which could already be discerned in Figure 4.33. This $T_{\text{EC max}}$ lowering in the ML elements could be due to the residual compressive stress discussed in Section 4.2.3.1, as it is known that the compressive stress can lower the $T_{\text{EC max}}$ [137], [138]. Although such an effect has not been anticipated, it certainly is favourable for cooling applications, as it brings $T_{\text{EC max}}$ closer to RT.

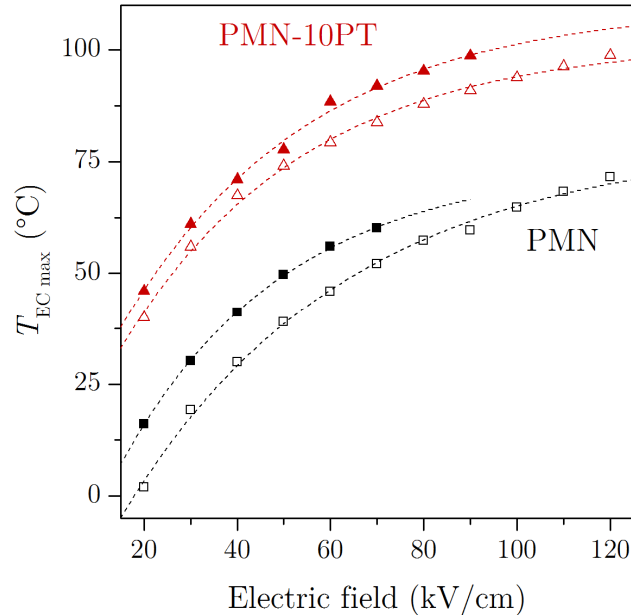


Figure 4.34: Comparison of the electric-field-dependent $T_{\text{EC max}}$ between ML elements (hollow symbols) and bulk ceramics (solid symbols) for PMN and PMN-10PT materials. Dashed lines were fitted with an asymptotic function and they are a guide for the eyes.

The PMN and PMN-PT ML elements as well as the bulk samples did not exhibit any Joule heating. As an example, the temperature change (ΔT) versus time (t) of the PMN-10PT ML and bulk samples obtained by the direct measuring method are collected in Figure 4.35a. Here, after the removal of the electric field the temperature relaxes back to the surrounding temperature. The difference between the bulk and the ML is in the time of relaxation (τ_{EC}), from the expression $\Delta T(t) = \Delta T_{EC} \exp(-t/\tau_{EC})$, where τ_{EC} and ΔT_{EC} are the fit parameters. τ_{EC} is 6.87 s for the bulk and almost two times longer for the ML, i.e., 11.16 s, which is simply due to the much larger mass of the ML element [73].

In our ML elements the outer layers are ceramic, thus they represent the passive mass in the EC measurements. Therefore, the heat has to pass first through this passive layer in order to reach the thermistor, see Figure 4.35b. Furthermore, the thermistor consists of an about 100- μm -thick insulating glass layer (Figure 4.35c), which also hinders the heat transfer, as reported in [23]. The thermalisation time of a thermistor glued to a sample, i.e., the time needed to reach thermal equilibrium, is about ~ 700 ms, as reported in [72]. In our case the thermalisation time, extracted from the graph in Figure 4.35a, is approximately 700 ms for the ML, and ~ 1000 ms for the bulk. This difference may be related to different experimental details, such as the quality of the contact between the thermistor and the surface of the sample or the thickness of the manually deposited glue, see Figure 4.35b,c. So, we may conclude that the geometry of our ML samples does not significantly affect the measurements as the heat conduction from the active to the passive ceramic layer is much faster than the heat conduction from the ceramic to the thermistor.

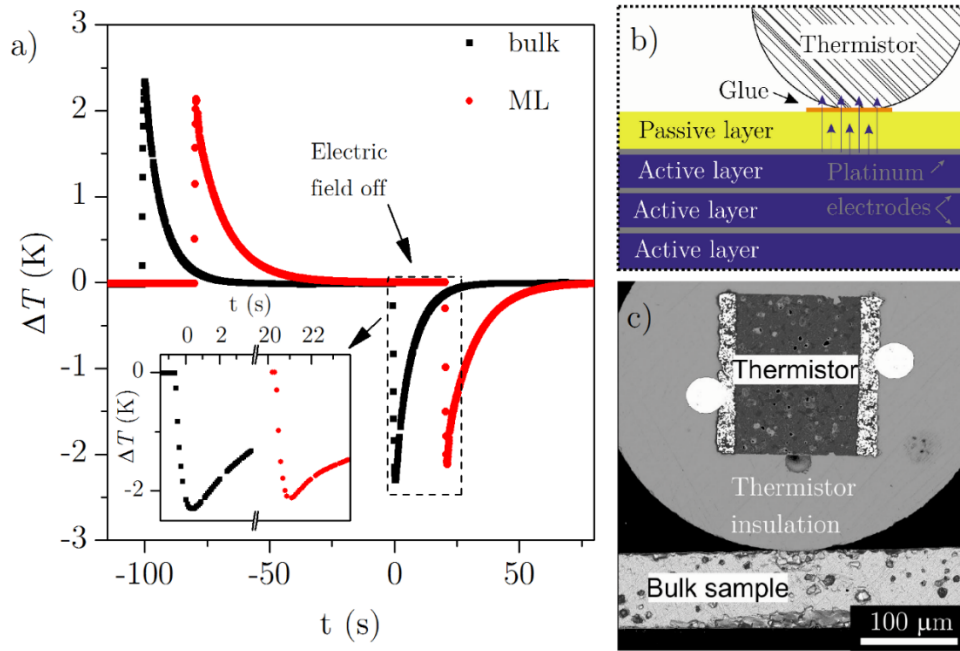


Figure 4.35: (a) Temperature change (ΔT) as a function of time (t) for bulk (black symbols) and ML (red symbols) PMN-10PT determined at 90 °C and under an electric field of 90 kV/cm. For better clarity the curves for the bulk are shifted and the temperature minima are magnified in the inset. (b) Sketch of the heat conduction in a ML cross-section with a glued thermistor on the top of the passive layer. (c) Cross-section micrograph of a thermistor glued to a sample.

4.2.6 Stability of the EC effect in multilayer elements

The EC stability of the PMN and PMN-10PT ML elements under electric-field cycling was investigated as described in Section 3.2.12. The frequency of the unipolar cycling signal ν_{cycling} was determined on the basis of frequencies used in EC demo devices, such as in Plaznik et al. [61], and Equation (1.9) where the data for the heat capacity and the thermal conductivity reported in [100] are used. The calculated values of ν_{cycling} are 6.1 Hz for PMN and 1.7 Hz for PMN-10PT, thus a frequency of 2 Hz was selected for our study. The results are presented as normalized ΔT_{EC} values versus the number of applied electric field cycles, see Figure 4.36. Joule heating was not observed in any of the EC stability measurements.

The PMN ML element was subjected to 10^6 electric field cycles at an amplitude of 110 kV/cm. The ΔT_{EC} value deviated during the cycling by about 1 %, which is in the range of the measurement uncertainty [7]. As examples, the plots of the temperature changes (ΔT) versus time before and after the cycling are included as insets in Figure 4.36a. The $\Delta T(t)$ values upon application and removal of the electric field are symmetrical, confirming the absence of any Joule heating.

Similarly, the PMN-10PT ML element was exposed to 10^6 electric field cycles at 100 kV/cm, see Figure 4.36b. A slight decrease of ΔT_{EC} is observed after 10^2 cycles; however, with further cycling the ΔT_{EC} increases again. After 10^5 cycles the ΔT_{EC} reaches its maximum, an about 2 % higher value than the initial ΔT_{EC} . Moreover, the ΔT_{EC} after 10^6 applied cycles is still marginally higher than the initial value. Note that the temperature of the environment during the electric field cycling was not controlled, and thus the ΔT_{EC} variations of a few percent could be a consequence of temperature variations of a few degrees.

In addition, the dielectric permittivity versus temperature and P-E hysteresis loops of both samples were measured before and after the electric field cycling. The dielectric permittivity plots of the PMN are shown in Figure 4.37a. The peak dielectric permittivity of the virgin sample is approximately 21 000 at 1 kHz and the T_m is at -10 °C. Upon electric field cycling the dielectric permittivity decreases, in our case by only about 5 % at 1 kHz, similar to other ferroelectrics/relaxors, where fatigue is usually dominated by domain-wall/polar-nanoregions pinning and the formation of a space charge field [65], [67], [68], [139]. Moreover, T_m is slightly down-shifted, presumably due to the fact that history-dependent effects, both fatigue and aging, influence the dielectric relaxation spectrum [140]. The peak value of the dielectric losses remains almost unchanged after cycling (see Figure 4.37b), i.e., $\tan \delta$ is 0.16 before and after the cycling. However, at RT, where the cycling was performed, $\tan \delta$ increases by a factor of 2, but still remains at a very low value of 0.0017.

In the PMN-10PT the dielectric permittivity also decreases upon cycling, and the peak value is approximately 13 % lower at 1 kHz. The T_m decreases by 3.5 K, and the dielectric losses remain almost unchanged, as with the PMN.

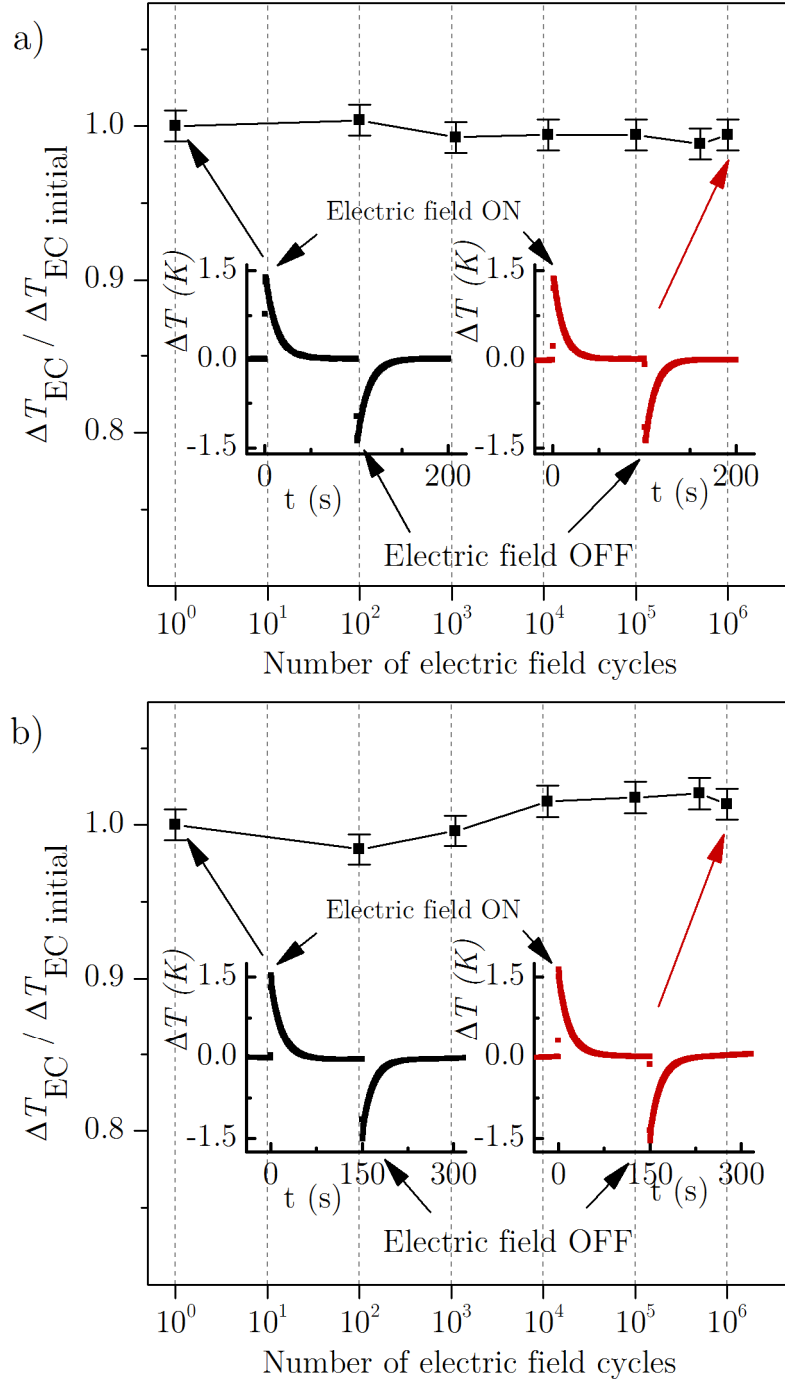


Figure 4.36: The EC temperature change normalized by the initial ΔT_{EC} value as a function of the number of the electric field cycles for the (a) PMN and (b) PMN-10PT ML elements. The time dependence of ΔT upon the applied step-like electric field before and after cycling are exhibited in the left- and right-hand insets, respectively.

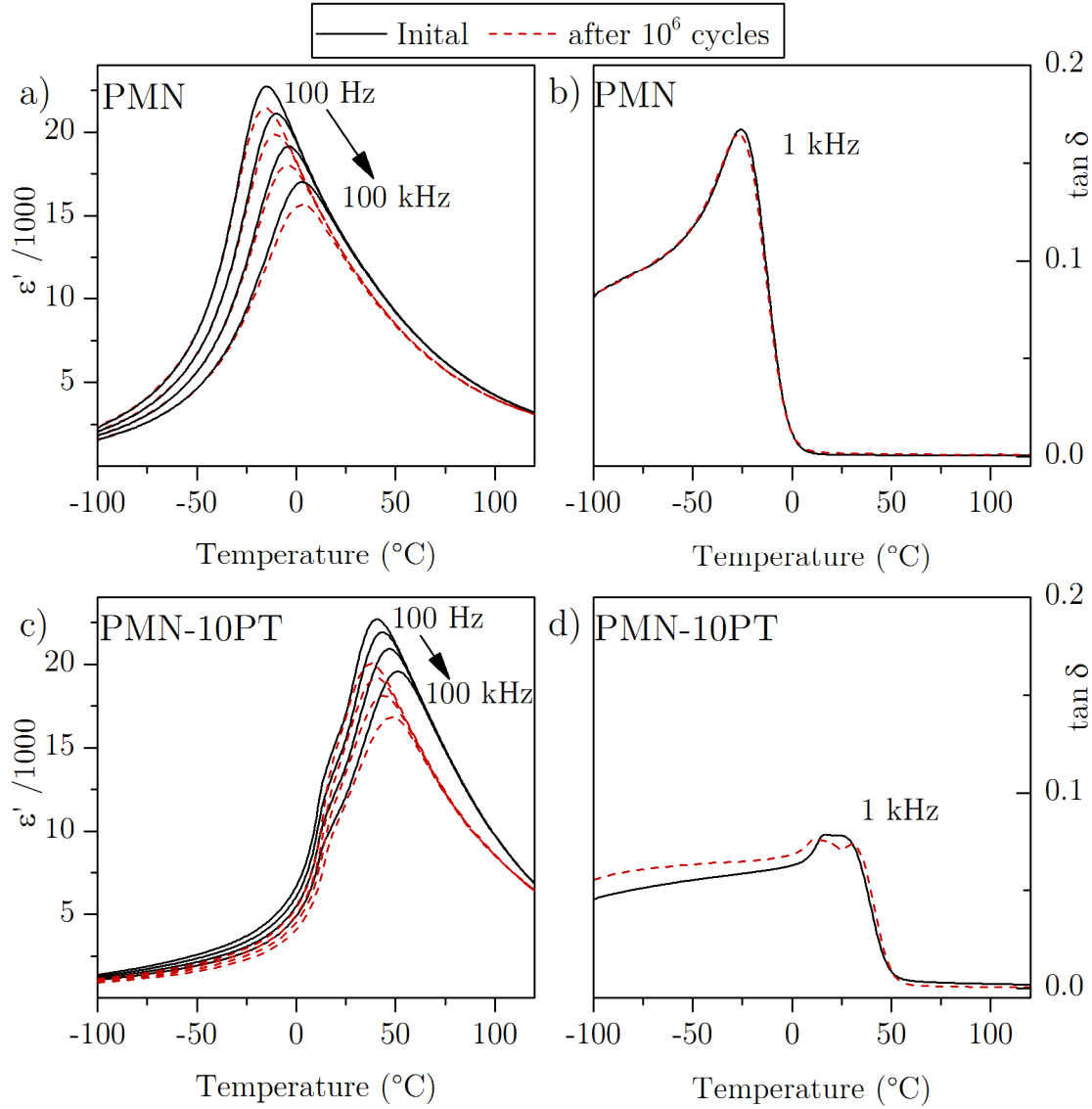


Figure 4.37: Temperature dependence of the dielectric permittivity measured at frequencies between 100 Hz and 100 kHz and dielectric losses ($\tan \delta$) at 1 kHz for PMN (a,b) and for PMN-10PT (c, d) before and after cycling.

The P - E hysteresis loops of the PMN before and after the cycling are compared in Figure 4.38. The initial hysteresis loop is slim with a P_s value of $29 \mu\text{C}/\text{cm}^2$, which decreases after cycling by 1 % in the orientation of the positive electric field, i.e., in the direction of the unipolar cycling. In contrast, the P_s in the negative electric field orientation is reduced by 3.6 %. The cycled hysteresis loop is slightly broader than the uncycled loop (the centres and maxima of both are enlarged in insets in Figure 4.38), which is in accordance with the higher $\tan \delta$ values. Similarly, in PMN-10PT a 3.5 % decrease of the P_s value and a slight broadening of the P - E loop develop after cycling, see the inset in Figure 4.38.

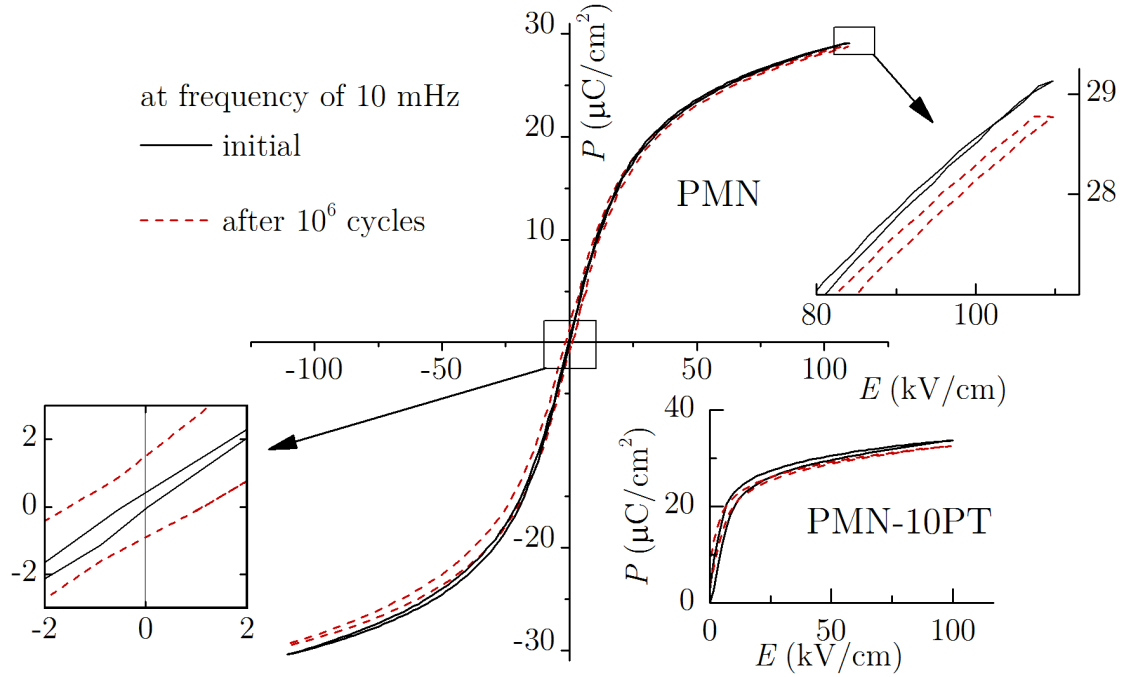


Figure 4.38: P - E hysteresis loops of PMN ML element before and after the electric field cycling. The left inset shows the enlarged centre of the loop, while in the upper-right inset the positive electric-field end of the P - E loop is enlarged. In the lower-right inset the positive electric field part (i.e., in the direction of the unipolar cycling) of the P - E loops of the PMN-10PT ML element before and after cycling are collected.

Unipolar electric field cycling might be one of the reasons for the low fatigue obtained in our experiments. This is because the electrical polarization is not completely reversed and, consequently, its pinning with charge defects is much less probable. Very importantly, we did not find any microcracks, not even at the ends of the inner electrodes, where they would be predominantly expected due to the strain incompatibility [64]. Note that microcracks at the electrode/ceramic layer interfaces are the usual origins of ML degradation upon electric-field cycling. Figure 4.39 includes FE-SEM micrographs of the polished (a), and thermally-etched (b) ML cross-section of the PMN ML sample after 10^6 electric-field cycles. In particular, the high-magnification micrograph of the end of the inner Pt electrode (Figure 4.39b) reveals the absence of any microcracks.

The fatigue effects in our ML relaxor elements upon cycling with a unipolar electric field, as used in EC applications, are negligible. A similar fatigue-less behaviour upon electric field cycling at 60 kV/cm has already been reported by Luo et al.[71] for a bulk lead-free relaxor and by Sapper et al.[70] for a ML lead-free relaxor. There is only one recent study of the EC effect's stability performed with a number of cycles that is relevant for cooling applications. The authors observed considerable Joule heating after 10^6 electric field cycles at 20 kV/cm in a $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ bulk ceramic due to the migration of oxygen vacancies. The problem was resolved by reversing the electric field every 10^5 cycles, which allowed for a redistribution of the oxygen vacancies, and consequently a fatigue-less behaviour was achieved up to 10^6 cycles. [75].

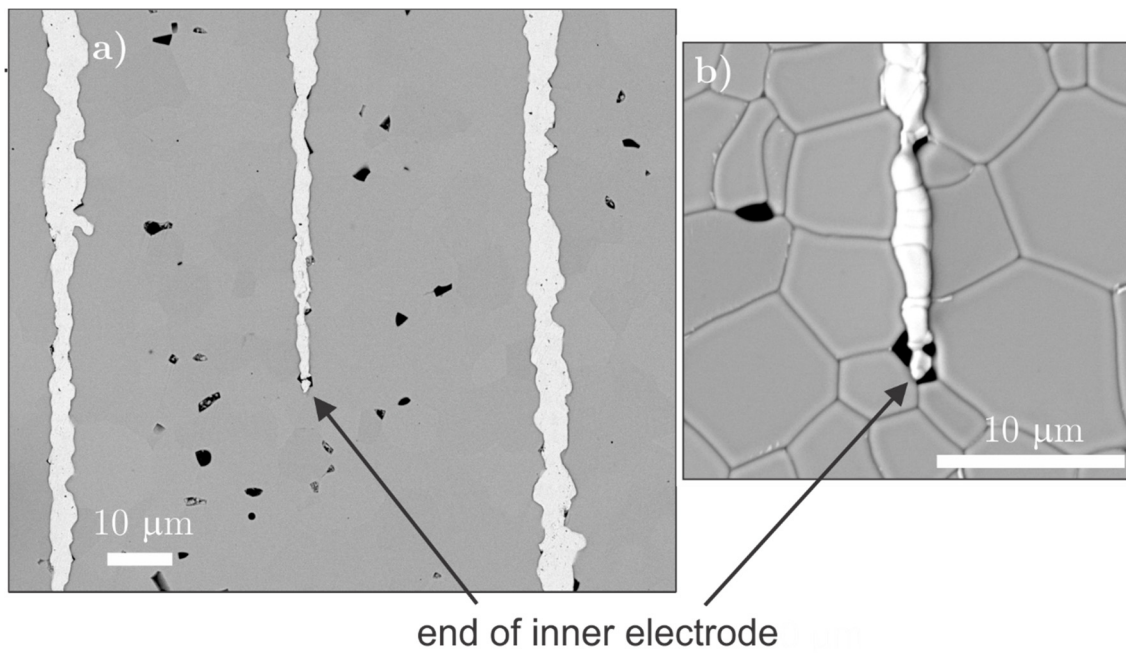


Figure 4.39: FE-SEM micrographs of (a) the polished and (b) thermally etched PMN ML cross-section after electric field cycling exhibiting the microstructure in the vicinity of the end of the inner Pt electrode.

Chapter 5

Summary and Conclusions

This thesis addresses the electrocaloric (EC) properties of relaxor $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) and PMN-rich solid solutions with PbTiO_3 (PMN-PT) and their viability for EC cooling in the form of multilayer (ML) elements.

5.1 PMN and PMN-PT Bulk Ceramics

The PMN, $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $x\text{PbTiO}_3$ (PMN-100xPT, $x = 0.05, 0.1$) bulk ceramics were prepared from mechanochemically synthesized powders. The choice of this synthesis made it possible to obtain phase-pure perovskite materials, which is challenging when using conventional solid-state routes. After sintering at 1200 °C the samples are very dense and according to the XRD results they crystallize in a pure perovskite phase. FE-SEM-WDXS analyses confirmed an almost stoichiometric composition, the absence of any secondary phases, and grain sizes of a few μm in all the samples. The dielectric spectroscopy revealed broad dielectric permittivity peaks with a strong frequency-dispersion characteristic for the relaxors. The temperatures of the dielectric anomalies (T_m) are up-shifted with increasing PT content, in agreement with the literature. The P - E loops are slim, and the values of the spontaneous polarization increase with increasing PT content. We note that the obtained low- and high-field properties are among the highest reported values for PMN and PMN-PT ceramics, which we relate to a high level of chemical homogeneity and the absence of any secondary pyrochlore phases.

Most importantly, the EC measurements reveal large EC temperature changes (ΔT_{EC}) in the PMN and PMN-PT materials. The maximum ΔT_{EC} values are 1.33 K at 70 kV/cm and at 61 °C for PMN, 2.2 K for PMN-5PT and 2.34 K for PMN-10PT at 90 kV/cm and at 91 °C and 93 °C, respectively. The temperature of the maximum EC temperature change ($T_{\text{EC max}}$) for a given field is composition-dependent; it is up-shifted with increasing PT content, similar to the dielectric permittivity peak. Consequently, at temperatures close to RT the ΔT_{EC} values of the PMN and PMN-PT materials are comparable for a given electric field. Moreover, the up-shifting of $T_{\text{EC max}}$ follows the same trend in both PMN and PMN-PT samples, only the absolute $T_{\text{EC max}}$ value depends on the chemical composition.

Combining the results of the electrocaloric measurements and the dielectric spectroscopy measured under DC bias field reveals a certain relationship between $T_{\text{EC max}}$ and T_m . By applying the DC bias above the threshold field, the ferroelectric state is induced in the PMN and PMN-PT. Consequently, the T_m is strongly up-shifted with increasing DC bias. The $T_{\text{EC max}}$ is always below T_m for a given field, and the temperature gap between the $T_{\text{EC max}}$ and T_m progressively increases with an increasing DC bias. Our results thus show that the electric-field-dependent T_m cannot be used for an estimation of the $T_{\text{EC max}}$.

In contrast, it can only roughly mark the temperature of the upper boundary of the temperature-electric-field window where the EC responsivity is the highest.

5.2 PMN and PMN-10PT Multilayer Elements

In the second part of the thesis PMN and PMN-10PT ML elements were prepared from the same powders as the bulk using tape-casting technology with screen-printed internal platinum electrodes. The PMN and PMN-10PT MLs, respectively, consisting of five 32- and 60- μm -thick layers, were obtained by sintering at $\sim 1000^\circ\text{C}$. According to the XRD analysis the ceramics crystallize in the pure perovskite phase. Furthermore, the FE-SEM analyses revealed homogeneous and highly dense microstructures with grains of a few μm . According to the WDXS analysis the samples exhibit a chemical composition very close to the perovskite stoichiometry and a high level of homogeneity across the individual layers.

The dielectric permittivity measurements of the PMN and PMN-10PT ML elements exhibited frequency-dispersive peaks with values comparable to those obtained for bulk ceramics. Interestingly, in the PMN-10PT ML element a kink in the dielectric permittivity was observed at $\sim 45^\circ\text{C}$ below T_m , which we tentatively attribute to the induced ferroelectric phase as a consequence of the residual thermal stress. The latter develops as a consequence of the different thermal expansion coefficients of the ceramic and platinum layers. The P - E loops of the ML elements are slim, with high values like those measured for bulk ceramics.

As both the low- and high-field dielectric properties of the ML elements were comparable to those of the bulk PMN and PMN-10PT we expected that the EC properties would also be comparable. The ΔT_{EC} values of the MLs are indeed only slightly lower than those of the bulk when compared at the same electric field. Due to their lower thickness the ML elements survive higher electric fields than the bulk and consequently they exhibit a larger maximum ΔT_{EC} . The maximum ΔT_{EC} obtained for PMN and PMN-10PT are 1.99 K and 2.72 K at 120 kV/cm and at 62°C and 99°C , respectively. While the EC properties of the PMN ML elements have not been previously reported, the EC results of our PMN-10PT ML elements are among the highest reported ΔT_{EC} values for MLs, as shown in Table 4.12.

The stability of ΔT_{EC} in the relaxor ML elements under electric field cycling is an important characteristic for cooling applications, but until our study this has not been addressed. We investigated the EC properties of PMN and PMN-10PT MLs upon cycling at 110 and 100 kV/cm, respectively. After 10^6 electric field cycles the ΔT_{EC} changed only by a few percent in both materials, exhibiting an almost fatigue-less behaviour. Similarly, both the dielectric and ferroelectric properties remained almost unchanged after the cycling. The ML elements survived the cycling experiments without any noticeable microstructural degradation related to fatigue.

Concerning the viability of the PMN and PMN-10PT ML elements in refrigeration technology, it is worth comparing the ΔT_{EC} values for a given temperature. At RT the PMN and PMN-10PT ML elements exhibit almost the same ΔT_{EC} , thus the choice of the optimum material depends on the operational temperature range. The PMN and PMN-10PT ML elements exhibit comparable ΔT_{EC} values to bulk ceramics, but they require significantly lower voltages due to the few-times-lower thickness of the individual layers, and in combination with a high EC stability they are very promising candidates for use in future EC cooling devices.

Appendix A

Indirect Measuring Method

The indirect EC method is usually performed as follows. The polarization-electric field (P - E) loops are measured at different temperatures (T) (see Figure A.a). From the measured data, $P(T, E)$ is extracted. Afterwards, the derivative $(\partial P / \partial T)_E$ is calculated and used in Equation (1.8) to obtain ΔT_{EC} , as in Figure A.b. For the indirect method to be valid, it is crucial to accurately measure the electrical polarization, which can be challenging in some cases. For instance, in relaxors the influence of the frequency on P - E loop measurements is still being debated. Moreover, it is not clear whether it is right to use Maxwell relations for relaxors, which are not in mechanical, polar or thermal equilibrium [12], [141], [142]. Another issue is related to leakage, which can distort a P - E loop and lead to an incorrectly determined $P(T, E)$. A further concern is the specific heat, which is required for the ΔT_{EC} calculation. The electric field dependence of the specific heat is often ignored in the literature, and thus the ΔT_{EC} values can be underestimated [12].

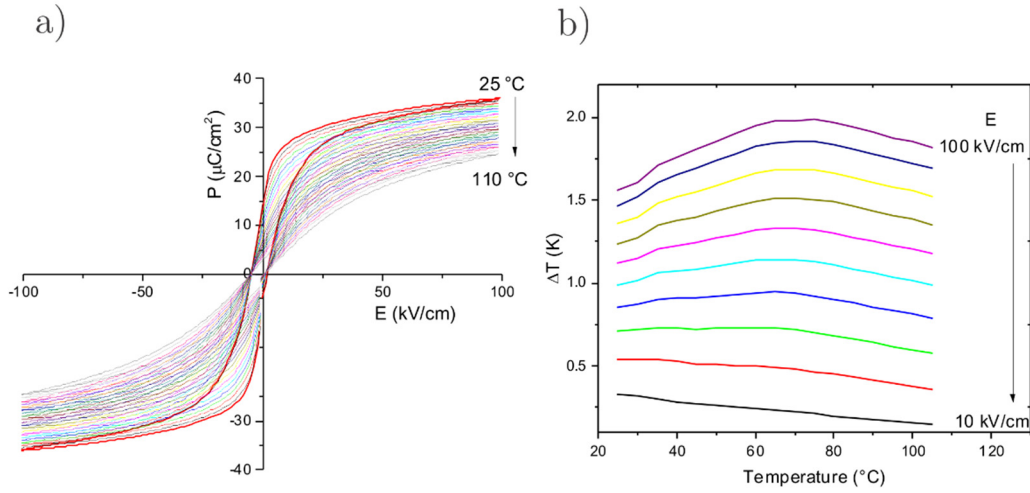


Figure A.1: (a) P - E hysteresis loops measured at temperatures from 25 °C to 110 °C, at an electric field of 100 kV/cm. (b) Calculated ΔT_{EC} versus temperature at electric fields of 10 to 100 kV/cm.

Appendix B

Tape Casting and the Fabrication of Multilayer Elements

Tape casting is a method for casting a slurry in the form of a tape (Figure B.1), also called a green tape. It is well known in many industries, including paper, plastic and paint manufacturing. Tape casting was first introduced for ceramic materials, and the description of the process was published [143] and patented [144] by Glenn Howatt for use in the electronics industry. The main idea of the 1952 patent has basically not changed, although many developments have been made. The main advantage of tape casting is that it is the best way of producing large-area, thin and smooth-surface ceramic sheets. These sheets can be produced with a thickness of less than 1 μm down to a few mm [145]. The process can be described as a sequence of three steps. The first step is mixing the ceramic powder with a solvent, binder and other additives to form a slurry. In the second step, the slurry is cast onto a moving carrier material and thinned by scraping with a blade. This blade is also called a doctor blade, which is essentially a knife-shaped hard material. The third step is drying of the tape and later the separation of the green tape from the carrier substrate.

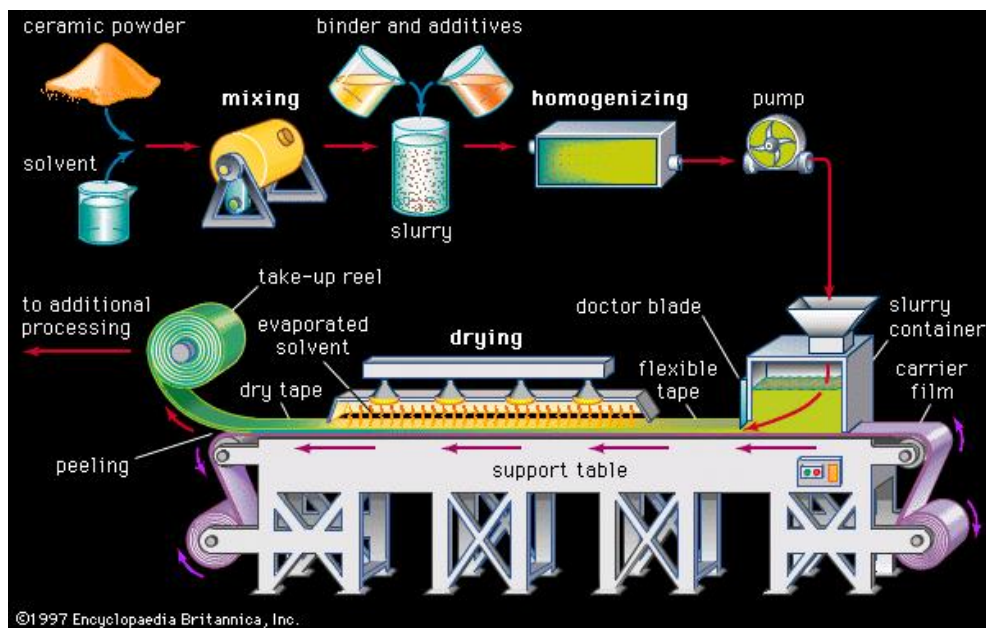


Figure B.1: Schematic representation of the tape-casting process [146].

The green tape is rubbery, flexible and has a very smooth surface. After the tape casting and drying, it is shaped and cut to various sizes, for applications in different electronic devices, including conductors, resistors and capacitors. These devices can have a single layer or multilayer structure, such as in multilayer capacitors. To become fully functional electronic materials, these shaped and stacked green tapes have to be consolidated.

B.1 Slurry Preparation

A slurry or a slip is a mixture of a ceramic powder, solvent, binder, surfactant, plasticizer and other additives. The last three are not essential for the slurry's preparation but are almost always present. The preparation of a slurry usually consists of at least two stages. In the first stage, the powder and solvent are mixed and milled from 2 to 48 hours. The surfactant is also added to the mixture at this stage. After milling, the plasticizer, binder and other ingredients are added. The order of mixing the components is often crucial, so the plasticizer should be added before the binder and other additives. The second-stage milling can also last from a few hours to 72 hours. The main point of this stage is to allow a complete dissolution of the binder along with a complete reaction between the binder and the plasticizer. It was shown that both the first and the second milling times have a significant impact on the final density of the ceramic tapes (Figure B.2) [145], [147].

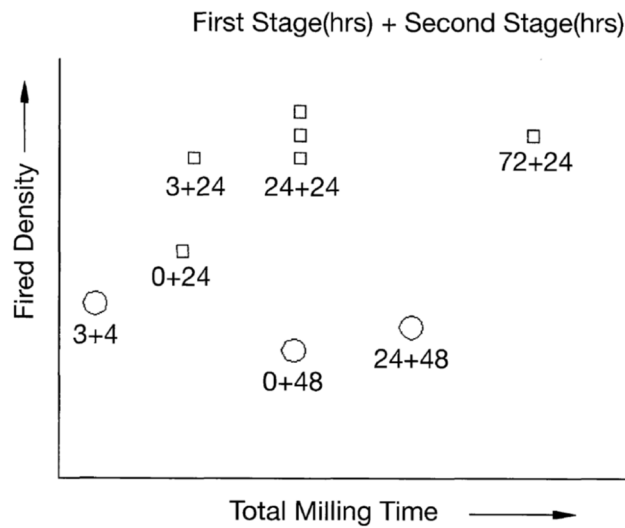


Figure B.2: The influence of the two-stage milling time on the final fired density. The first and the second numbers are the durations of the respective milling stages in hours [145].

After milling the slurry should be de-aired to remove the residual air bubbles. The latter can cause defects in the tape, such as pinholes that can lead to cracking. Moreover, the air bubbles can cause elongated streaks or thin spots in the tape-casting direction. De-airing is usually performed with a low vacuum accompanied by gentle stirring.

B.2 Tape Casting of the Green Tape

When the slurry is prepared, it has to be fed to the tape-casting machine. In continuous processing, the feeding is performed with a pump and piping system, while for smaller, lab-scale batches, manual feeding and gravity are used. The slurry is usually filtered prior to

casting to remove large inhomogeneities or agglomerates, which are larger than the thickness of the green tape. Sieves or meshes with apertures as fine as 10 μm are normally used [147]. In continuous processes, the pumping and filtration system prevents the slurry from stagnating, i.e., its tendency to thicken.

As can be seen from Figure B.2 and Figure B.3 the slurry is firstly fed to the reservoir positioned close to the doctor blade. From that point the slurry is thinned under the blade, which involves moving the carrier under a fixed doctor blade or conversely by pushing the doctor blade over a fixed carrier. The former principle is used for large amounts of slurry and large tape-casting machines, while the latter is more suitable for laboratory-scale tape casting.

A doctor blade is a knife-shaped piece of a hard material, such as stainless steel or hardened carbon steel, and for more abrasive slurries tungsten carbide or aluminium oxide blades are used. The surface in contact with the slurry should be flat and smooth. At the opposite side from the blade, thus from the bottom, the carrier and the slurry should also be supported with a flat and smooth surface. A polished granite block is often used as the support. The distance between the doctor blade and the granite block is referred to as the blade gap. The tape thickness depends on the blade gap, and also on other factors such as the carrier speed and the viscosity of the slurry. The blade gap can be fixed for certain blades, but it is more practical if it is adjustable.

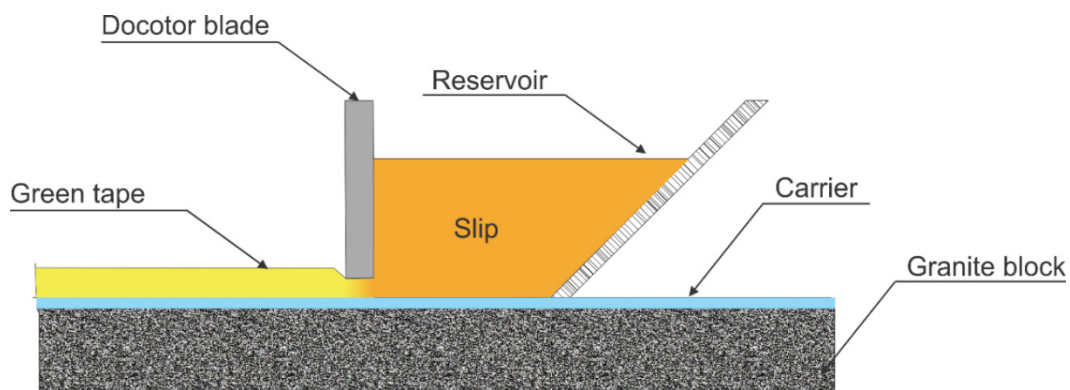


Figure B.3: Simplified doctor-blade assembly of a tape caster.

The carrier or the substrate holds or carries the green tape. It can be stationary or in motion, which is more often the case. Carriers are composed of various materials, the majority are made of polymers, but also stainless steel, paper or glass are used. Polyester and polypropylene carriers in the form of films are a favourite choice, often coated with silicon to more easily detach the green tape. The carrier needs to hold the green tape, but at the same time allow easy removal when needed.

Drying of the as-cast green tape starts after the doctor-blade thinning. The length of a tape caster is to a large extent determined by the drying system, i.e., the segment of the equipment where the solvents are removed from the tape. In most cases the drying system is complex, and it is composed of a few to a dozen bottom heaters and almost the same number of chambers with different air temperatures. Regardless of the tape caster's length, the drying temperature is increasing from the beginning to the end. Close to the blade, the drying temperature is usually set to room temperature, while at the end of the drying system, the temperature is increased to the values of the solvent-evaporation temperature. The air flow, air temperatures and bottom heaters have to be regulated in such way that the solvent is evaporating from both the upper and lower parts of the green tape. If they are not correctly set, defects like the skin effect, edge curling, centre cracking, etc. start to appear.

After drying, the green tape is rolled and stored on the take-up roll or it is moved for further shaping, cutting or thermal treatments. The final green tape is typically composed of 55–60 volume % of ceramic powder, 35 volume % of organic material and about 15 volume % of porosity [145].

B.3 From Green Tape to Multilayer Elements

A schematic presentation of the fabrication of multilayer (ML) elements from a green tape is shown in Figure B.4. After casting, the tape is cut into sheets, usually about 15 cm × 15 cm that allow for easy manipulation. Then the electrode paste is screen-printed onto the sheets [147]. The screen-printing is performed with a squeegee, either manually or automatically. The thickness of the screen-printed electrodes is between 2 and 25 μm . The lamination is the following step in which the electrode sheets are precisely stacked. In the case of ML capacitors, such as in our case, every other sheet is slightly shifted, so that the final ML element has interdigitated internal electrodes, see Figure 4.19a. Such stacked layers are pressed, usually isostatically, at 3 to 30 MPa and at temperatures between 50 and 80°C. Pressing ensures better bonding between the screen-printed electrodes and the green sheets and increases the green density. The subsequent step is cutting of the stacked green sheets into ML elements. The last step is the thermal treatment, which includes a pre-sintering step to remove the organic additives followed by sintering.

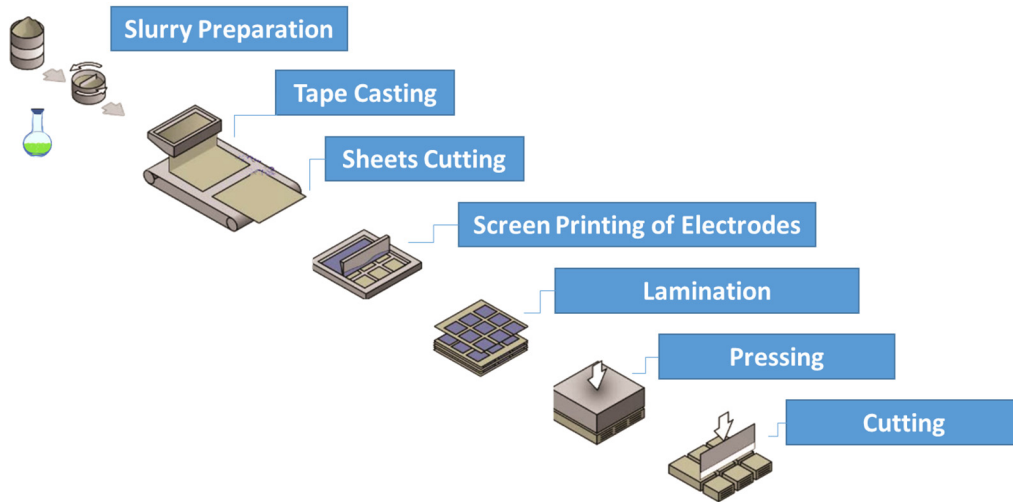


Figure B.4: The multi-step process of fabricating multilayer elements, after [148].

Appendix C

Temperature versus Electric Field Contour Graphs of Electrocaloric Responsivity

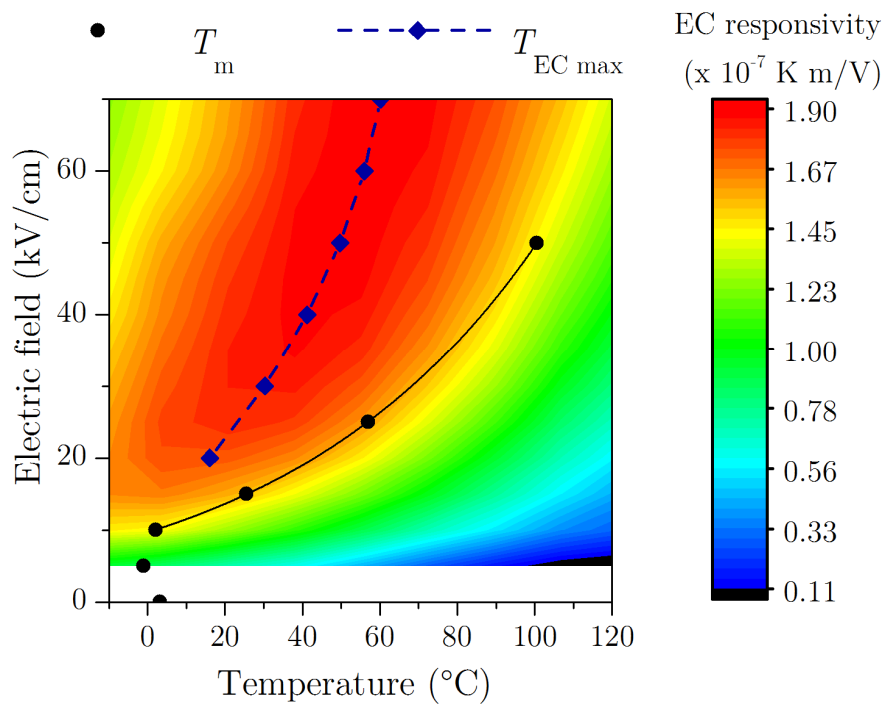


Figure C.1: The EC responsivity as a function of electric field and temperature expressed for PMN. Black symbols denote T_m versus electric field, while blue symbols represent $T_{EC \text{ max}}$ versus electric field. Lines are guides for the eyes.

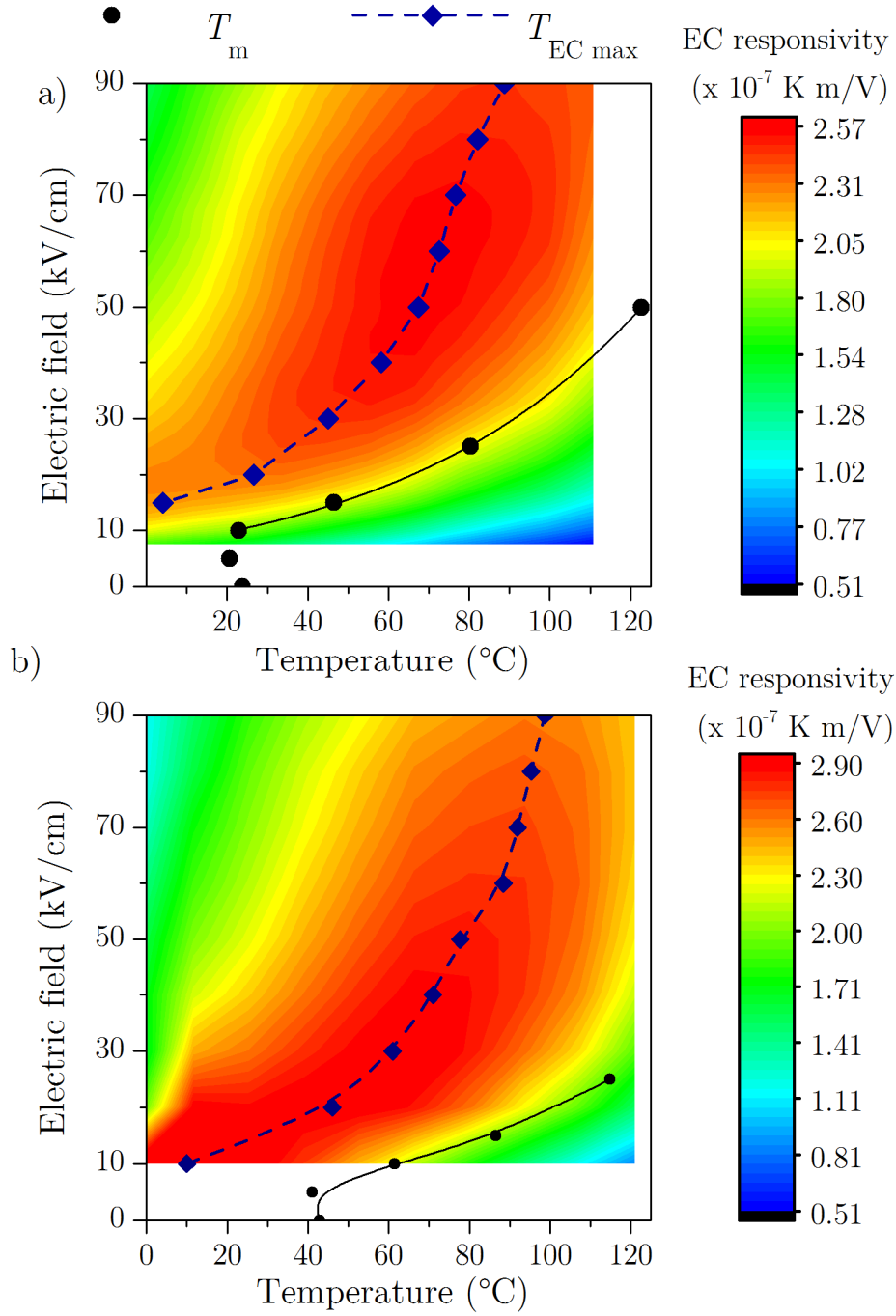


Figure C.2: The EC responsivity as a function of electric field and temperature field expressed for (a) PMN-5PT and (b) PMN-10PT. Black symbols denote T_m versus electric field, while blue symbols represent $T_{\text{EC max}}$ versus electric field. Lines are guides for the eyes.

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Publications related to the thesis

Journal Articles

Lovro Fulanović, Silvo Drnovšek, Hana Uršič, Marko Vrabelj, Danjela Kuščer, Kostja Makarovič, Vid Bobnar, Zdravko Kutnjak, Barbara Malič, "Multilayer $0.9\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.1\text{PbTiO}_3$ elements for electrocaloric cooling", *J. Eur. Ceram. Soc.*, vol. 37, no. 2, p. 599-603, 2017, doi: [10.1016/j.jeurceramsoc.2016.09.010](https://doi.org/10.1016/j.jeurceramsoc.2016.09.010).

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Hana Uršič, Lovro Fulanović, Marko Vrabelj, Zdravko Kutnjak, Brigita Rožič, Silvo Drnovšek, Barbara Malič, "Electrocaloric properties of $0.7\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.3\text{PbTiO}_3$ ceramics with different grain sizes", *Advances in applied ceramics*, vol. 115, no. 2, p. 77-80, 2016, doi: [10.1080/17436753.2015.1116724](https://doi.org/10.1080/17436753.2015.1116724).

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Monographs and other completed works

Andraž Bradeško, Lovro Fulanović, Marko Vrabelj, Silvo Drnovšek, Tomaž Kos, Barbara Malič, Tadej Rojac, *Izdelava merilnega sistema za karakterizacijo elektrokaličnih sprememb temperature keramičnih materialov v temperaturnem območju med $-50\text{ }^{\circ}\text{C}$ in $200\text{ }^{\circ}\text{C}$* , (*Measurement system for characterization of temperature changes of ceramic materials between $-50\text{ }^{\circ}\text{C}$ and $200\text{ }^{\circ}\text{C}$*), (IJS technical report, 12294), 2017.

Unpublished conference contribution

Lovro Fulanović, Marko Vrabelj, Silvo Drnovšek, Hana Uršič, Danjela Kuščer, Kostja Makarovič, Zdravko Kutnjak, Vid Bobnar, Barbara Malič, *Electrocaloric properties of $0.9\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.1\text{PbTiO}_3$ multilayered structures prepared by tape casting*, [\(Link\)](#).

Other publications

Andreja Eršte, Lovro Fulanović, Lucija Čoga, M. Lin, Y. Thakur, Qiming M. Zhang, Vid Bobnar, "Stable dielectric response of low-loss aromatic polythiourea thin films on $\text{Pt}/\text{SiO}_2\text{Pt}/\text{SiO}_2$ substrate", *Journal of advanced dielectrics*, vol. 6, no. 1, p. 1650003-1-1650003-4, 2016, doi: [10.1142/S2010135X1650003X](#).

Biography

I was born on the 18th of August 1988 in Zagreb, Croatia. In 2012, I obtained my Master's degree at the Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb, (UNIZAG FSB), in the field of mechanical engineering. For the next year and a half I was employed at UNIZAG FSB, where I was investigating mechanical properties of polymer thick films used for retention of helium. In 2014, I received an international exchange grant for 6 months to perform dielectric spectroscopy investigation of polymer and ceramic materials under supervision of Assoc. Prof. Vid Bobnar, Condensed Matter Physics Department, Jožef Stefan Institute. In November 2014 I was hired as a young researcher at the Electronic Ceramics Department, Jožef Stefan Institute, and at the same time I started my PhD study at the Jožef Stefan International Postgraduate School under supervision of Prof. Dr. Barbara Malič and Assoc. Prof. Dr. Vid Bobnar. In 2016 I was granted a two-months research visit to the group of Prof. Dr. Jürgen Rödel at Technische Universität Darmstadt. My research is mainly focused on ceramic materials, particularly relaxor ferroelectric $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$, in the form of bulk ceramics and multilayer elements, and their dielectric, ferroelectric and electrocaloric characterization.

Attendance at workshops and courses:

- Mladi upi 2014 – Izobraževanje za mlade raziskovalce, Center za prenos tehnologij in inovacij, Institut Jožef Stefan, Ljubljana, Slovenija, 19.12.2014.
- Fundamentals of vacuum techniques, Slovenian Society for Vacuum Technique, Jožef Stefan Institute, Ljubljana, Slovenia, 12.-13.1.2015.
- EDS/WDXS X-ray microanalysis, European Microbeam Analysis Society, Jožef Stefan Institute, Ljubljana, Slovenia, 3.5.2015
- The Summer School on “Innovative technologies in the field of ceramic manufacturing”, organized by European Ceramic Society in Budapest, Hungary, from 7.-8.7.2017.
- Workshop on materials for energy conversion and their applications: electrocalorics and thermoelectrics, at the “53rd International Conference on Microelectronics, Devices and Materials”, Ljubljana, Slovenia, 5.10.2017.

Award:

Winner of the Student competition for the best poster entitled “*Electrocaloric ceramic multilayer elements prepared by tape casting for future cooling applications*” at the SHAPING VI Conference, Montpellier, July, 2016.