

GIANT ENERGY-CONVERSION EFFECTS IN SOFT AND SOLID ADVANCED MATERIALS

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RAZISKAVE POJAVOV Z OGROMNO PRETVORBO ENERGIJ V MEHKIH IN TRDNIH NAPREDNIH MATERIALIH

Doktorska disertacija

Supervisor: Prof. Dr. Zdravko Kutnjak

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Življenje je potovanje, za katerega nihče ne dobi zemljevida. Vsakdo potuje po svoje in si riše svoj zemljevid. Vsaka risba je nov smerokaz čudovitih poti življenja.



“Decidez ce que vous voulez et allez-y” (Niagara Falls, August 2011)

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Abstract

This thesis presents the results of our experimental work in the field of new advanced materials such as liquid crystal elastomers (LCEs), electrocalorics and magnetoelectrics.

In the first part, the conversion of thermal to mechanical energy is addressed in LCEs. The three important, newly discovered, chemical and physical parameters for controlling their critical behavior are presented. Via these parameters it is possible to influence the phase transition from an isotropic to a nematic phase. Since the nature of this transition is directly connected to the temperature profile of a thermomechanical or thermoelastic response, it is thus possible to influence the type of the thermoelastic response. Therefore, the LCE materials can expand/contract either quickly, i.e., discontinuously or slowly, i.e., continuously, depending on the proper tuning of the above-mentioned parameters. These scientific findings could help chemists in synthesizing the LCEs with proper thermomechanical properties, as well as engineers in constructing the final product of a particular application, such as, for instance, an artificial muscle by using the appropriately engineered LCEs. This part of the thesis has been done in collaboration with the research group of Prof. Dr. Heino Finkelmann, Institut für Makromolekulare Chemie, Freiburg, Germany, which kindly supplied most of the LCE samples we studied, and with Dr. George Cordoyiannis, EN-FIST Centre of Excellence, JSI, who made experiments related to the impact of the cross-linker concentration on the nature of the PN-N phase transition in LCEs. The NMR studies of LCEs were made by the research group of Prof. Dr. Boštjan Zalar, from the Condensed Matter Physics Department, JSI.

In the second part the electrocaloric effect (ECE) related to the conversion of the electrical to thermal energy is addressed. The section on electrocaloric materials presents the first direct measurements of the giant electrocaloric effect in several organic and inorganic materials. These studies have been done in collaboration with two research groups: the research group of Prof. Dr. Marija Kosec, from the Electronic Ceramics Department, JSI, Slovenia, and with the group of Prof. Dr. Qiming Zhang, from Pennsylvania State University, USA. These groups supplied inorganic and organic ECE materials, respectively. In addition, collaboration with Prof. Dr. Raša Pirc who has done the theoretical part of the ECE research studies is also acknowledged. Our direct observations of the ECE are compared with recent predictions based on indirect measurements in the above mentioned materials and moreover, they show a characteristic peak of the effective ECE responsiveness near the critical point (CP). This indicates the potential relevance of the CP for the enhancement of the giant ECE.

The last third part of the thesis addresses the magnetoelectric effect, i.e., the control of the magnetic properties via electrical ones, and vice versa. In this section the first ever prepared soft magnetoelectric material, i.e., a mixture of ferroelectric liquid crystal and ferromagnetic nanoparticles is presented. This research work has been done with Dr. Sašo Gyergyek and Prof. Dr. Miha Drofenik from the Materials Synthesis Department, JSI, with Dr. Marko Jagodič and Prof. Dr. Zvonko Jagličić, the Institute of Mathematics, Physics, and Mechanics, Ljubljana, and with Prof. Dr. Samo Kralj from the Department of Physics, Faculty of Natural Science and Mathematics, University of Maribor.

To conclude, the main purpose of this dissertation is a contribution to a better understanding of the studied advanced materials, and, consequently, to help to

manufacture new, even more improved, advanced materials that will find a place in relevant applications, which could improve our lives.

The scientific accomplishments of thesis have been published in twenty-four scientific articles in various international scientific journals. Also, four new scientific articles have already been accepted for publication and one article is unpublished.

Povzetek

V disertaciji so predstavljene osnovne raziskave, ki so v tesni povezavi z možnimi aplikacijami v vsakdanjem življenju, na področju novih naprednih materialov, t.j., tekočerkristalnih elastomerov (TKE), elektrokalorikov in magnetoelektrikov.

V prvem delu je obravnavana pretvorba toplotne energije v mehansko v tekočerkristalnih elastomernih sistemih. Predstavljeni so trije pomembni, na novo odkriti kemijski in fizikalni parametri, preko katerih lahko vplivamo na aplikativno najbolj uporaben fazni prehod v teh materialih, prehod iz izotropne v nematsko fazo. Zaradi neposredne povezanosti narave tega prehoda s temperaturno odvisnostjo termomehanskega ali termoelastičnega odziva, je mogoče nadzorovati tudi slednjega. S tem dosežemo možnost za ustrezno uporabo oz. aplikacijo, t.j., da se tekočerkristalni elastomerni material razteza/krči bodisi hitro oz. nezvezno ali pa počasi oz. zvezno, odvisno od omenjenih parametrov. Te znanstvene ugotovitve bodo lahko v pomoč tako kemikom, ki bodo TKE z ustreznimi termomehanskimi lastnostmi sintetizirali, kot tudi inženirjem, ki bodo naredili končni produkt za posebno aplikacijo kot je npr. umetna mišica, katere glavni del bo lahko ustrezno pripravljen tekočerkristalni elastomer. Omenjene znanstvene raziskave so bile opravljene v sodelovanju z raziskovalno skupino Prof. Dr. Heina Finkelmannja z » Institut für Macromolekulare Chemie« iz Freiburga, Nemčija, kjer so nam pripravili večino merjenih TKE materialov ter z Dr. Georgom Cordoyiannisom, z EN-FIST centra odličnosti, IJS, ki je opravil eksperimente, ki pokažejo, da gostota zamreževalcev vpliva na naravo PN-N faznega prehoda. NMR meritve so bile opravljene v skupini Prof. Dr. Boštjana Zalarja z Odseka za Fiziko trdne snovi, IJS.

V drugem delu je obravnavan elektrokalorični pojav, kjer gre za pretvorbo električne energije v termalno. Predstavljene so prve neposredne meritve ogromnega elektrokaloričnega pojava v anorganskih in organskih materialih. Omenjene znanstvene študije so bile narejene v sodelovanju z raziskovalno skupino Prof. Dr. Marije Kosec, na Odseku za elektronsko keramiko na IJS, ter v sodelovanju z znanstvenimi kolegi z inštituta Materials Research Institute, The Pennsylvania State University, ZDA, pod vodstvom Prof. Dr. Qiminga Zhanga. Obe skupini sta pripravili ustrezne materiale. Prav tako pa smo sodelovali s Prof. Dr. Rašo Pircem, ki je prispeval teoretični del raziskav elektrokaloričnega pojava. Dobljeni znanstveni rezultati so primerljivi s preteklimi napovedmi, ki temeljijo na posrednih meritvah. Poleg tega pa so pokazali, da je vrednost odzivnosti elektrokaloričnega pojava največja v bližini kritične točke. Slednje dokazuje pomemben vpliv kritične točke na elektrokalorični pojav.

V zadnjem, tretjem delu je obravnavan magnetokalorični pojav, t. j., nadzor magnetnih lastnosti preko električnih in obratno. Predstavljen je prvi primer mehkega magnetoelektričnega materiala. To je mešanica feroelektričnega tekočega kristala in feromagnetnih nanodelcev. Omenjeno raziskovalno delo je bilo opravljeno v sodelovanju z Dr. Sašom Gyergyekom in Prof. Dr. Miho Drogenikom z odseka za Sintezo materialov, IJS, z Dr. Markom Jagodičem in Prof. Dr. Zvonkom Jačličičem, z Inštituta za Matematiko, Fiziko in Mehaniko v Ljubljani, ter s Prof. Dr. Samom Kraljem z oddelka za Fiziko, Fakulteta za Naravoslovje in Matematiko, Univerza v Mariboru.

Za zaključek, namen te doktorske disertacije je, da pripomore k boljšemu razumevanju

preučevanih naprednih materialov in k izdelavi novih, ki bodo našli mesto v številnih ustreznih aplikacijah, in s tem prispevali k izboljšanju našega življenja.

Znanstveni dosežki doktorske disertacije so objavljeni v štiriindvajsetih znanstvenih člankih v mednarodnih znanstvenih revijah. Prav tako so bili sprejeti v objavo štirje novi znanstveni članki, eden članek pa je še neobjavljen.

Abbreviations

CNT = Carbon nanotube
 CP = critical point
 Cu = Cupper
 DMM = Digital multimeter
 DSC = differential scanning calorimetry
 ECE = electrocaloric effect
 FE –PE = ferroelectric-paraelectric
 FJC model = freely jointed chain model
 FWHM = the full-width at half maximum
 I-N = isotropic-nematic
 JSI = Jožef Stefan Institute
 LCs = liquid crystals
 LCEs = liquid crystal elastomers
 LSCEs = liquid single crystal elastomers
 MCE = magnetocaloric effect
 MC-LCEs = main-chain LCEs
 ME = magnetoelectric
 MNPs = magnetic nanoparticles
 NMR = nuclear magnetic resonance
 NPs = nanoparticles
 PDMS = poly(dimethylsiloxane)
 PLZT = Lead Lanthanum Zirconate Titanate
 PMN = Lead Magnesium Niobate
 PMN-xPT = Lead Magnesium Niobate-xLead Titanate
 PN-N= paranematic-nematic
 PNRs = polar nanoregions
 PRT = Platinum thermometer
 Pt = platinum
 P(VDF-TrFE) = Poly(Vinylidene Fluoride-Trifluoroethylene)
 P(VDF-TrFE-CFE) = Poly(Vinylidene Fluoride-Trifluoroethylene-Chlorofluoroethylene)
 P(VDF-CTFE) = Poly(Vinylidene Fluoride-Chlorotrifluoroethylene)
 SC-LCEs = side-chain LCEs
 SAXS = small-angle X-ray scattering
 SEM = scanning electron spectroscopy
 SmA = smectic A
 SmC = smectic C
 SmC* = ferroelectric smectic C
 SQUID = superconducting quantum interference device
 SRBRF model = spherical random-bond-random-field model
 TEM = transmission electron microscopy
 USA = United States of America
 WGM = whispering-gallery-mode

1 Introduction

In recent years, the interest in materials that are promising for different applications in everyday life has started to grow. This innovative research will increase the quality of our lives. However, I believe that our research work, a part of it is presented in this thesis, will contribute in a mosaic of science and one day it will be used in various real applications.

Our interest is focused on studying the various effects related to energy conversions and the physical properties of new, advanced materials, i.e., liquid crystal elastomers, electrocalorics, and soft magnetoelectrics. These materials can be important in the development of new, high-end technology. In particular, we have studied different conversions of energies in advanced materials, such as the giant conversion of thermal to mechanical energy, i.e., the thermomechanical effect, in nematic liquid crystal elastomers, the giant conversion of electrical to thermal energy, i.e., the electrocaloric effect in soft and solid relaxor ferroelectrics, and the electric control of magnetization, i.e., the magnetoelectric effect in soft multiferroics, such as mixtures of ferroelectric liquid crystal and magnetic nanoparticles.

1.1 Liquid crystal elastomers (LCEs)

Liquid crystal elastomers are one of the so-called smart materials, which are very promising for many applications such as artificial muscles, actuators, sensors and adaptive smart materials [1-11]. As the name suggests, these are materials that combine the properties of liquid crystals and elastomers, i.e., the orientational order of conventional liquid crystals (LCs) is combined with the elastic properties of elastomers [12-14]. The most interesting and potentially most attractive feature for the application of LCEs is so-called thermomechanical effect, which means that LCEs spontaneously stretch or shrink due to the temperature change in the vicinity of a particular phase transition for several tens or even several hundred percent. It is important to mention that these strains considerably exceed the elongations of other known actuation materials. This property was already explored theoretically [15-23] and it makes LCEs the best candidates for many application niches, some of them already mentioned above. Due to this large potential, LCEs have also been intensively studied experimentally [24-32], and in terms of simulations [33-35].

The most promising for applications is the phase transition from an isotropic to a nematic (I-N) phase. So far due to the several theoretical and the few experimental studies [21, 23, 25, 27, 28, 36-42], the nature of this transition was not clear and generally it was thought to be supercritical. It was considered that in the nematic LCEs a supercritical evolution of the physical properties from the I-N phase is a consequence of either an internal mechanical field conjugate to the order parameter or quenched random effects.

The main studies in LCEs have been related to the I-N phase transition in view of the elasticity in these materials, whether it is soft, semi-soft or non-soft [12]. It was observed that the stress-strain diagram is strongly related to the orientational order of the nematic director field [43, 44]. The degree of this order is closely related with the crosslinking

history [45]. This finding shows that the elasticity is directly linked to the thermomechanical effect in LCEs. Furthermore, all synthesis work was supported by important physical experiments that characterized the stress-strain behavior and stress-induced alignment [1, 19, 24, 27, 28, 36, 39, 45].

The nematic-elastic coupling in LCEs gives rise to the following important effect, i.e., soft elasticity. This phenomenon, when there is no rubber-elastic energy in the response of LCE systems to different strains, was first discovered by Warner et al. in 1994 [46]. The applicability of this concept was confirmed by measurements of the dynamical shear modulus [19, 20].

Soft elasticity is related to the local rotations in nematic LCEs, i.e., the extension of a rubber with no elastic energy cost accompanied by characteristic director rotations, and it is a consequence of the symmetry [12, 17]. The idea is related to accommodate the distribution of polymer chains via mechanical deformations without its distortion as it rotates. It is known that a typical solid includes its volume and shape, and both of them cost energy when they change. On the other hand, as already mentioned, in LCEs under the applied stress, changes in their shapes cost practically no energy. However, liquid crystal elastomers correspond to the category of liquids, but their part, i.e., rubbers show non-soft deformations, and this is a reason that LCEs are classified as solid-like materials. This is in accordance with the argument that the softness exists in a solid with an internal degree of freedom and with an accessible isotropic state [12, 17].

In a non-ideal case the elasticity is semi-soft. This means a threshold before the director rotation, i.e., before the rotation of the director is completed, the deformation proceeds with a little additional resistance. This is shown as a stress plateau on the stress-deformation graphs [45]. It was found that chemically identical networks with different thermomechanical histories can show very different stress-strain diagrams in their semi-soft regions of deformations.

The non-linear strain-induced director reorientation and the related plateau-like behavior in the stress-strain relation are characteristic for the nematic monodomain LCEs. This was in comparison to the experimental observations theoretically described by a nonlinear macroscopic model [47]. The model includes two materials with two preferred directions, i.e., in the case of LCEs one direction is related to the LC director, and the other is anchoring in the polymer network during the procedure of synthesis.

The nature of the I-N phase transition in LCEs can be described by two different theories [28]. In the first one, LCEs are considered as heterogeneous materials composed of domains. The average order parameter is then calculated as superposition order parameter profiles related to the individual microdomains and it can be attributed to the supercritical character of the I-N phase transition. The second scenario is related to the supercritical behavior as a consequence of the coupling between the nematic order parameter and a conjugate internal or external field that can drive the I-N phase transition into a supercritical regime. This is happening whenever the field exceeds its critical value.

In order to distinguish between these two scenarios, Selinger et al. [28] exploited two models and it was found that the mentioned two scenarios show totally different temperature-dependent order parameter curves. They found that the internal field was far below the critical value. This is the first observation of the possibility that a critical point exists in LCEs. Later it was shown that LCEs prepared by famous "Finkelmann procedure" [1] are supercritical systems with a low heterogeneity, and when they are doped with an amount of conventional nematogen, they can be driven towards the critical regime [36].

The idea that the critical behavior of LCEs could be influenced by varying the geometry and density of the crosslinkers was introduced in early theoretical studies [16]. Indications that an increasing crosslinking density leads to a supercritical-like

thermoelastic response and a birefringence temperature can be found in various studies [39,48]. It was also predicted that the local variations in the crosslinking density could lead to the quenched randomness, i.e., a random-field induced smearing of criticality [23, 41].

Before continuing, it is important to mention that due to the non-zero order parameter observed in LCEs by nuclear magnetic resonance above the I-N transition temperature [29], we will use in this thesis the term paranematic (PN) instead of isotropic (I). In order to confirm the theoretical prediction [16, 28], it was recently experimentally demonstrated that a critical point exists in liquid crystal elastomer systems [29], i.e., LCEs show discontinuous or subcritical behavior. This development was obtained for side-chain LCEs (SC-LCEs) [29, 31]. Recently, it was shown that the thermomechanical response of SC-LCEs can be controlled by changing a chemical parameter, i.e., the crosslinker concentration [31]. It was found that with increasing the crosslinking density, the paranematic to nematic (PN-N) phase transition can be tuned from first order to the supercritical one [31]. This means that in these materials both the on-off, i.e., discontinuous or the smeared or continuous temperature profile of the spontaneous elongation/contraction can be achieved.

In recent times considerable attention has also been paid to the main-chain LCEs (MC-LCEs) due to the large thermomechanical effect observed in these systems. A few studies have already investigated MC-LCEs [48-52] related to the studies of thermomechanical, stress-strain, and shear response, but systematic studies of the nature of the PN-N phase transition were not made until now.

It was predicted that MC-LCEs should have better mechanical and optical properties in comparison to SC-LCEs due to the direct coupling of the mesogens with the polymer backbone [53]. This was later experimentally confirmed by thermoelastic measurements, the results of which exceeded those observed in SC-LCEs [43, 54].

The first MC-LCEs were synthesized by Donnio et al. [49] by crosslinking the liquid-crystalline polymer chains by a flexible siloxane-based crosslinker. Later on, new main-chain LCEs were synthesized, where the synthesis of well-defined monodomain MC-LCEs is obtained by the hydrosilylation of new mesogens [55]. The investigated thermoelastic experiments confirm that all the designed samples presented a prolate conformation of polymer chains. Furthermore, it was found that the flexible crosslinker increases the clearing temperature in MC-LCEs and the most important is the observation that the mechanical properties such as elastic modulus and the spontaneous elongation/contraction could be tuned via the chemistry of the mesogen and crosslinking density.

The combination of mesogens incorporated directly within the polymeric backbone lead theoretically to a stronger coupling between the polymer chain orientation, network strain and the intrinsically high orientational order of LC mesogens, and thus to a great enhancement of the mechanical properties [52]. The prediction was confirmed experimentally by Wermter and Finkelmann [50]. They found that increasing the proportion of the main-chain component in a nematic monodomain LCE mixed of SC- and MC-LCEs results in an increased elongation up to 300% at the I-N phase, in comparison to pure SC-LCEs, where this value is typically six times smaller.

A study related to the design and synthesis of new MC-LCEs has shown that small changes in the mesogen symmetry have a strong impact on the phase transition temperature and on the stability of mesophases. Thus it is possible to predict the different properties of a LCE by tuning the cross-linker density [52].

However, as mentioned above, it was recently experimentally demonstrated that a critical point of the water-type indeed exists in side-chain LCEs. In this thesis a systematic experimental study of the main-chain LCEs is made in order to clarify which

mechanisms affect LCEs. It was found that one can play with different parameters, i.e., chemical and physical ones, such as an internal random stress field, which can be controlled by a crosslinking density, an external stress field, and a crosslinking temperature [56-60]. This is very useful and important for future technological development because the thermomechanical response can now be tailored to the specific application demand.

As mentioned above, the LCE systems consist of LCs and elastomers (rubber-like materials). In the next paragraphs we will briefly present the basic properties of these materials since they are the building blocks of LCEs.

Generally, most materials exhibit only one phase transition when changing the state from the solid to the liquid, or vice versa. The simplest example is ice, which with increasing temperature melts into water. However, there also exist materials that have more than one phase state, i.e., they exhibit more than one phase transition between the solid and liquid state. Examples of such systems that are also related to our work are so-called liquid crystal materials, shortly liquid crystals (LCs). These are optically transparent organic materials consisting of anisotropic molecules and exhibiting the mechanical properties of liquids and some properties of solid crystals as they display one or more phases between the crystalline solid and the liquid state [61]. Rod-shaped LC molecules that have an elongated, anisotropic geometry are responsible for the unique optical properties that can be useful in a variety of applications.

According to their molecular ordering mechanisms, LCs are divided into two groups: lyotropic and thermotropic LCs. Specifically, in the case of lyotropic LCs the ordering is reached for an appropriate concentration of LC molecules, while in thermotropic LCs the ordering is established over a given temperature interval. In this thesis we will focus on thermotropic LCs, in particular, on LCs exhibiting a nematic (N) and ferroelectric smectic C* phase. This is directly related to our work on nematic LCEs and soft magnetoelectrics.

As we have already mentioned, the LCs typically exhibit several different phases during the transition from the solid to the liquid state. The arrangement of LC molecules, which is different in each phase, can be described by two types of order, i.e., the positional and orientational order. A typical sequence of phases in thermotropic LCs with decreasing temperature is as follows. At a high enough temperature the LCs exist in the isotropic phase. Here the molecules have no positional and no orientational order. By decreasing the temperature T the LC phases appear in the following sequence: below the isotropic phase, at $T = T_{IN}$ the nematic phase is reached. Here the molecules have no positional order, however, they tend to be aligned along a LC director $\bar{n}$. Below the nematic phase the smectic phases can be found in some materials. Here the molecules are arranged in layered structures. First a smectic A (SmA) phase is established at $T = T_{NA} < T_{IN}$. In this phase the molecules are arranged on a macroscopic level in equidistant and parallel layers. Molecules are on average oriented along the layer normal $\bar{\nu}$. Further on, at $T = T_{AC} < T_{NA}$ a smectic C (SmC) phase is reached, where molecules become tilted with respect to $\bar{\nu}$. In the case of chiral molecules the structural ordering exhibits a helical structure, and due to symmetry reasons the electrical polarization, $\bar{P} \propto \bar{n} \times \bar{\nu}$, appears. As a result the ferroelectric phase (SmC*) is established.

So, the difference between LCs and the other states (solid, liquid) is a tendency of the liquid crystal molecules to establish an orientational order, i.e., mesogens to point along a director. In a liquid state the intrinsic positional order does not exist and on the other hand, in the solid state the molecules are highly positionally ordered. As we saw above, the orientational order of the LC phases is between traditional solid and liquid phases.

Today, LC systems play an important role in modern technology. They can be used in a variety of optical applications due to their ability to significantly change their

macroscopic properties under the various external stimuli like, the change in the electric or magnetic field. Their ordering properties can also be controlled by various surface anchoring and wetting effects.

Elastomers are rubbery materials which after the removal of the external force quickly return in the initial state, i.e., in the state with the initial shape and size. Their basic structure is the fixed polymer topology consisting of polymer chains linked together via crosslinking elements into a gel network [12]. The crosslinkers play an important role in the elastic behavior of elastomers. They prevent the disentanglement of the polymer chains in the case of deformation.

Therefore, the main characteristic of elastomers is that they respond via a reversible deformation of the polymer chains on the external perturbations. An applied external force changes the elastomer material from an isotropic disordered into an anisotropic ordered state. In relation to the polymer chains' perturbations a free energy can be introduced. The polymer network chains have the minimum free energy in their non-deformed, natural state, and the free energy increases with deformation. Due to this property, elastomers are considered as solids without regard to properties like flexibility, fluidity and disorder that are typical for liquids. However, elastomers are an important class of polymers. They are very elastic, i.e., they can extend up to eight times of their original length without any irreversible transformation after the deformation removal [12]. This property makes elastomers widely used for different applications.

It is natural to expect that a combination and the interaction of both LCs and elastomers in the LCEs will bring about some new, interesting physical properties, which will be discussed later in Chapter 3.

1.2 Electrocalorics

The electrocaloric effect, i.e., the conversion of electrical energy to heat and vice versa, is potentially of great importance in a broad range of applications like sensors and heating and cooling devices of the new generation, which could be friendlier to the environment. The effect has been known for about 80 years, but it was not considered to be useful for commercial applications, due to its small magnitude in previously known materials [62]. The recent revival of ECE research is related to an increasing interest in alternative cooling technologies. Lately, a giant ECE was predicted in some organic and inorganic materials [62-69]. These predictions were based solely on indirect measurements of the electric polarization P as a function of the electric field and the temperature and not on direct measurements of the ECE itself. The ECE response was actually calculated from the $P(T, E)$ by using Maxwell thermodynamic relations, assuming reversibility of the thermodynamic process [62]. More details about the indirect method will be provided in Chapter 4.

The microscopic mechanism of the ECE is not fully established yet [62, 63], but the general idea how to explain it revolves around the change of the entropy S , which is stimulated by an electric field, i.e., induced by the change of the ferroelectric dipolar state in a dielectric material. Until recently, it was not even clear whether the maximum in ECE occurs above, below or at the phase transition [62]. The experimental and theoretical results presented here, investigate these issues with any special focus on the behavior of the ECE in the vicinity of the critical point.

In recent times the needs around energy capacities for production increase, and consequently there is a pressure on the environment. In order to solve this problem, some measures were taken to reduce energy consumption, like for instance, the energy labeling of household devices. However, such measures are not enough. The solution could be

found in the development of more energy efficient and environmentally acceptable technologies. Here, the new, advanced electrocaloric cooling devices based on electrocaloric materials can play a significant role.

Nowadays, we are familiar with the cooling devices that use classic compression/expansion type cooling cycles as well as thermoelectric [70, 71] and magnetocaloric cooling devices [72, 73]. In the case of thermoelectrics the temperature change of the material is achieved due to the direct current through the material. This, so-called Peltier element, is used, for example, in wine refrigerators and in micro-cooling devices, such as portable cooling boxes and CCD chip coolers. The weakness of these elements is in the low energy efficiency and in the additional resistive or Joule heating due to the current through the thermoelectric material. At higher powers for each watt of heat taken out on cooling side, three watts of excessive heat are produced on the hot side of the thermoelectric device, thus significantly limiting their use. The magnetocaloric effect is analogous to the ECE except that in the case of magnetocalorics the temperature change in the material is achieved by changing the magnetic field. Here a disadvantage lies in the difficulty of producing inexpensively and with small devices, large magnetic fields. For example, to produce magnetic fields above 5 T, large and expensive superconductive magnets are required. Currently, magnetocalorics are only used for very special purposes in laboratories and perhaps for some large cooling devices.

The alternatives for an energy-efficient and environmentally friendlier cooling technology are devices based on electrocaloric materials. In contrast to magnetocalorics these materials exhibit a temperature change under an applied/removed electric field. As dielectrics these materials are typically very good insulators and usually they do not suffer problems related to the resistive Joule heating. Due to the possible miniaturization they are very promising for a broad variety of applications. Besides having strong potential to be used in different standard cooling and heating devices, such as commercial refrigerators and heating pumps, they can also be tailored for almost any application in microrobotics, and in microelectronics for cooling the electronic elements.

In this thesis, direct measurements of the ECE in various inorganic and organic ferroelectrics and relaxor ferroelectrics will be presented [74-85]. Some of them were first direct measurements confirming the existence of a giant ECE in relaxor bulk and thin film materials. It was shown that the observed ECE magnitude is, generally, in ferroelectrics, consistent with a recent prediction based on indirect measurements via electric polarization. However, in relaxor ferroelectrics a significant discrepancy was observed between the ECE results obtained in the indirect and direct way indicating the breakdown of the Maxwell thermodynamic expression in relaxor materials, most likely related to the breakdown of the ergodicity in these systems. Since the ECE studies have been made in normal ferroelectrics and also in relaxor ferroelectrics, in the next paragraph the basic properties of these materials will be presented.

The ferroelectricity and relaxor behavior were already investigated in the 1950s in different inorganic materials [86]. Due to a very large dielectric constant, polarization, and electromechanical response, the relaxor ferroelectrics were especially promising for various applications like capacitors, transducers, sensors, medical ultrasound devices, etc. Besides the inorganic relaxor materials it has been known that organic materials, for example, certain types of polymers, also show relaxor ferroelectric properties that include a giant electromechanical response [87, 88].

Ferroelectrics are defined as materials whose intrinsic lattice polarization P can be reversed, if the applied electric field is larger than the coercive field. Usually, they have a phase transition temperature T_C above which they are paraelectric, i.e., above which the spontaneous polarization vanishes [64]. Besides the usually inorganic ferroelectrics, ferroelectric polymers have also attracted considerable attention [87, 88]. They have

certain advantages, like for instance, they are flexible and light weight and they can be prepared in different shapes.

A universal property of the relaxor state is a broad frequency-dependent peak in the real part of the temperature-dependent dielectric susceptibility or dielectric constant $\varepsilon'(T)$ [89]. The temperature T_m of the peak is shifted to higher temperatures with increasing frequency and it defines the dynamic freezing, i.e., the glass-like transition temperature T_f . Above this temperature the strong frequency dispersion in $\varepsilon'(T)$ is observed, associated with the slowing down of dipolar fluctuations within the polar nanodomains. At a low enough temperature all the dipolar motion freezes and the dispersion vanishes [69, 89]. A similar dispersion can also be observed in the imaginary part of the dielectric constant ε'' due to the Kramer-König relations.

The schematic diagram of a typical relaxor has three different regions [90, 91]. At high temperatures the ergodic relaxor state exists and below the freezing temperature a nonergodic state is observed. The ferroelectric properties in the electric field (E)-temperature (T) phase diagram are only observed when the applied dc bias electric field is higher than the critical electric field $E_C(T)$. Therefore, relaxors are materials that combine the properties of ferroelectrics and glassy materials [69, 92].

The phase transition from the ergodic to ferroelectric phase can be induced with a large external dc bias electric field [90]. The polar micro-regions start to merge into a normal ferroelectric. This transformation is shown in a frequency-independent step change in the dielectric susceptibility and polarization [90, 91].

Next, let us take a look at the major differences between ferroelectrics and relaxors.

In normal ferroelectrics the temperature dependence of the dielectric susceptibility shows a sharp, narrow peak and it follows a Currie-Weiss law [90]. Its temperature position is typically frequency independent. Furthermore, spontaneous polarization in the ferroelectrics sharply (in the case of the first order phase transition) or continuously (in the case of the second order phase transition) vanishes at the ferroelectric (FE) transition temperature T_C . Above this so-called Currie-Weiss temperature no polarization is observed. Next, the P-E hysteresis loop in the FE material is rather wide and the large remanent polarization is a manifestation of the strong cooperative nature of the ferroelectrics [89].

In contrast, the relaxor materials exhibit a very broad temperature-dependent dielectric susceptibility peak and a strong frequency dispersion in the peak temperature T_m and in the values of ε' below T_m [69]. Relaxors exhibit a strong deviation from the Currie-Weiss law for temperatures of some few hundred degrees above T_m . Here the slim P-E hysteresis loops can persist even at high temperatures.

The difference between ferroelectrics and canonical relaxor materials, like Lead Magnesium Niobate (PMN), also results in the nature of the low-temperature phase transition. The FE transition involves a macroscopic symmetry change at T_C and it can be of the first or the second order. In a canonical relaxor material like PMN there is no phase transition across T_m . Thus, the peak in $\varepsilon'(T)$ is a consequence of the slowing down of the dipolar motion which freezes below the freezing temperature T_f [69, 92]. In general, the glassy properties of relaxor materials closely resemble those observed in dipolar glasses [92].

From all the presented features it is clear that the physical properties of normal ferroelectrics are very different from those of relaxors.

There also exist materials that possess characteristics of both, i. e., ferroelectrics and canonical relaxors. These systems were first proposed by Burns and Dacol [93]. There exists the coexistence of the polar micro-domains and polar nanoregions [94]. In these materials it is possible that on cooling the material a spontaneous transformation towards a long-range ferroelectric ordering occurs even without an electric field, if the thermal

fluctuations are not strong enough [95].

The large polarization and the large number of polar nanoregions that can lead to an extra entropy contribution in relaxor ferroelectrics result in the giant electrocaloric effect in these materials [74, 96]. It has already been reported that a normal ferroelectric can be converted into a relaxor ferroelectric by using either high-energy radiation [97] or by chemical synthesis [63, 98].

Utilizing direct measurements of the ECE change of temperature, the electrocaloric effect has been studied as a function of the electric field step in various bulk, thick and thin films of relaxor ferroelectric ceramics [74, 76, 80, 83, 85] and also in thin films of normal ferroelectric and relaxor ferroelectric polymers [75-79, 81, 82, 84]. Details of the sample preparations will be presented later in Chapter 4. The relatively large temperature change ΔT_{EC} of 2-3 K was obtained at a modest field of 90 kV/cm, even in the case of bulk ceramic materials, while in thin films the ECE was in the range between 10 and 40 K. The ECE temperature changes were obtained by using a high-resolution calorimeter [99-101] with a small modification to the experimental setup and the software. Details will be presented later in Chapter 4 along with the details of the ECE data analysis by using the zero-dimensional model, which can be used due to the fast internal thermal response times in the measured ECE materials.

The experimental studies also indicated that the effective ECE responsiveness shows a characteristic peak near the critical point [91, 102-106], demonstrating its relevance for the enhancement of the ECE [74-85]. It is shown that the ECE behavior determined from the direct measurements is in a good agreement in the vicinity of the critical point with the theoretical predictions [83, 107, 108].

However, in order to find the effective materials for ECE applications the refrigerant capacity that measures the quality of the cooling materials is presented at the end of Chapter 4. It indicates that the relaxor ferroelectric thin films are the most prominent materials that show an extremely large ECE [83] and thus very good cooling potential.

1.3 Magnetoelectrics

Magnetoelectrics have recently been attracting considerable attention due to their properties, i.e., in such materials it would be possible to control the magnetic properties via electrical ones, and vice versa, and also due to their potential for applications, for example, in the information-storage industry [109]. The magnetoelectric effect is well known to exist in solid materials and solid composites. Recently, the development of a soft material based on mixtures of a liquid crystal and magnetic nanoparticles (NPs), which would show magnetoelectricity, has become a holy grail. It has turned out that it is difficult to produce stable colloidal mixtures of LC and magnetic NPs due to the rapid separation of the magnetic nanoparticles from the mixture.

The systems involving NPs are becoming of great interest to the scientific community. In recent years there were several efforts to synthesize new nanoparticles with extraordinary properties. It is known that mixtures of NPs mixed with some conventional materials could exhibit special behavior not found in the individual components [110]. Lately, attention has been paid among other NPs also to more complex nanostructures, like for instance, carbon nanotubes (CNTs). These materials exhibit remarkable properties in a single direction along the tube axis. Due to their symmetry, size and mechanical properties, they are a very promising material for applications in nanotechnology [111]. The different production methods of CNTs [112-114] result in complex aggregates in which the anisotropic properties are reduced. The standard techniques that can align the CNTs, like field-assisted alignment [115], shearing [116] and molecular combing [117]

processes, are either too complicated for applications or they do not align CNTs well over the macroscopic scales. Thus, attention was paid to the development of an efficient and relatively simple technique that will be appropriate for CNT alignment. Such a technique could be the preparation of a mixture of CNTs and the liquid crystal.

Namely, it was found that LC alignment can control the assembly of organized CNTs and also other nanomaterials [118, 119]. Specifically, it was found that CNTs in nematics orient parallel to the director and that the order in CNTs can be controlled via the alignment of LC molecules by an external electric or magnetic field. However, LCs can also control the order in the other nanometer and micro-sized building blocks. In recent years a wide range of nanoparticles have been studied, like quantum dots, clusters, fullerenes, etc.

Earlier studies are related to the bulk LC alignment in solutions of the small magnetic particles in nematic solvents [121]. In these systems the particles increase the response of the LC to the weak magnetic fields. Particles can align parallel or perpendicular to the director, depending on the particle size and the nature of the LC anchoring to the particle surface [121]. Several theoretical studies on rod-like particles immersed in nematic LCs [121-127] have shown that the functionalisation of NPs is important.

The surface coating of the NPs was originally used to avoid the phase separation of NPs [128]. Later, it was found that the surface coating of NPs also has an impact on the interaction between NPs and LCs. Some studies were also made on ferrosmectics, i.e., in mixtures of smectic LCs and magnetic NPs [128]. Actually, LCs and NPs affect each other. The LCs help to align the NPs and the NPs have the opposite impact on the LC phases and phase transitions. In particular, it was shown for example that the magnetic nanoparticles with a different surface coating have an impact on the phase transition of an octylcyanobiphenyl (8CB) liquid crystal [129].

In addition, the quenched random disorder (QRD) effects of the phase transitions and critical phenomena in the LCs in porous media were investigated [130, 131]. These effects are interesting for many areas of soft condensed matter [130, 131]. T. Bellini et al. showed that the behavior of the nematic phase is distorted by QRD. This experimental work proved the so-called Imry-Ma argument [132], i. e., that even a small amount of disorder would suppress the long range nematic order.

Furthermore, aerogels [133, 134], hydrophilic and hydrophobic silica aerosils [135-139], controlled porous glasses (CPGs) [140, 141], vycor glasses [142], and anopores [143] were studied to observe their impact on LCs. Different dispersions, like those of colloidal [144], ferroelectric [145], gold [146] and magnetic [147] NPs have been investigated. These systems are very promising for various photonic applications [144, 146, 147]. The mentioned studies are also important to better understand the impact of QRD and confinement on LCs. In the case of aerosil nanoparticles the strong impact of the aerosil concentration upon the transition was observed. The calorimetric studies [137, 138] show several finite size effects when the concentration of the aerosils is increased. For instance, it was observed that the heat capacity anomaly is shifted to a lower temperature and it becomes smeared and suppressed [137, 148, 149].

Considerable attention was also paid to the impact of NPs on the liquid-crystalline blue phases (BPs) observed in chiral LCs. BPs exhibit a large potential for applications in photonics and display technologies [150]. Their application potential is mainly hindered by the narrow temperature range in which they appear. In recent years intensive research efforts have been in progress to achieve stabilization of these phases over a wide temperature range [151-153]. In particular, the blue phase III is of great technological interest [153]. It was shown that the temperature range where the BPIII phase is stable is greatly enhanced in homogeneous mixtures of LCs and NPs with the appropriate size and surface functionalisation [154-156].

Studies of magnetic colloids started in the 1960s. Attention was paid to the systems composed of liquid carries and magnetic NPs [157]. The originality of such systems is based on the magnetic properties of the NPs. Each nanoparticle is a magnetic monodomain. This means it has a permanent magnetic dipole, which is fixed, and its direction can fluctuate inside the gain. Studies were also performed in the field of magnetic NPs in self-assembled surfactants, i.e., dispersed in a confined geometry [157].

Since the main feature of magnetoelectrics is the so-called magnetoelectric effect, in the next paragraph the basics of this effect will be briefly introduced.

The magnetoelectric (ME) effect was first predicted in the 19th Century when in 1888 Röntgen found that a moving dielectric becomes magnetic when it is placed in an electric field [158] and more than ten years later the reverse effect, i.e., the existence of the polarization of a moving dielectric in a magnetic field was shown [159]. The possibility of an intrinsic magnetoelectric behavior in non-moving crystals was discovered in 1894 by Curie. Later on, the first experiments to demonstrate the static ME effect were carried out [160]. But these attempts were unsuccessful.

Curie predicted in his work that symmetry is a key issue in the existence of the ME effect [161]. Many decades later it was recognized that the ME response can happen only in time-asymmetric media [162]. Time-asymmetry was first shown by Dzyaloshinskii [163] in antiferromagnetic Cr_2O_3 material. Later on, in this system the electric-field-induced magnetization and magnetic-field-induced polarization were experimentally confirmed [164, 165]. However, in these first studies the ME effect was small and thus it was not useful for applications [109, 160].

In 1990 studies of the ME effect gained momentum due to the possibility of the existence of a large ME effect in composite materials. Composites can show the ME response even in the case when their constituents do not show the ME response [109, 160]. The very idea to synthesize a composite material that could show the ME response was already discussed in 1948 by Tellegen [166]. It was suggested to prepare suspensions of macroscopic particles that have both electric and magnetic dipole moments. It was also suggested by H. Zheng [167], experimentally, that self-organized nanocomposites can show an efficient coupling between the phases. Later on, there were several attempts to develop a magnetoelectric material consisting of two components, one ferromagnetic and the other ferroelectric, at room temperature [168].

Magnetoelectric coupling describes the coupling between the magnetization and the polarization of a material [109]. This coupling can be measured indirectly by measuring the changes in either the magnetization near the ferroelectric transition temperature or the dielectric constant near the magnetic transition temperature. More relevant are the direct measurements that investigate either a magnetic response to an applied electric field or an electric response to an applied magnetic field [109].

The ME effect is mathematically described by the ME coefficient that coupled the magnetic and the electric field and it is large if this coefficient is large [169].

ME composites are very promising for various technological applications like magnetic sensors, transducers, filters, ME recording heads, memory devices, etc. [109, 169]. The coupling between the two composites can permit data to be written electrically and read magnetically depending on parallel or anti-parallel magnetic and electric fields [109, 169].

It is suggested that the proper nanoparticle size for ME applications is between 10 and 20 nm [170, 171]. But the problem is the colloidal intrinsic instability over a long time. Particles tend to form agglomerates in the colloidal suspension, thus reducing its stability. Therefore, it is necessary to find a strategy to stabilize the colloidal suspension. One of the suggested methods is coating the NPs with organic polymers to increase the viscosity. This strategy helps to prepare the stable and robust magnetic NP suspensions in various

solvents [170]. However, so far it did not help to stabilize the suspensions of magnetic NPs and LCs, at least not on a long time scale exceeding weeks.

In this thesis a way to avoid the problems related to producing stable colloidal mixtures of LC and magnetic NPs and how to successfully prepare the first mixtures of LCs and magnetic NPs that are stable on a time scale exceeding several months is presented [172-174]. In due process the first soft magnetoelectric materials were thus produced. Such materials can lead to the production of new, enhanced, soft magnetoelectrics, which can potentially find applications in electronics, spintronics, for the detection of low magnetic fields, etc.

To conclude, our studied materials mentioned above (liquid crystal elastomers, electrocalorics, and soft magnetoelectrics) are currently hot topics of condensed matter physics because of their potential perspective for various applications and also, due to the basic research point of view, very interesting physical properties which are not yet fully examined and understood.

2 Experimental techniques and methods

In order to study all three systems, i.e., LCEs, electrocalorics and soft magnetoelectrics, a variety of experimental techniques have been employed.

The LCE systems were investigated by using a high-resolution ac calorimetry [99-101]. The calorimetric data described in this thesis were supported by deuteron-perturbed nuclear magnetic resonance (deuteron NMR) data performed by Dr. Andrija Lebar [29, 31, 175]. The ECE in various organic and inorganic materials have been studied using a new method, so called electrocaloric thermometry. This technique exploits the benefits of an excellent temperature stabilization and measurement accuracy of the high-resolution calorimeter. Electrocaloric thermometry is similar to high-resolution calorimetry up to the point that instead of driving the sample with heat power a special form of electric field is applied to the sample. New soft magnetoelectric materials were characterized by using a SQUID susceptometer [176], X-ray spectroscopy [177], and transmission electron microscopy (TEM) [178].

Here, a high-resolution calorimetry and dielectric spectroscopy will be presented in detail. The details of the electrocaloric thermometry will be presented later in Section 4.

2.1 High-resolution calorimetry

The heat capacity measurement technique is a useful tool for studying the critical behavior in the vicinity of different phase transitions. The obtained informations about the heat capacity C_p and the enthalpy as functions of the temperature T for various classes of transitions play an important role in characterizing the phase transitions that occur in condensed systems [100]. In comparison to the several known calorimetric techniques like differential scanning calorimetry (DSC) [100] and traditional adiabatic calorimetry [179], the most widely used high-resolution methods are high-resolution ac- and relaxation calorimetry. Both the ac and relaxation mode can be used to obtain the heat capacity $C_p(T)$ in the vicinity of the selected phase transition, and to distinguish between the first, i.e., discontinuous and the second, i.e., continuous order of the particular transition. The combination of both modes can be used to detect the latent heat L when present.

Traditional adiabatic calorimetry is a classical method for enthalpy and heat-capacity measurements. It measures the total heat capacity of the sample and the sample cell, and because the sample cell's heat capacity is usually quite large, a relatively large sample is needed. To achieve a good resolution the scanning rate, i.e., the temperature change step should be small. This makes the method slow. On the other hand, the most common technique used in studies related to phase transitions in LCs is DSC. Its advantages are reflected in its very high sensitivity to enthalpy changes of around 0.01 J/g, a small sample size of around 10 mg, and in good operation procedure using commercial instruments with flexible computer software. DSC is an ideal initial technique, useful for discovering a new phase transition, but it is not useful for detailed measurements near the phase transitions [100].

The high-resolution calorimetry technique was developed in the middle of the previous

century, and in the following years it was used in various studies in soft and also in solid materials for characterizing their phase transitions and critical phenomena [91, 180].

In our studies a home-made, dual-mode computerized calorimeter (Figure 1) operating in the ac and relaxation modes over a broad temperature range between 80 and 470 K has been used. The ac mode provides only quantitative information related to the continuous changes of the enthalpy and the relaxation mode also detects the discontinuous part of the enthalpy, i.e., the latent heat L .

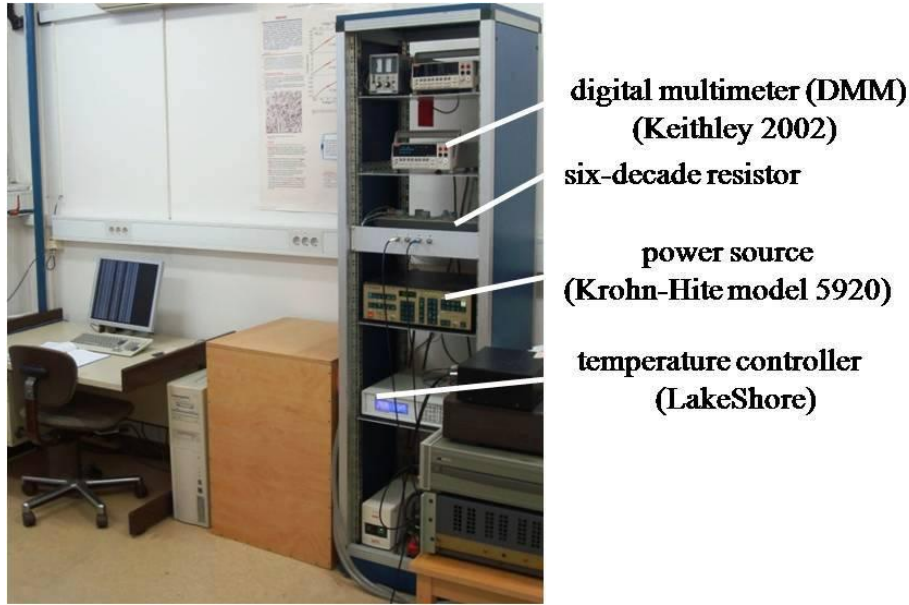


Figure 1: *Home-made calorimeter at the Jožef Stefan Institute.* The whole calorimeter setup consists of different parts, i.e., a thermal bath, electronic devices and a computer.

The high-resolution calorimeter setup can be represented by a simple diagram of a thermal system consisting of a sample with a heat capacity $C_{p, \text{sample}}$ and a heater. A sample with the attached thin resistive heater that provides the input power is connected to a temperature-controlled bath stabilized to within 0.1 mK. This thermal link is represented by the thermal resistance R , typically between 200 and 250 (Figure 2). Such a model called the “zero-dimensional” model of thermal analysis [99] can be used in the case when the internal thermal diffusion time τ_{INT} of the sample is small enough and the temperature gradients in the sample can be neglected. The sample temperature $T_s(t)$ is detected by a small-bead thermistor that is attached on the opposite side of the sample to the heater.

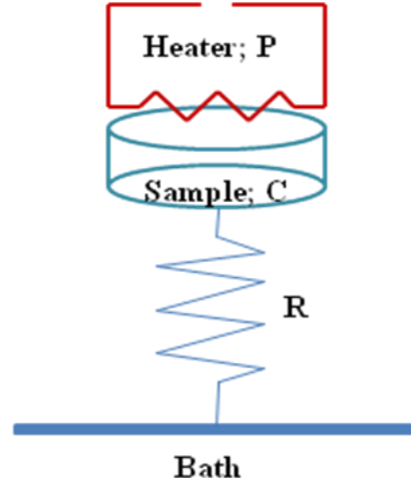


Figure 2: Simple diagram of the calorimeter thermal system. A sample with an attached heater is connected with a temperature-stabilized bath via a thermal link represented by the thermal resistance R .

Generally, the heat input power $P=dW/dt$ usually causes dissipating electrical work in the system. The conversion of energy in the calorimeter for a constant pressure process is given by [99, 100]

$$P = C_p^{\text{sys}} \frac{dT}{dt} + \frac{dL}{dt} + \frac{T - T_B}{R} \quad (1)$$

where $dL=L_1dm$ with L_1 is the latent heat per gram related to the first order phase transition and dm is the mass of material converted from one coexisting phase to another. T and T_B denotes the temperatures related to the sample and the bath, respectively, and the $C_p^{\text{sys}} = C_{p,\text{sample}} + C_{p,\text{cell}}$ is the total heat capacity of the sample and the cell.

In the case when the two-phase coexistence is absent it follows from Eq. (1) that

$$C_p^{\text{sys}} = \frac{dH/dt}{dT/dt} = \frac{P - (T - T_B)/R}{dT/dt}. \quad (2)$$

In the presence of the two-phase coexistence during a first order phase transition, and if the phase interconversion occurs, an effective heat capacity is defined by

$$C_{\text{eff}}^{\text{sys}} = \frac{P - (T - T_B)/R}{dT/dt}. \quad (3)$$

The released or absorbed latent heat is given by

$$L = \int_{T_a}^{T_b} \{ C_{\text{eff}}^{\text{sys}} - [C_{p,\text{coex}} + C_{p,\text{cell}}] \} dT, \quad (4)$$

where $C_{p,\text{coex}} = X_\alpha C_p(\alpha) + X_\beta C_p(\beta)$ is the heat capacity of the two coexisting phases, $\alpha+\beta$, over a narrow coexistence range from T_a to T_b . X_α and X_β represent the mass fractions of the α and β phases. Since the coexistence range is small, one can take $C_p(\alpha)=C_p(T_a)$ and $C_p(\beta)=C_p(T_b)$. Eq. (4) is equal to

$$L = \int_{t_a}^{t_b} \left(P - \frac{T - T_B}{R} \right) dt - \int_{T_a}^{T_b} [C_{p,coex} + C_{p,cell}] dT, \quad (5)$$

where t_a and t_b are the corresponding times related to the appearance of the coexisting temperature T_a and T_b during the temperature variation.

A good design feature of the high-resolution scanning calorimeter is the very precise control of the thermal shield and the high-resolution measurements of the sample temperature $T(t)$ [99, 100]. The calorimeter is able to operate in several modes during cooling and heating. The most attractive mode includes heating with a constant power ($P=const.$) and with the shield temperature equal to the sample temperature. Here Eq. (3) becomes simply

$$C_{eff}^{sys} = \frac{P}{dT/dt} \quad (6)$$

and Eq. (5) becomes

$$L = H(T_b) - H(T_a) - \int_{T_a}^{T_b} [C_{p,coex} + C_{p,cell}] dT. \quad (7)$$

The ac calorimetry method was first introduced in 1960s [181] and later on it was used in various studies [99, 100]. This method could be employed for small samples around 10-100 mg and it can operate with a sufficiently slow heating and cooling rate with perfect resolution in the $C_p(T)$ since the oscillating temperature amplitude ΔT_{AC} can be small, i.e., around 5 mK.

A disadvantage of this method is related to the fact that it measures C_p directly and not the enthalpy H . In addition, it cannot measure quantitatively the latent heat in the case of the first order phase transition. However, a clear qualitative indication of two-phase coexistence in the phase shift of the signal $T(t)$ can usually be found [182].

For ac calorimetry the sinusoidal oscillating power $P_{AC}e^{i\omega t}$ is applied to the sample by a thin resistive heater, and the frequency value ω is chosen so that it prevents any gradient in the temperature inside the sample, and enables a good thermal link between the sample and the bath. The typical frequency value in our case, for the calorimeter at Jožef Stefan Institute (JSI) is $\omega = 0.0767s^{-1}$, so that $1/\omega \ll \tau_{INT}$, where τ_{INT} is the characteristic internal time for the thermal diffusion in the sample cell. The sample temperature oscillations $T_{AC} = P_{AC}/(1/R + i\omega C)$ are detected by the thermistor with a room temperature resistivity ranging from 1 k Ω to 1 M Ω . Here C denotes the complex heat capacity $C = C'(\omega) - iC''(\omega)$, which is in most cases frequency independent, real quantity, i.e., $C'' = 0$.

The phase shift of T_{AC} is given by

$$\tan(\phi) = \frac{1}{\omega RC'} + \frac{C'}{C''} \quad (8)$$

and it is useful for detecting the presence of the latent heat because it exhibits the anomalous peak in the two-phase coexistence range [59, 182] (Figure 3). As mentioned above, the ac mode can reliably observe only the second-order transition. It precisely measures the heat capacity as a function of the temperature $C_p(T)$, i.e., the continuous part of the enthalpy changes

$$\delta H = \int C_p(T) dT, \quad (9)$$

but it does not provide any quantitative information about the latent heat. For this reason the relaxation mode is required.

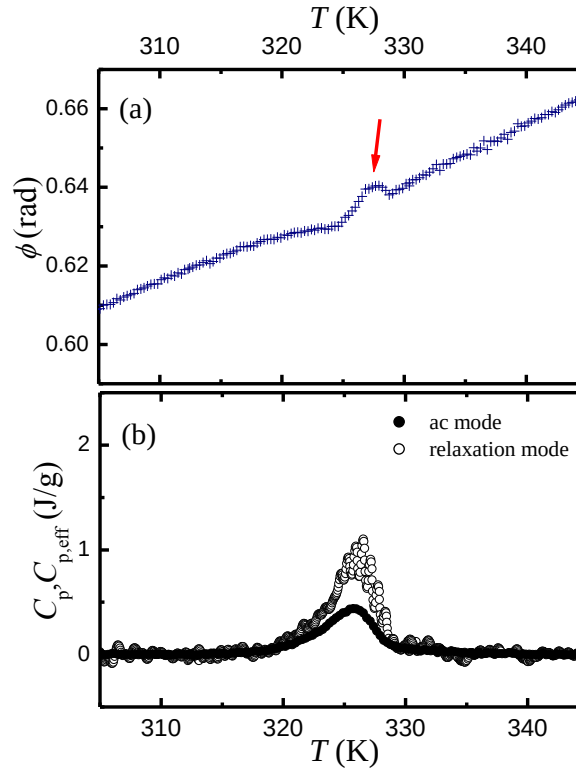


Figure 3: The $\phi(T)$ profile extracted from the ac mode. $\phi(T)$ shown in (a) indicates a first order transition (red arrow). For comparison the ac and relaxation data are shown in (b). See explanation around comparison between the ac and relaxation runs below [59].

Relaxation or non-adiabatic scanning calorimetry was first developed and experimentally used in 1974 [182], after which it was upgraded [99]. The basic advantage of this technique is that it can detect a very small latent heat (a few mJ/g) in relatively small samples. But on the other hand, this method exhibits somewhat larger noise in $C_{p,eff}(T)$ data than the ac mode [99, 100].

Here the applied heater power P_{RELAX} can be a step or a linearly ramped function of time [99, 100]. In the case of a step power function, for a heating run, the power is switched from 0 at time $t=0$ to a constant value P_0 , and the opposite for a cooling run. From solving Eq. (1) in the absence of latent heat it follows that the sample temperature $T(t)$ behaves exponentially when R and C_p are taken as constants over the range from $T(0)$ to $T(\infty)$. Thus for the heating regime

$$T(t) = T_B + \Delta T_\infty [1 - \exp(-t / \tau_{ext})] \quad (10)$$

and

$$T(t) = T_B + \Delta T_\infty \exp(-t/\tau_{\text{ext}}) \quad (11)$$

for cooling. Here, T_B is the constant bath temperature and $\Delta T_\infty = RP_0$. The quantity $\tau_{\text{ext}} = RC_p$ represents the external time constant for the heat flow from a sample to the bath. Usually, runs are made in pairs, first a cooling and then a heating run, or vice versa [99, 100].

If a first-order phase conversion occurs between $T(0)$ and $T(\infty)$, the latent heat is given by

$$L = \int_0^\infty [C(t) - C_0] \dot{T}(t) dt. \quad (12)$$

The expression is equivalent to Eq. (5).

In the case when the applied external power is a linear ramped function, the situation is as follows.

During the heating the applied power is

$$P_{\text{RELAX}} = \begin{cases} 0, & t < 0 \\ \dot{P}t, & 0 \leq t \leq t_1 \\ 0, & t > t_1 \end{cases} \quad (13)$$

where t_1 is typically around 480 s for the calorimeter at the JSI. For $t \leq 0$, the initial sample temperature T_{INT} is equal to the bath temperature T_{BATH} , and for $t \gg t_1$ the sample temperature reaches a plateau $T(\infty) = T_{\text{BATH}} + RP_0$. In the cooling run the power profile is given by

$$P_{\text{RELAX}} = \begin{cases} P_0, & t < 0 \\ \dot{P}t, & 0 \leq t \leq t_1 \\ 0, & t > t_1 \end{cases} \quad (14)$$

Here the initial sample temperature T_{INT} is $T(\infty)$ and the final temperature is equal to T_{BATH} . The effective heat capacity $C_{\text{p,eff}}$ is calculated from

$$C_{\text{p,eff}} = \frac{dH}{dT} = \frac{P - [(T - T_{\text{BATH}})/R]}{dT/dt}, \quad (15)$$

where $R = (T(\infty) - T_{\text{BATH}})/P_0$ and P is the power corresponding to the sample temperature between T_{BATH} and $T(\infty)$ at some time $0 \leq t \leq t_1$. This mode can detect not only the continuous part of enthalpy δH , but also the discontinuous part, i.e., the latent heat.

The total enthalpy obtained here is calculated from

$$\Delta H = \int C_{p,\text{eff}}(T) dT. \quad (16)$$

This so-called ramp-relaxation method, where the applied power is a linear ramped function, is called non-adiabatic scanning calorimetry. In comparison to the previous relaxation technique when the power is a step function, it allows much better control of the T_B to be constant. The other advantage is the optimal behavior of dT/dt [100], which is now a much smoother function outside the coexistence range.

The difference between the integrals expressed by Eq. (16) and (9) obtained in the relaxation and ac modes, respectively, gives the latent heat value

$$L = \Delta H - \delta H \quad (17)$$

that provides information about the type of the phase transition. The non-zero latent heat L indicates the first order, i.e., discontinuous phase transition, and the absence of L shows the second order, i.e., continuous transition.

Some more details related to the calorimetry with respects to different problems studied in this thesis will be given in the corresponding chapters.

2.2 Linear Dielectric spectroscopy

Dielectric spectroscopy measurements were utilized in the case of the ECE and soft magnetoelectric studies.

The dielectric properties as function of temperature were measured in different electrocaloric materials in order to determine the ferroelectric-paraelectric phase transition temperature. This is important information, because it was shown that the maximum of the ECE takes place in the vicinity of this temperature [74-85, 91]. And the ECE temperature variation could also be predicted from the dielectric constant temperature behavior. For example, if the dielectric constant shows a smooth variation of temperature then the ECE is expected to be nearly constant in a broad temperature range [74, 75, 84].

In the case of soft magnetoelectrics, the dielectric measurements were used to check the impact of the NPs on the dynamical properties of the LC director field and to see their impact on the soft and the Goldstone mode [172, 173].

The complex dielectric constant $\varepsilon^*(T, \omega) = \varepsilon'(T, \omega) - i\varepsilon''(T, \omega)$ was measured as a function of the temperature using the HP48282A precision LCR meter. The dielectric constant was scanned at a few selected frequencies usually in the range between 20 Hz and 1 MHz on cooling or heating the sample with typical rates of 10 K/h.

More details about the dielectric measurements in these cases and the results will be presented in the corresponding chapters. Here the basics about the dielectric spectroscopy method are given.

As mentioned above the complex dielectric constant ε^* or the complex dielectric susceptibility χ^* ($\chi^* = \varepsilon^* - 1$) measurements were performed using the LCR meter. These quantities can be obtained via measurements of the complex resistivity $Z = R + 1/(i\omega C)$. The schematic diagram of the dielectric experimental setup is presented in Figure 4.

A dielectric constant is a measure of the response of polar entities to the applied external stimulus, for instance caused by the change of the electric field. To minimize the energy, the polar molecules tend to be oriented in a way that the dipole moments are parallel with the direction of the applied electric field E . Thus, the orientation of the molecules is time dependent after the external stimulus, i.e., the polarization relaxes to a

new equilibrium state. Since the susceptibility is a proportional factor between the electric field and the polarization, it is thus a frequency-dependent quantity.

The polarization P consists of two parts: the induced (P_{IND}) and the static (P_{STAT}) polarization [183, 184]. The induced polarization contribution reaches the value $P_{\text{IND}} = \chi_{\infty} \epsilon_0 E$ almost instantaneously at the beginning when the electric field is applied, i.e., it represents high-frequency polarizable contributions. After the electric field is applied the polarization typically exponentially relaxes to the static polarization value $P_{\text{STAT}} = \chi_s \epsilon_0 E$. Here, the quantities χ_{∞} and χ_s denote the high-frequency and the static dielectric susceptibility. The difference between the static and the induced polarization value is a consequence of the orientational polarization.

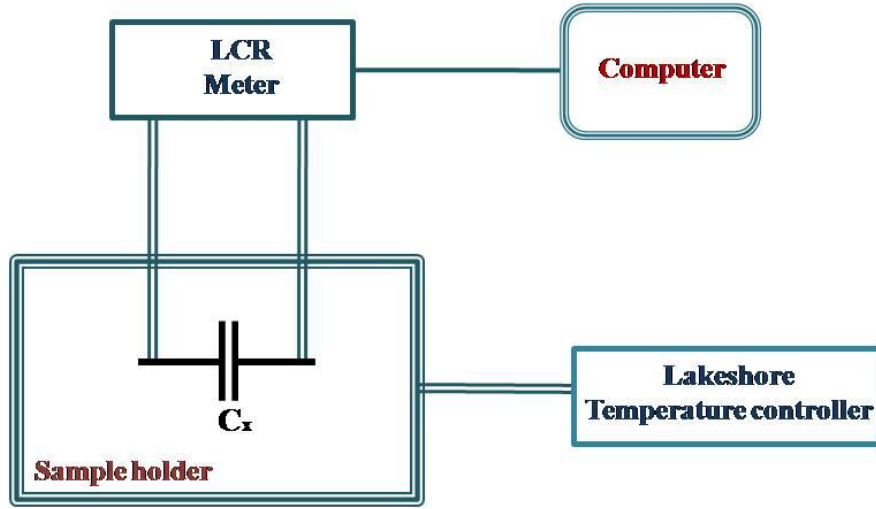


Figure 4: Schematic diagram of the experimental setup for the dielectric constant measurements; C_x denotes the sample capacitance.

The polarization P in the time interval $[t_1, t_1 + dt_1]$ is given by

$$P(t - t_1) = \chi_{\infty} \epsilon_0 \alpha(t - t_1) \epsilon_0 E(t_1) dt_1, \quad (18)$$

where $t_1 < t < t_1 + dt_1$ and the time-dependent orientation progress $\alpha(t - t_1)$ has the exponential form $\alpha(t) = \alpha(0) \exp(-t/\tau)$. Here, τ denotes the relaxation time that is a function of the temperature and the material's viscosity. For the applied electric field in the form $E(t_1) = E_0 \exp(i\omega t_1)$ at times $t > t_1 + dt_1$ the polarization is expressed as

$$P(t) = \chi_{\infty} \epsilon_0 E(t) + \epsilon_0 \int_0^t E(t_1) \alpha(t - t_1) dt_1 \quad (19)$$

and also it holds that

$$P(t) = P_0 e^{i(\omega t + \psi)} = \chi \epsilon_0 E(t). \quad (20)$$

Thus the complex dielectric susceptibility χ^* can be written as

$$\chi^* = \chi_{\infty} + \int_{-\infty}^t e^{i\omega(t-t_1)} \alpha(t - t_1) dt_1. \quad (21)$$

The constant $\alpha(0)$ can be obtained from the assumption that at $\omega=0$ the polarization P is parallel to the electric field E , and thus $\chi^* = \chi_s$. Thus it follows that

$$\alpha(0) = \frac{\chi_s - \chi_\infty}{\tau}. \quad (22)$$

With the use of Equations (21) and (22) and the integration by parts it follows that

$$\chi^* = \chi' + i\chi'' = \varepsilon' - 1 + i(\varepsilon'' - 1) = \chi_\infty + \frac{\chi_s - \chi_\infty}{1 + i\omega\tau} \quad (23)$$

or

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau}. \quad (24)$$

This is a Debye expression for a monodispersive relaxation process. The polydispersive relaxation process is described by making a convolution of the above equations with the appropriate distribution function of relaxation times $g(\tau)$, see more details in [184].

In the case of a non-ideal dielectric material with the final resistivity, Eq. (24) is written as

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau} + \frac{i}{RC_0\omega}. \quad (25)$$

Here, R denotes the sample resistivity and C_0 is the capacity of the empty measuring cell. This expression contains an additional imaginary part in comparison to Eq. (24). Here it was considered that for such a material

$$\frac{1}{Z} = \frac{1}{R} + i\omega C = i\omega C_0 \varepsilon^*. \quad (26)$$

More details about the dielectric spectroscopy techniques and measurements can be found in Refs. [183] and [184].

3 Nature of the PN-N transition in nematic LCEs and the thermo-mechanical response as a function of the chemical and physical parameters

Everyone knows that muscles play an incredibly important role in our bodies. Everything that we coerce with our brain, is expressed as muscular motion. Muscles are some kind of engine. Actually they work differently than, for example, electric motors, but they do the same thing, i.e., turn energy into motion. However, without muscles our body would not be able to move.

Many years ago scientists started playing with the idea of a merger between man and technology. At the beginning they produced simple limbs from wood, and later on they began looking for more comfortable materials. They successfully replaced natural limbs, for example, the knee or elbow, with artificial ones. Over the past decade many new materials that can be used as artificial muscles have been developed. Attention was paid to materials that can replace natural muscles when they fail, or assist them when they become weak. A muscle-like technology would also be useful for other medical implants and different human-assisting devices. However, muscle-like materials are important for a wide range of different applications like sensors, biomimetic devices, different nanoscale machines, micro-electronical systems, and others [2-11]. The important applicable property of such promising materials is the change of their dimension due to the different perturbations, like electric field, light or temperature change.

Nevertheless, in the quest to find a replacement for our natural muscles we need first to know the fundamental muscle properties, i.e., to understand their structure and the mechanical basics of their function. The primary purpose of a muscle is to generate a movement which is manipulated by nervous systems. Muscles are anisotropic substances that shrink and stretch along the muscle fibers [185-187]. The basic parameters that describe their operation are contraction/elongation, mechanical tension and the time of expansion. Muscle motion is limited by the maximum values of those parameters whose typical values are 25% for contraction, 350 kPa for tension and 0.2 to 0.1 s for the duration of the response [185, 187]. So, nowadays we know the muscle composition and their functions, but we are still not able to produce a real artificial muscle. The problem is that we cannot find the proper materials, i.e., materials with properties similar to natural muscles. However, around 1994 a new type of materials was developed that is very promising for different applications, also potentially for artificial muscles. These materials are liquid crystal elastomers. As the name suggests these materials possess properties of liquid crystals and elastomers (Figure 5), i.e., the orientational order of liquid crystals is combined with the elasticity of polymer networks [12]. Their interesting and potentially the most attractive feature is the thermomechanical response. This means their large spontaneous change in geometry, i.e., spontaneous shrinking and stretching with the temperature change.

In this thesis we limit ourselves to nematic LCEs because they are the most promising materials for artificial muscles and other applications.

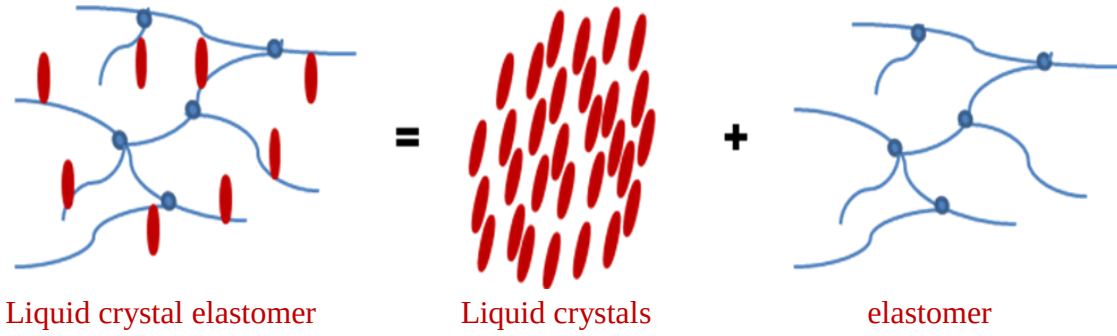


Figure 5: *Schematic presentation of liquid crystal elastomers (LCEs)*. LCEs bring together the orientational order of LCs and the rubber elasticity of crosslinked polymers.

It is common knowledge that there exist four states of matter: gases, liquids, solids and plasma. However, there also exists the state that does not belong clearly to one of the above mentioned states, i.e., liquid crystals. These materials contain phases between the liquid and the solid state, and they consist of anisotropic molecules called mesogens. Typically, with decreasing temperature isotropic, nematic and smectic phases can be observed in many LCs (Figure 6). As we mentioned in the Introduction, LCs can be divided into two classes, thermotropic and lyotropic LCs. The difference between them lies in a parameter that controls the liquid crystallinity. In our case, we focused on thermotropic LCs formed by anisotropic rod-like molecules with a long-range orientational order. The important feature of these molecules is a rigid aromatic core to which one or more alkyl chains are attached [61]. In order to define a few physical quantities that will be needed later, we will first consider within next few paragraphs the properties of nematic ordering and later on some basic properties of the polymer network like elastomers.

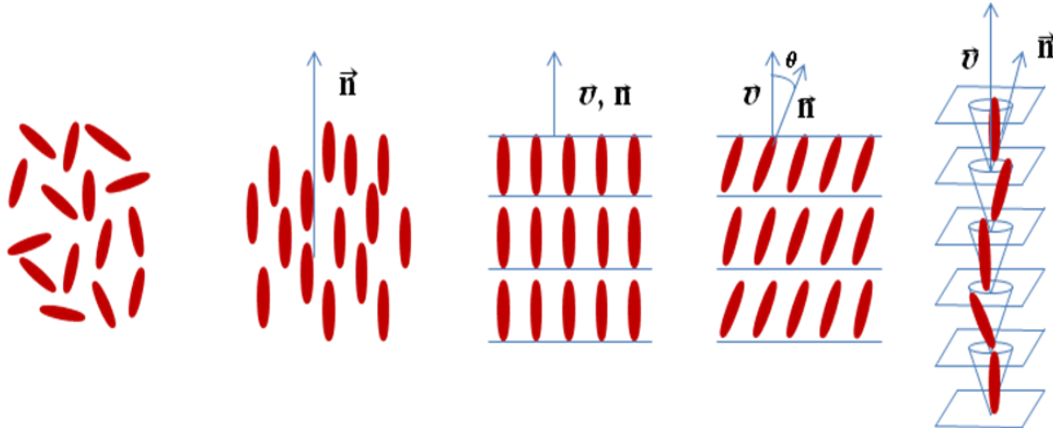


Figure 6: *A simple presentation of liquid crystal (LC) phases*. From the left to the right the isotropic, nematic, smectic A, smectic C and the helical structure of the smectic C* phase are shown.

The nematic phase is the simplest of all LC phases after the isotropic one. As it was mentioned above, in the nematic phase molecules do not possess positional order, but they self-align into the long-range orientational ordered state with their long axes roughly parallel. This means the molecules are free to flow, while having an orientation along the average direction of all the molecules, i.e., along the nematic director $\vec{n}$. Here, $\pm \vec{n}$ orientations are equivalent due to the physical point of view. The fluctuations of LC

molecules around $\bar{n}$ are described by the nematic order parameter, defined via the average of the second Legendre polynomial [12, 61]

$$\bar{S}(\bar{r}) = \langle P_2(\cos \theta) \rangle = \left\langle \frac{1}{2} (3 \cos^2 \theta - 1) \right\rangle, \quad (27)$$

where θ is the angle between the average and temporal orientation of the LC molecule at a given point in space defined by $\bar{r}$. The brackets $\langle \dots \rangle$ denote a temporal and spatial average. The isotropic phase is characterized by $\bar{S} = 0$, and a perfectly aligned ordering along $\bar{n}$ yields $\bar{S} = 1$. Typically, the value of $\bar{S}$ is found to be between 0.3 and 0.8, and generally decreases with increasing temperature (Figure 7). A discontinuous jump in the order parameter $\bar{S}$, which was experimentally observed in many nematics, demonstrates that nematics should be considered in principle as first order systems.

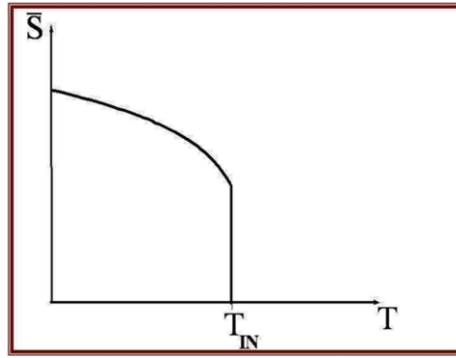


Figure 7: A presentation of the typical temperature profile of the nematic order parameter $\bar{S}$. T_{IN} denotes the phase transition temperature from I to N phase. It is known that the I-N phase transition of conventional LCs is weakly first order, i.e., $\bar{S}$ shows discontinuous behavior at T_{IN} .

As an important consequence of the nematic symmetry, the Landau expansion for the nematic free energy is defined by the following expression [12]

$$F_{nem} = \frac{1}{2} A \bar{S}^2 - \frac{1}{3} B \bar{S}^3 + \frac{1}{4} C \bar{S}^4 + \dots - f \bar{S}. \quad (28)$$

Here $-f\bar{S}$ represents the impact of some external, conjugate field to the order parameter, for example, an electric field. If an external field is present, it usually defines the direction of molecular alignment. The presence of the term $-\frac{1}{3} B \bar{S}^3$ is directly related to the discontinuous character of the nematic phase transition. Due to the elastic properties of LC phases, in the case of unaligned samples where the director $\bar{n}$ varies through space, i.e., $\bar{n} = \bar{n}(r)$, a continuum theory is used. To take into account the different possible distortions of the director, such as splay, twist or bend, the well-known Frank elastic free energy is used [12]

$$F_{nem} = \frac{1}{2} K_1 [\nabla \cdot \bar{n}]^2 + \frac{1}{2} K_2 [\bar{n} \cdot (\nabla \times \bar{n})]^2 + \frac{1}{2} K_3 [\bar{n} \times (\nabla \times \bar{n})]^2, \quad (29)$$

where K_1 , K_2 and K_3 are the nematic elastic constants associated with the splay, twist and bend deformations of the director field. These constants control the variation of the director orientation, and they can be determined from the light-scattering experiments and also in special cases where a magnetic or electric field induces a nematic transition in well-defined geometries, such as for instance, the Freedericksz transition [12, 61]. The mesogens composing the LCEs possess the same nematic properties as described above and are thus nematogens, i.e., if isolated, they would form the nematic phase below a certain nematic transition temperature T_{IN} .

The anisotropy of LC molecules is an important property of these systems. It reflects in the anisotropic response of the LCs on different external perturbations which is important for different applications, as for example, in well-known nematic LCs displays [188], where the Freedericksz transition plays an important role. Moreover, LCs could be used in optical microresonators that are interesting for various applications, as for example, an electrically tunable low-loss whispering-gallery-mode (WGM) resonator made of nematic liquid crystal droplets in a polymer matrix [189].

From a macroscopic point of view, elastomers are macromolecular rubber materials that after the removal of the external force quickly return in the position with the initial state, i.e., in the state with the initial shape and size (Figure 8). The basic building blocks of the elastomers, so called monomers, are mostly light hydrocarbons and silicones. If one of the hydrogens in a monomer that is connected with silicon is replaced by some reactive element or group, monomers can be linked into polymers via bonds between the reactive groups (Figure 9). Such polymers can form a network, i.e., an elastomer via the binding elements. These elements play an important role in the elastic behavior of elastomers. They prevent disentanglement of the polymer chains in the case of deformation. Therefore, the main characteristic of elastomers is that they respond with reversible deformation of the polymer chains on the external force.

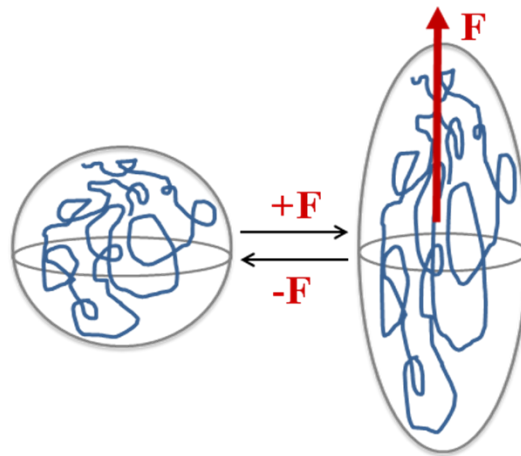


Figure 8: A presentation of elastomer shape change due to the external force. After the removal of the external force, elastomers return to the initial position, i.e., in the state with the initial size and shape.

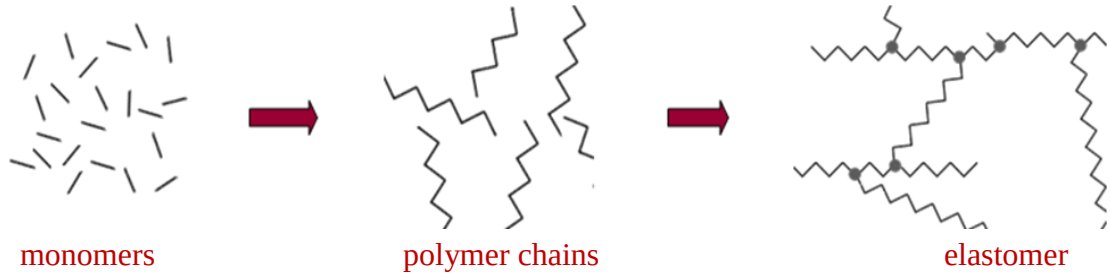


Figure 9: *The construction of elastomer.* Monomers are linked into a polymer via reactive elements. And polymers form the elastomer via binding elements.

Elastomers are highly complex disordered systems. They consist of polymer chains. Each chain can be modeled by a simple model, called the freely jointed chain (FJC) model [12]. A polymer chain with N monomers of molecular length a_M , has a length, called the arc length, $l = Na_M$. Each monomer is randomly oriented with respect to other monomers, i.e., no interactions between monomers are considered, since it can be freely jointed with respect to its two neighbors. The distance between the end-to-end points of the polymer chain is represented by the end-to-end vector

$$\bar{R} = \sum_{i=1}^N \bar{r}_i, \quad (30)$$

where $\bar{r}_1, \dots, \bar{r}_N$ are vectors corresponding to individual monomers (Figure 10). Those random vectors have components in all three dimensions of space.

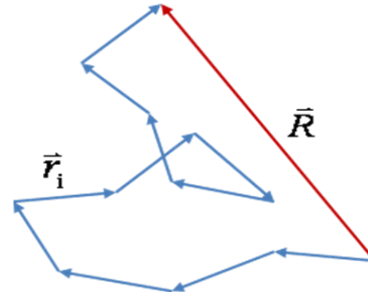


Figure 10: *A sketch of the ideal polymer chain.* $\bar{R}$ denotes the end-to end vector between end-to-end points of a chain, and $\bar{r}_i$ are vectors corresponding to the individual monomers.

The mean square end-to-end vector for a random walk of N steps in each direction is

$$\langle R_x^2 \rangle = \langle R_y^2 \rangle = \langle R_z^2 \rangle = \langle R^2 \rangle = \frac{1}{3} a_M^2 N = \frac{1}{3} a_M l, \quad (31)$$

since the vectors $\bar{r}_i$, $i=1, \dots, N$ are independent. The total number of possible configurations of an idealized chain, i.e., the number of possible random walks with restriction on the starting and end points, is given by the formula

$$Z_N(\bar{R}) = p_N(\bar{R})Z_N, \quad (32)$$

where Z_N presents the number of possible conformations without chain restriction, i.e., the chain ends are not fixed. The coefficient $p_N(\bar{R})$ represents the probability of the existence of end-to-end vector $\bar{R}$ for a given conformation, and it is defined by a Gaussian distribution

$$p_N(\bar{R}) = \left(\frac{3}{2\pi R_0^2} \right)^{3/2} \exp\left(-\frac{3\bar{R}^2}{2R_0^2} \right). \quad (33)$$

The distribution is characterized by the variance $R_0 = a_M l$. The free energy of a single polymer chain is expressed by

$$F(\bar{R}) = F_0 + k_B T \left(\frac{3\bar{R}^2}{2R_0^2} \right) + C, \quad (34)$$

where k_B is the Boltzmann constant, T temperature, $F_0 = -k_B T \ln Z_N$ the free energy of an unconstrained chain, and C represents the normalization of the probability distribution. Both F_0 and C are additive constants independent of the chain end-to-end distance. Due to this, they can be neglected. Thus we get

$$F(\bar{R}) = k_B T \left(\frac{3\bar{R}^2}{2R_0^2} \right). \quad (35)$$

The $F(\bar{R})$ includes configurations with equal internal energy. For the energy related to the distortion of chemical bonds with the internal energy per molecule $U(\bar{R})$ the free energy of a single chain is

$$F(\bar{R}) = U(\bar{R}) - TS(\bar{R}). \quad (36)$$

Here S is the entropy per molecule given by

$$S(\bar{R}) = -k_B \frac{3\bar{R}^2}{2R_0^2}, \quad (37)$$

because $U(\bar{R}) = 0$ in classical freely jointed model. This shows that the stretched polymer chains can be treated as entropic springs with the spring constant $k_B T / R_0^2$.

When the external force is applied on a single isolated chain the chain extends and its free energy increases. Rubber elasticity is a simple illustration of entropic-mechanical effects [12]. An applied force will result in a change of the average shape of a block of rubber with the polymer network (Figure 11).

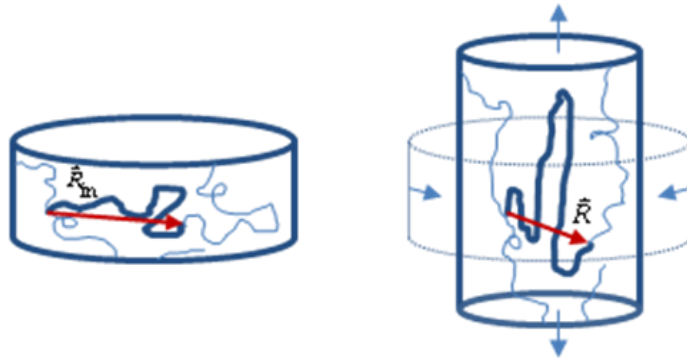


Figure 11: A block of rubber with the polymer network. An applied force changes the shape of a block. $\vec{R}_{in}$ is the end-to-end vector of unstressed chain, and $\vec{R}$ denotes the equal vector but for the deformed chain.

Let us take one polymer chain. Due to the applied force, a chain deforms in the geometric proportion of the whole block deformation. The new end-to-end vector is

$$\vec{R} = \underline{\lambda} \vec{R}_{in}, \quad (38)$$

where $\underline{\lambda}$ is a tensor, due to a possibility that a chain can be deformed in all three space directions x, y, z , and $\vec{R}_{in}$ denotes the initial end-to-end vector. The free energy for an extended chain is

$$F_C(\vec{R}) = \frac{3}{2} k_B T \frac{\vec{R}_{in} \cdot \underline{\lambda}^T \cdot \underline{\lambda} \cdot \vec{R}_{in}}{R_0^2}. \quad (39)$$

The sum of all the chain energies in a deformed body also shows a Gaussian distribution (Eq. 33) as in the case of the ideal chain presented before. The average free energy per chain is then expressed as

$$F_C(\vec{R}) = \frac{2k_B T}{3R_0^2} \left\langle \vec{R}_{in} \cdot \underline{\lambda} \cdot \underline{\lambda}^T \vec{R}_{in} \right\rangle_{p_N(\vec{R}_{in})}. \quad (40)$$

The final result related to the free energy of a deformed rubber is [12]

$$F_C = \frac{1}{2} n_c k_B T (\lambda_{xx}^2 + \lambda_{yy}^2 + \lambda_{zz}^2), \quad (41)$$

where n_c is an average of chains per unit volume and the term $n_c k_B T$ defines the characteristic rubber modulus μ . In the case of a uniaxial deformation of a rubber in the z direction, and assuming a conservation of volume ($\lambda_{xx} \lambda_{yy} \lambda_{zz} = 1$) then $\underline{\lambda} = (1/\sqrt{\lambda}, 1/\sqrt{\lambda}, \lambda)$. Eq. 41 becomes

$$F_C = \frac{\mu}{2} \left(\lambda^2 + \frac{1}{\lambda} \right). \quad (42)$$

In the model presented above, each polymer chain in rubber polymer networks is modeled by using a so-called three-dimensional Gaussian random walk. If the average length of the network is very large ($N \rightarrow \infty$) the chain will always remain in the Gaussian limit [12].

As was already mentioned, liquid crystal elastomers are materials in which the anisotropy of LCs, i.e., the orientational order, is combined with the elastic properties of elastomers. Thus the macroscopic properties provided by polymer networks (shape deformation) are connected with the microscopic properties of mesogens (orientation, positional order). The combination of both leads these systems to be extremely promising soft materials for different applications, due to the resulting thermomechanical response, i.e., a huge spontaneous change in geometry with temperature. Our focus has been related to the nematic LCEs since they show an extremely large thermomechanical effect. This effect in LCE systems is in direct connection with a type of LCE elasticity, which can be soft, semi-soft or non-soft [12].

The building blocks of elastomers consist of polymer backbones, crosslinkers and mesogens. Depending on the way how mesogens are attached to the backbone, two distinct types of LCEs are known. The liquid crystal mesogens molecules are incorporated directly into the polymer network in the case of main-chain LCEs (MC-LCEs), and in the side-chain LCEs (SC-LCEs) the mesogens are attached on the polymer backbone as lateral monomers, i.e., mesogens hanging from the backbone (Figure 12).

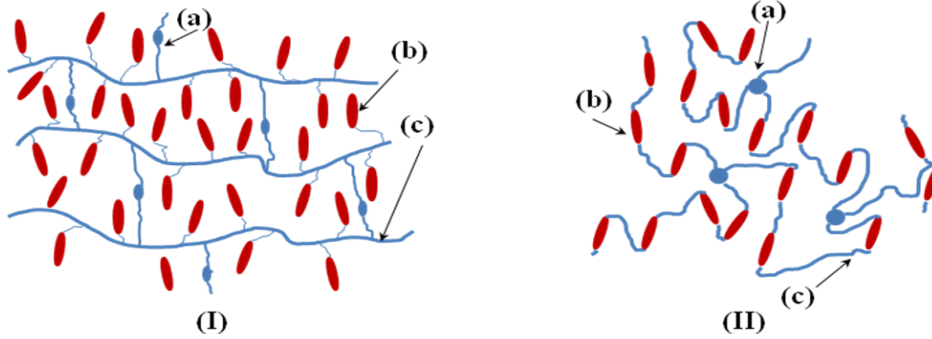


Figure 12: *Schematic presentation of two distinct types of LCEs. (I) SC-LCEs consist of (a) crosslinkers, (b) mesogens and (c) polymer backbone; (II) Building blocks of MC-LCEs are (a) crosslinkers, (b) mesogenic molecules, and (c) chain extenders.*

In comparison to the above presented FJC model for an isotropic elastic polymer chain let us take a look at a polymer chain as a part of a LCE system [12].

In LCEs, where the mesogens are incorporated into the polymer chains, the latter ordering depends on the mesogenic ordering. The change in the mesogenic order parameter gives rise to the macroscopic deformations. The focus will be on MC-LCEs. In the case of MC-polymers the average shape of gyration is elongated along the direction $\vec{n}$.

When the elastic chain is elongated in one direction, for example, in z , its dimensions in the x, y and z directions are $R_x = R_y = R_{\perp}$ and $R_z = R_{\parallel}$ (Figure 13) and the anisotropic elastic chain gyration is given by

$$g = r_{||} / r_{\perp}, \quad (43)$$

where $r_{||}$ and $r_{\perp}$ are monomer step lengths, and $R_{||}$ and $R_{\perp}$ are radii of gyration, in directions parallel and perpendicular to the director $\bar{n}$. The main square end-to-end vector that characterizes the shape of a chain is

$$\langle R_i R_j \rangle = \frac{1}{3} r_{ij} l, \quad (44)$$

where the step length now forms a tensor r_{ij} (analogous to isotropic form, Eq. 31).

The nematic order parameter $\bar{S}$ is directly related to the shape anisotropy of the polymer chain

$$r_{||} = a_M(1+2\bar{S}) \text{ and } r_{\perp} = a_M(1-\bar{S}). \quad (45)$$

Further, the step length gyration could be given in terms of the mesogenic order parameter

$$g = r_{||} / r_{\perp} = (1+2\bar{S}) / (1-\bar{S}), \quad (46)$$

and

$$r_{||} / r_{\perp} = (R_{||} / R_{\perp})^2. \quad (47)$$

When the nematic MC-LCE goes from isotropic to an ordered nematic phase without external load, the free energy per chain is given by

$$F_C = \mu/2[\lambda^2(a_M/r_{||})+2/\lambda(a_M/r_{\perp})]. \quad (48)$$

Minimizing the free energy $dF_C/d\lambda=0$ leads to the spontaneous deformation, i.e., in this case to the elongation of the MC-LCE

$$\lambda = (r_{||} / r_{\perp})^{1/3}. \quad (49)$$

Basically, the nematic liquid crystal elastomers are polydomain, i.e., they include many non-aligned domains. The applied stress on such LCEs results in orientation of these domains into a single aligned domain, i.e., the LCEs become monodomain. The LCE sample with one oriented domain is called liquid single crystal elastomer (LSCE). In our work all samples were nematic liquid single crystal elastomers (LSCEs), but in this thesis, for simplicity we will use the words LCEs instead of LSCEs.

The most attractive and applicable property of monodomain LCEs is a reversible thermomechanical effect. This means that LCEs elongate/contract spontaneously with temperature change. For different applications, the nematic-paranematic phase transition is observed to be the most promising due to a giant change in the elastomer length as a

consequence of the coupling between the elastic properties of elastomers and the orientational order of mesogens (Figure 13). Any stress on a polymer network has an impact on the orientational order of liquid crystals and, vice versa, any change in the orientational order affects the shape of the elastomers. Thus a change in temperature near the PN-N phase transition induces a large change in orientational order that causes the elastomer to extend or contract [28].

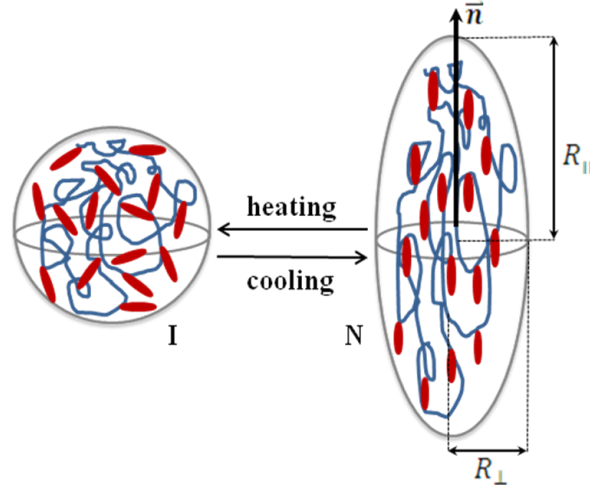


Figure 13: A representation of LCE shape change due to the temperature change at the PN-N phase transition. Polymers are ordered isotropically in the PN phase, which is represented by a spherical shape and they become elongated along the director $\vec{n}$ when nematic order appears by cooling into the N phase. $R_{||}$ and $R_{\perp}$ represent the radii of gyration, in directions parallel and perpendicular to the director $\vec{n}$.

The temperature dependence of the thermomechanical response approximately resembles the temperature evolution of the nematic order parameter $\bar{S}(T)$ (Figure 14), i.e., as already mentioned it can be tuned from on/off, where elongation/contraction takes place in a narrow temperature range, via CP to continuous, i.e., a supercritical response with most of the elongation/contraction taking place in the broad temperature interval [31, 56, 57].

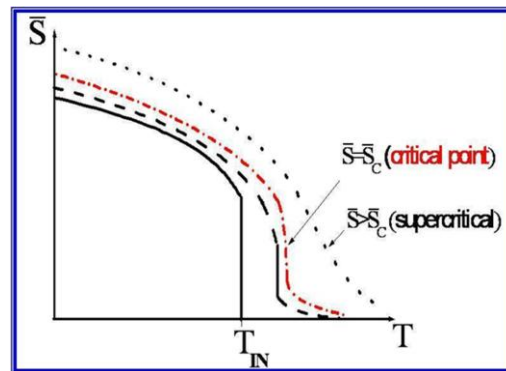


Figure 14: Schematic representation of the nematic order parameter $\bar{S}$ in LCEs. In contrast to conventional nematic LCs where it shows discontinuous behavior at T_{IN} , in LCEs it can be continuous at the CP or even supercritical.

As mentioned in the Abstract, all the LCE samples studied in this thesis were prepared by the research group of Prof. Dr. Finkelmann using the well-known two-step Finkelmann procedure [1]. This procedure paved the way how to prepare an elastomer with a permanent, macroscopically uniform alignment. In addition, it allows us to have a control over the contributions of the mesogens alignment and polymeric elasticity. Let us briefly describe the main points of this procedure.

In the first step of the Finkelmann procedure, a well-defined network is synthesized and deformed with a constant stress larger than the threshold stress to induce the network anisotropy and to obtain a uniform director orientation. In the second step the anisotropy is locked in the system by completing the crosslinking before the final elastomer is produced. This preparation method is used for SC-LCEs as well as for MC-LCEs with a small difference during the preparation, i.e., in MC-LCEs, due to the high elasticity the speed of reaction is slower and in the second preparation step a larger strain is needed.

Specifically, at first all three constituents of LCEs, i.e., for example in the case of SC-LCEs, liquid-crystalline molecules, crosslinkers and polymer backbone monomer poly(dimethylsiloxane) (PDMS) with the platinum (Pt) catalyst were added together in toluene to get a reaction between them. Such a solution is then rotated at a speed of around 4000 rpm at a temperature around 343 K, and at the end it is left to dry. As a result a non-aligned polydomain LCE is observed.

In the second step a uniaxial load larger than the threshold stress is applied to realign many domains into a one single aligned domain, and thus convert a polydomain LCE into a monodomain. The LCE is strained to the point where most of the mesogenic rotation is finished and then heated to the temperature below T_{IN} under this fixed load, i.e., the load is locked in the LCE before the final crosslinking step. This is described in a Landau-de-Gennes free-energy equation as the term $f\bar{S}$ (see Eq. 50) below.

The mesogens usually present around 90% of the final LCE mass. This shows that the mesogens have control over most of the parameters in LCE systems.

Before the calorimetric measurements it was important to prepare a sample in a proper way. A simple presentation of a final sample preparation is shown in Figure 15. A cell consisting of a cup and a lid with a proper shape was prepared by using high-purity silver. Both cell parts were cleaned with chloroform, acetone and ethanol absolute in an ultrasound bath. After that, melted indium was spread on the edges of the cups and lids in order to ensure good bonding during the sealing off of the cell by a cold welding method. Before the cell was loaded with the sample, final cleaning was made in the same way as before.

All the added masses during the cell preparation were weighed, and later taken into account during the data analysis. An LCE sample was put between the two thin (~ 0.1 mm) layers of Teflon, in order to prevent any additional stress related to the sample sticking on the cell walls. The stretching of the LCE was not influenced by the stretching resistance of the properly oriented Teflon layer, which was freely placed in the cell, because the Young's modulus of the Teflon is much smaller than that of the elastomer.

Further, a sample was put into the cup and finally closed by the lid via the cold welding method, in which the two silver pieces were pressed together using a press. After sealing the cell, the heater in the form of a small strain gauge and the small bead thermistor were attached to the cell on opposite sides. A diagram of the calorimeter instruments is shown in Figure 1, in Chapter 2. The thermal bath is a cylindrical copper block with an inner part, on which the sample cell is mounted. The thermal link between the cell and the bath is mainly achieved by the air and wires of the flexible heater which is attached to the cell. The bath is heated and stabilized by another flexible heater mounted around the inner can.

A programmable arbitrary wave-form generator is used as the power source for a cell

heater. A six-decade resistor is connected with the heater for measurements of the current through the heater and for changing the heater power. A bath temperature is measured with a platinum resistance thermometer. A constant current from a current source is passed through the thermometer. The voltage across the resistor is measured by a multimeter. The temperature of the outer can is kept at a constant value by a temperature controller with a thermistor attached to the can. The measurements and data acquisition are made with a computer. In the ac mode the scan sequence can be either heating or cooling with a scanning rate larger than 5 mK/h.

The prepared sample is mounted in a sample holder of the calorimeter (Figure 16(a)). Two contacts are reserved for a thermistor, and on the opposite site the other two for the heater. After mounting a sample, the calorimeter cell is closed by a cover and put into a thermal bath (Figure 16(b)). Then it is connected with all the instruments mentioned above.

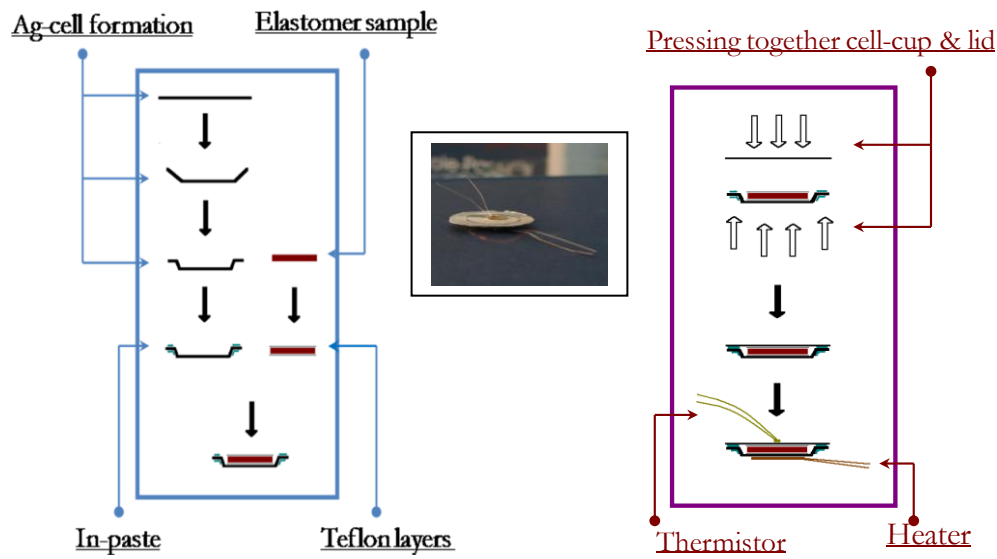


Figure 15: *Presentation of LCE samples preparation for heat capacity measurements.* A LCE sample is put between two thin Teflon layers and placed in the home-made silver cell. At the end the thermistor and the heater are attached to the sample. The final sample is shown in the middle.

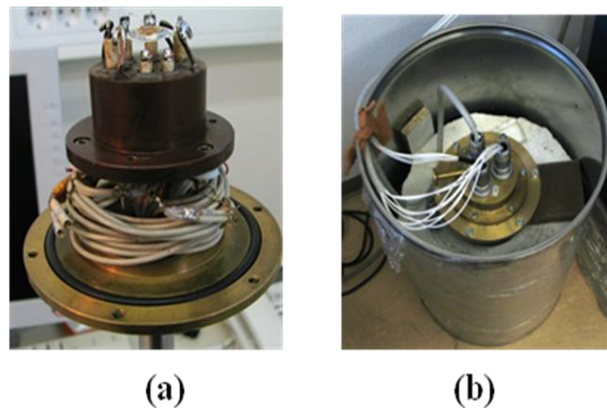


Figure 16: *Photos of the sample holder and an outer thermal bath of the calorimeter.* (a) A sample cell with attached thermistor and heater is mounted in the sample holder and then it is closed with a cover and put in to (b) the thermal bath.

3.1 PN-N transition as a function of crosslinkers density

As was mentioned, the nature of the PN-N phase transition in nematic LCEs was not clear until a few years ago. It was considered that this transition is supercritical, i.e., neither first order or discontinuous nor second order or continuous phase transition. Such behavior can be a consequence of either an internal mechanical field conjugate to the order parameter or quenched random disorder effects [28].

Recently it was shown that a subcritical or discontinuous behavior of side-chain LCEs (SC-LCEs) can be achieved by swelling the supercritical nematic liquid crystal elastomer samples with a proper amount of the conventional nematic liquid crystal [29].

Not long ago it was demonstrated that the thermodynamic response of SC-LCEs can also be adjusted by a variation of a single chemical parameter, i.e., crosslinking density [31]. It was shown that with increasing this parameter the paranematic-to-nematic (PN-N) phase transition behavior of SC-LCEs can be tuned from first order to critical and even to supercritical via a liquid-vapor type critical point. The criticality of the phase transition is accordingly reflected in different temperature profiles of the thermomechanical response.

In order to find a universal picture of the impact of the crosslinking density on the thermodynamic behavior of LCEs, we investigated the PN-N phase transition in the nematic main-chain LCEs (MC-LCEs). These LCEs consist of isotropic crosslinkers with five crosslinking points (HD5), rod-like mesogenic molecules and of a backbone with siloxane-based chain extenders (Figure 17). Five samples with different concentrations, $x = 0.025, 0.04, 0.06, 0.08$, and 0.12 , were prepared by using the well-known Finkelmann procedure [1]. Here x denotes the ratio of the number of the cross-linker and mesogen molecules. As mentioned above the LCE samples were prepared in a two-step process. In the first step, network anisotropy with a uniform director alignment was introduced by the well defined network, deformed with a constant load that is larger than the threshold load. In the next step, a second crosslinking step, which was taken in the nematic phase at around 330 K, locks-in the network anisotropy. Thus the network anisotropy was produced before the final elastomer sample was obtained.

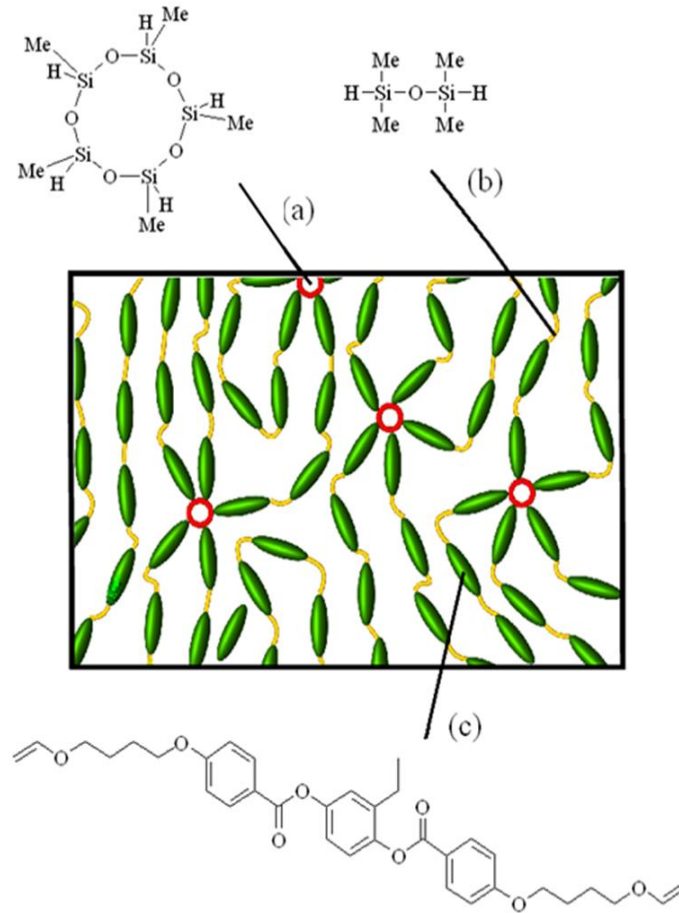


Figure 17: *Two dimensional schematic representation of a nematic main-chain LCE*. MC-LCEs consist of (a) an isotropic crosslinkers, (b) siloxane-based chain extenders, and (c) mesogenic molecules [56, 57].

For studying the impact of the crosslinking density on the nature of the PN-N phase transition two techniques were used: high-resolution calorimetry [99-101] and deuterium quadrupole-perturbed nuclear magnetic resonance (deuterium NMR) [29, 31, 56, 175, 190]. In this thesis we will present the results of the calorimetric measurements and just mention the basic conclusion results obtained by NMR.

The heat capacity (C_p) measurements as a function of temperature were made by the high-resolution calorimetry, with a scanning rate of 0.8 K/h in the ac mode where data were collected during the cooling. As described in Section 2.1 the ac mode mainly detects the continuous changes of enthalpy. In order to check the presence of the latent heat in the case of a first order transition, ac measurements must be combined with the relaxation calorimetric data. The relaxation mode is sensitive to the total enthalpy changes including both continuous and discontinuous changes. By subtracting the integral below the ac C_p data from the integral of the relaxation C_p data the latent heat can be discerned (Figure 18). The typical temperature step ($\sim$ amplitude of the scanned temperature) in relaxation runs was around 0.7 K.

Figure 19 presents the excess heat capacity (ΔC_p) as a function of temperature [56]. It is shown that at low crosslinker concentrations the differences between the C_p anomalies obtained in ac and relaxation runs are clearly seen. This demonstrates the presence of the latent heat, i.e., the occurrence of the first order phase transition. Further, with increasing crosslinker concentration the difference between the ac and relaxation modes decreases, i.e., the latent heat slowly goes to zero, and it vanishes for high concentrations

(approximately at $x = 0.12$). The vanishing latent heat defines the single point in the crosslinker density-temperature ($x - T$) phase diagram at which the transition becomes continuous.

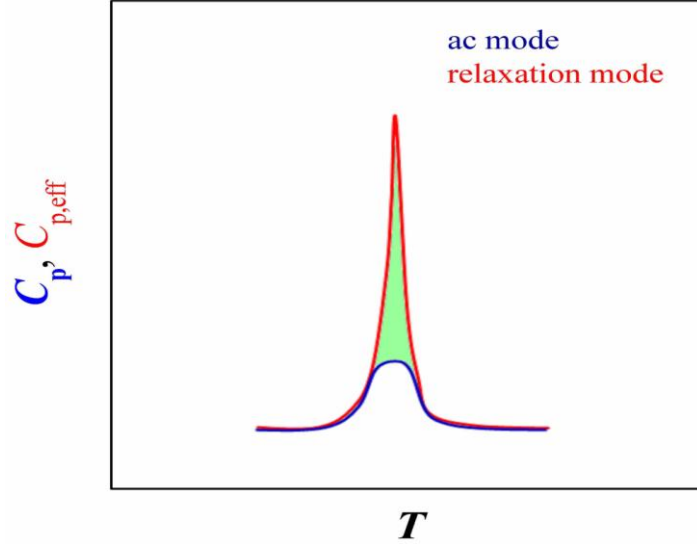


Figure 18: Heat-capacity profiles of the ac (C_p) and relaxation mode ($C_{p,eff}$) in the case of a first order phase transition. The difference of the integrals (green colored area) shows that the latent heat is present in the transition.

Above $x = 0.12$ PN-N the phase transition vanishes in the strict sense of the term and only gradual or supercritical evolution in certain physical quantities can be observed resulting in the broad noncritical anomalies following the so-called Widom line [191, 192] in the $x - T$ phase diagram (Figure 20). The solid and open symbols denote the data obtained in the ac and relaxation runs. For all the results the excess heat capacity ΔC_p data were derived after subtracting a background and for clarity they were shifted along the ΔC_p axis.

The comparison of the latent heat L as a function of crosslinker density x for MC-LCEs with isotropic crosslinkers (HD5) and SC-LCEs with a point-like (V3) and a rod-like (V6) crosslinkers (data taken from reference [31]) is presented in Figure 21 [56]. It should be noted that due to the different crosslinking topology in the mentioned systems, x denotes a different but similar quantity, i.e., in the case of MC-LCEs x stands for the crosslinkers density [56] and in the case of SC-LCEs x denotes the coverage of active chain groups of the polymer backbone [31]. It was found that the thermodynamic behavior in MC-LCE systems is similar to that in SC-LCEs, where the latent heat also slowly disappears with increasing crosslinker concentration. This clearly shows the existence of the liquid-vapor type critical point in the $x - T$ phase diagram of main-chain LCEs.

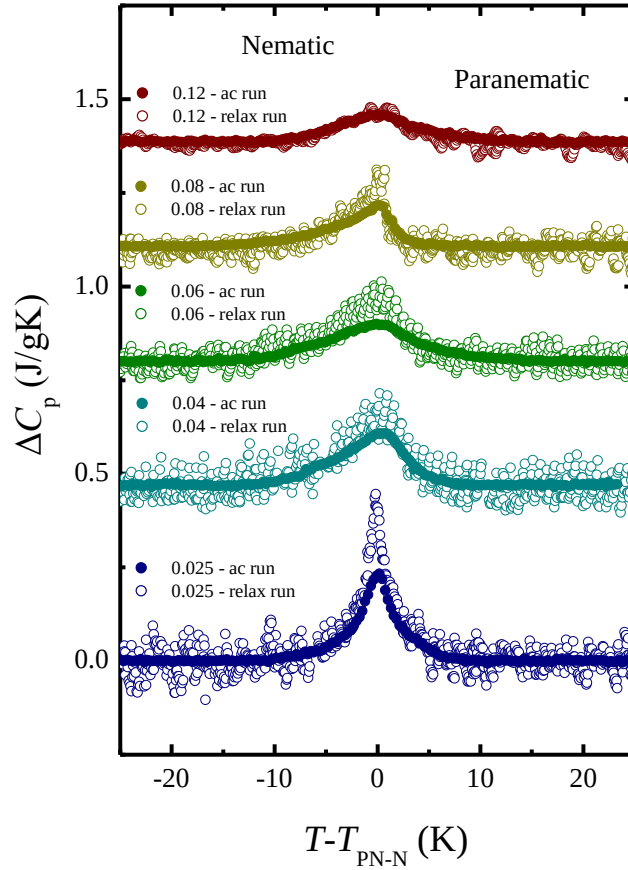


Figure 19: The excess heat capacity ΔC_p data as a function of temperature for five different crosslinking concentrations of MC-LCEs. ΔC_p data were obtained in the ac (solid circles) and relaxation runs (open circles) [56].

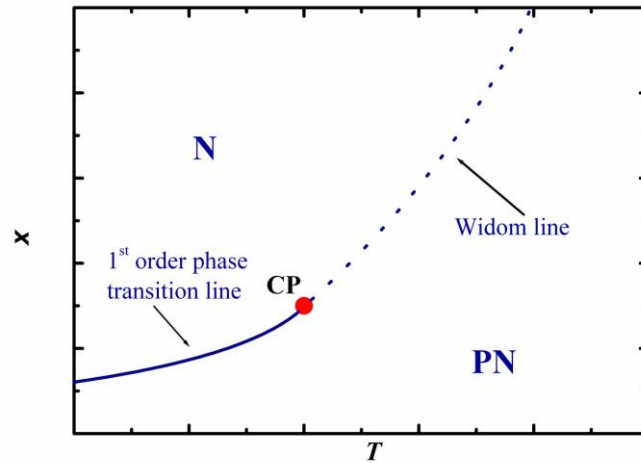


Figure 20: Crosslinker density-temperature (x - T) phase diagram of the LCE systems. The solid line denotes the region of the first order phase transitions, and the dashed line stays for a Widom line along which the supercritical evolution of physical properties occurs. At a single critical point (CP) the transition becomes continuous, thus ending the first order phase transition line.

In fact, it was observed that with increasing the crosslinkers density the nature of the PN-N phase transition changes from discontinuous via continuous at the critical point, to supercritical for densities above critical. The theoretical predictions of critical phenomena that such observations are expected whenever a field conjugate to the order parameter exists, and its value increases across the respective critical value, leads to the conclusion that by increasing the crosslinkers' density the strength of the local mechanical fields is increased. As we mentioned above, the same has been demonstrated for side-chain LCEs [31]. In respect of both observations we can conclude that the impact of the crosslinkers' density on the nature of the PN-N transition is universal for all types of LCEs.

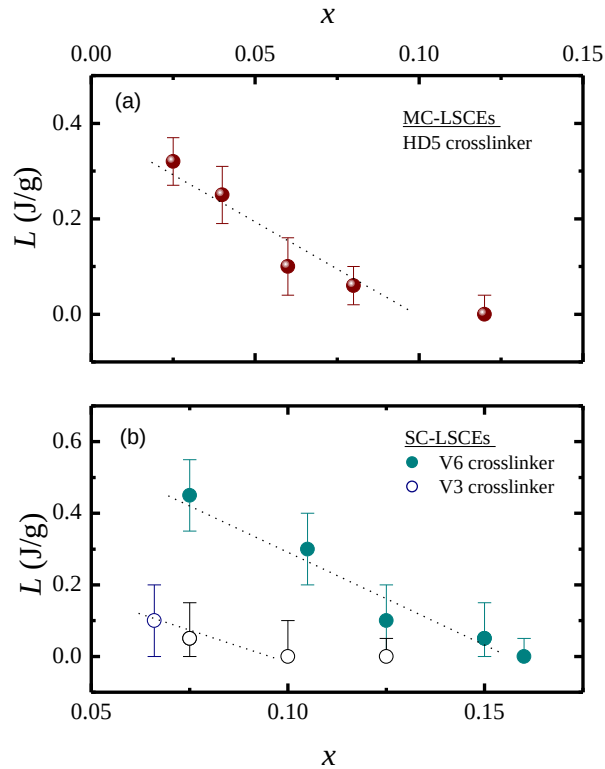


Figure 21: *The latent heat L as a function of crosslinker density.* Data are presented for (a) MC-LCEs and for (b) SC-LCEs samples taken from [31]. Similar impact of crosslinkers density variation observed in both MC-LCE [56] and SC-LCE [31] indicates the universal behavior in all types of LCEs.

NMR is a suitable method for studying the local nematic order of mesogenic groups $\bar{S}(T)$ [29, 31, 56, 175, 190]. A typical result of NMR measurements performed by A. Lebar is a doublet NMR spectrum with its splitting proportional to the local order parameter. In studies related to LCE systems presented above, well-separated doublets, but broader than in SC-LCEs, were observed [56]. Such a difference could be a consequence of the slow dynamics in MC-LCEs, where mesogens are attached to the backbone at both their ends in comparison to SC-LCEs, where only one end of mesogens is attached, and the second one is free [56].

The obtained $\bar{S}(T)$ results qualitatively confirm the calorimetric results. It was clearly observed how with decreasing the crosslinker density the $\bar{S}(T)$ changes from the continuous, i.e., supercritical, to discontinuous like [56]. This means that a sufficient decrease in the crosslinker density leads to the discontinuous PN-N phase transition in

MC-LCEs.

3.2 Influence of the external stress field during the crosslinking procedure on the PN-N transition

The next mechanism that can drive the type of phase transition is a frozen-in uniform external mechanical field. That means an external mechanical stress is used during the preparation of the LCE samples. Our aim was to study how the sample preparation conditions influence the transition behavior. For this reason we took two main-chain LCEs with the same crosslinking concentration $x = 0.04$ oriented during the preparation by two different external mechanical fields, 91 kPa and 24 kPa. The masses of both samples were around 40 mg, and the second crosslinking step was made at 373 K, i.e., above the PN-N phase in order to eliminate the impact of the crosslinking temperature on the final results.

We would like to mention that the type of LCEs used was exactly the same as in the previous study of the crosslinking density's impact on the nature of the PN-N phase transition. Thus we used main-chain LSCEs consisting of siloxane chain extenders, flexible isotropic crosslinkers and the mesogenic molecules. Because both applied mechanical loads were larger than the critical stress threshold that aligns the sample, i.e., both loads were larger than 10 kPa, thus our samples were monodomain [56].

The results of the calorimetric measurements, i.e., the temperature dependence of the excess heat capacity (ΔC_p) obtained during the heating in the temperature range between 315 and 355 K, are presented in Figure 22. Results were collected during the ac (solid circles) and relaxation (open circles) runs with scanning rates of 1 K/h in ac runs and 0.5 K step in relaxation runs. It is shown that for a higher magnitude of the external mechanical field 91 kPa a more suppressed PN-N ΔC_p anomaly and a smaller latent heat L of around 0.05 J/g are observed. In contrast, at a smaller external field of 24 kPa a much sharper heat capacity anomaly and larger latent heat of 0.49 J/g were observed [56].

These results obtained on two main-chain LSCEs samples with the same concentration but stretched with different mechanical loads during the second crosslinking step show that increasing external mechanical field reduces the latent heat towards zero. This implies that the increasing the external mechanical field drives the PN-N phase transition towards the critical point. Therefore, it is clearly shown that the external mechanical field used during the sample preparation plays a similar role in changing the nature of the PN-N transition in MC-LSCEs as internal random mechanical fields, which can be tuned by changing the crosslinkers' density.

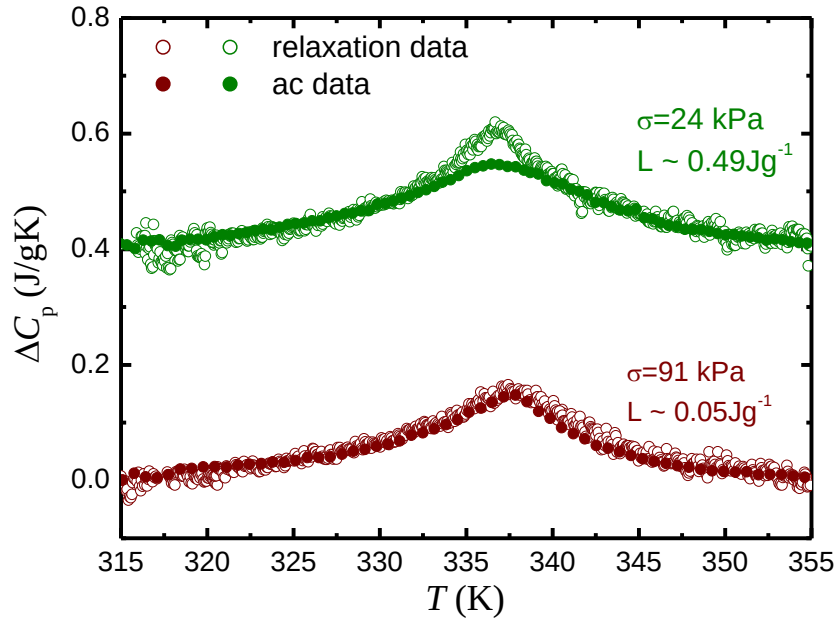


Figure 22: The excess heat capacity data ΔC_p as a function of temperature for two MC-LCE samples prepared under two different external mechanical fields σ . ΔC_p data were determined during the relaxation (open symbols) and ac (solid symbols) runs [56]. Note the much smaller difference in both runs for the sample prepared at a higher external mechanical field, indicating a significantly reduced latent heat.

The observations presented above are in good agreement with the theoretical predictions that the coupling between the nematic order parameter and conjugate internal or external field can drive the PN-N phase transition into a supercritical one and maybe to a subcritical regime [28]. This can be explained by using the well-known Landau de Gennes expression for the free energy F of a PN-N phase transition in MC-LCEs

$$F = \frac{1}{2} A \bar{S}^2 - \frac{1}{3} B \bar{S}^3 + \frac{1}{4} C \bar{S}^4 - f \bar{S}, \quad (50)$$

where the term $f \bar{S}$ represents the coupling between the applied mechanical fields f and the orientational order. In the LCEs f is a mechanical stress field consisting of the internal random fields f_{int} , imprinted into the system during the preparation and of the uniform external mechanical field f_{ext} related to the applied uniform external stress field applied between the two crosslinking steps

$$f = f_{\text{int}} + f_{\text{ext}}. \quad (51)$$

These fields conjugate to the nematic order parameter $\bar{S}$, besides inducing some orientational order in the isotropic phase can also drive the PN-N phase transition from the discontinuous to the continuous one.

It was found that in the case when f is increasing below the critical value f_c the discontinuity in the temperature profile of the order parameter $\bar{S}$ slowly vanishes and it completely disappears at $f = f_c$ where the transition becomes continuous. When the applied

mechanical field f exceeds the f_c value, then the PN-N evolution becomes gradual and non-critical [28]. The term “supercritical” actually denotes the non-critical behavior where only a smooth evolution of the order parameter is observed from the high temperature state to the low temperature state, both possessing the same local symmetry.

In studies presented above, the internal mechanical field f_{int} can be tuned by the crosslinkers’ density and the external mechanical field f_{ext} is the external stress that was applied between the two crosslinking steps. Our results presented above show the impact of both the internal as well as external mechanical fields on the PN-N transition and thus two possible ways of controlling the type of the thermoelastic response.

3.3 Influence of crosslinking temperature on the nature of the PN-N phase transition

Above we have already presented the role of the two parameters on the critical behavior of PN-N phase transition of LCEs, i.e., the chemical parameter crosslinkers density and the mechanical load applied during the sample preparation. Here the third, till now unexplored, parameter for controlling the LCEs’ critical behavior is introduced. It was observed that two main-chain LCEs of identical composition but crosslinked at two different temperatures, each in a different thermodynamic phase, exhibit dramatically different thermal behavior [57].

Therefore, the impact of crosslinking temperature on the critical behavior of LCEs is studied on two monodomain main-chain LCEs with the same composition as reported in the previous subsection. Both samples consist of chain extenders, the crosslinkers of density $x = 0.04$ and the mesogens shown in Figure 17. In addition, the two samples with masses around 40 mg were prepared by applying the same mechanical stress prior to the second crosslinking step, i.e., 91 kPa. However, the difference between them lies in the temperature where the second crosslinking took place. In the case of the first sample (LCE1) the second crosslinking step was made at 373 K, i.e., much above the PN-N phase transition, and in the second LCE sample (LCE2) the final crosslinking was performed at 323 K, i.e., deep in the nematic phase. Both samples were swollen in toluene to eliminate any nonreacted components, and then dried. It should be mentioned that the first crosslinking step is always made in the isotropic phase by swelling all the components in toluene to react.

Before measurements samples were put in a silver cell and annealed twice above the temperature of the PN-N phase transition. The results were obtained during heating the LCEs, between 310 K and 360 K with scanning rates of 1 K/h for ac and 0.5 K steps for relaxation runs. The high-resolution calorimetry results are presented in Figure 23 [57]. The final net heat capacity C_p was obtained from the initial C_p results by subtracting the C_p of silver and Teflon. At the end the noncritical background was subtracted and the excess heat capacity ΔC_p of the ac run and the effective excess heat capacity $\Delta C_{p,\text{eff}}(T)$ of the relaxation run were derived.

In the case of LCE1 a broad and suppressed anomaly is observed in both ΔC_p and $\Delta C_{p,\text{eff}}(T)$. The small latent heat L of (0.09 ± 0.007) J/g indicates the proximity to the critical point. On the other hand, LCE2 shows a much sharper ΔC_p anomaly. In addition, a much larger latent heat L of (0.78 ± 0.05) J/g indicates the first order character of the PN-N transition. Consequently, the crosslinking of the LCEs at a lower temperature in the nematic phase results in a strongly first order PN-N phase transition. From this it is also possible to conclude that a critical point is shifted to higher crosslinking concentrations when the second crosslinking step is made in the nematic phase [57].

In Table 1 the total enthalpy change ΔH , the latent heat L , the temperature range $\Delta T_{1/2}$, where the half of ΔH is observed, and also the full-width at half maximum

(FWHM) of the C_p peaks related to the PN-N phase transition are presented [57]. It is interesting to mention an observation from previous study [56], where the latent heat of $L = (0.25 \pm 0.05)$ J/g is reported for another sample of identical composition but crosslinked in the second step at a temperature of around 330 K. The crosslinking temperature for the above-mentioned sample was just below the transition temperature T_{PN-N} and it lies between the crosslinking temperatures of the samples presented here. In agreement the $L = (0.25 \pm 0.05)$ J/g lies between the latent heat values of the LCE1 and LCE2 samples presented here. This demonstrates the monotonous increase of the latent heat with the decreasing crosslinking temperature, i.e., increasing distance from the critical point.

Since the concentration of crosslinkers remains constant at $x = 0.04$ the CP must be shifted toward higher crosslinking concentrations in the $x - T$ phase diagram. This shows that it is possible to control the thermomechanical response in LCEs from discontinuous to continuous one by changing the second crosslinking temperature of the LCE samples with the identical compositions. The explanation from a chemical point of view is as follows. In the nematic phase the second crosslinking process results in a more ordered network. The free chains are more organized before they become crosslinked. This leads to larger oriented domains or smaller random fields. In the case of isotropic or PN phase the order of the network is much smaller, leading to stronger random fields [57].

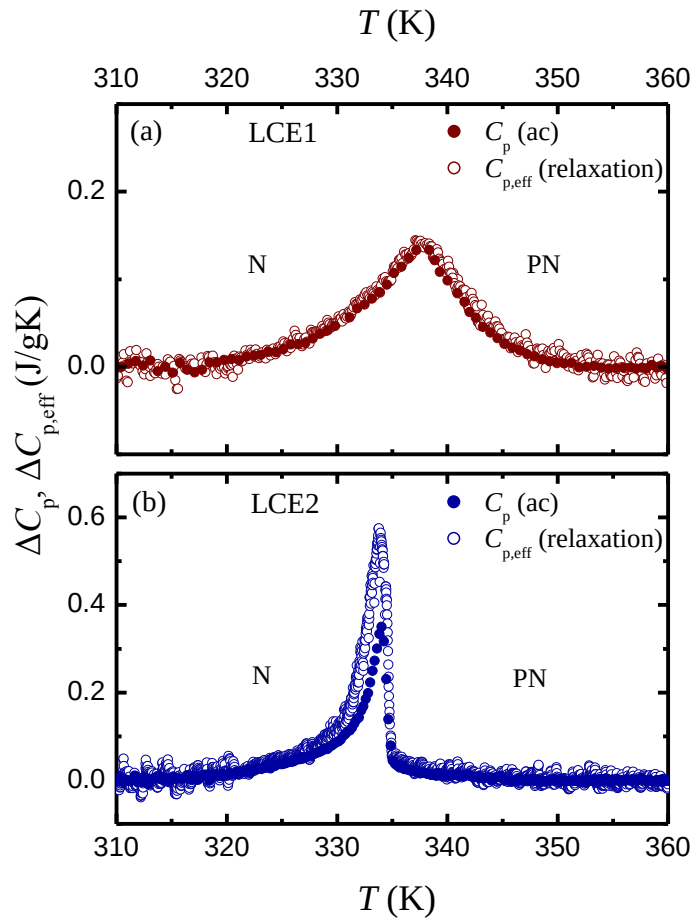


Figure 23: The excess heat capacity data as a function of the temperature for two MC-LCE samples prepared at two different temperatures in the second crosslinking step. ΔC_p and $\Delta C_{p, \text{eff}}$ data were determined during the ac and relaxation runs, respectively [57].

Therefore, we found that the crosslinking temperature plays an important role in the LCEs' critical behavior. Its impact on the nature of the PN-N phase transition is much stronger in comparison to the two previously mentioned parameters, i.e., the crosslinking density and the frozen-in external mechanical field [56].

Table 1: *The ac and relaxation data for LCE1 and LCE2.* The total enthalpy change ΔH , the latent heat L , the temperature range data $\Delta T_{1/2}$, where the half of ΔH is observed, and also the FWHM of the C_p peaks related to the PN-N phase transition are presented [57].

	Rate (K h ⁻¹)	ΔH (J g ⁻¹)	$\Delta T_{1/2}$ (K)
Sample	[T-step (K)]	[L(J g ⁻¹)]	[FWHM (K)]
LCE1	1	1.73 ± 0.04	7.30 ± 0.02
	[0.5]	$[0.09 \pm 0.07]$	$[10.76 \pm 0.03]$
LCE2	1	2.23 ± 0.04	2.85 ± 0.02
	[0.5]	$[0.78 \pm 0.05]$	$[2.43 \pm 0.04]$

3.4 Control of the thermomechanical response

Here a summary of the above-described observations related to the control of the PN-N phase transition in LCEs is given. We discuss how the control of the PN-N phase transition in LCEs helps to control the large thermomechanical response of LCEs, which can be used in various applications.

Let us reiterate, the combination of LC and rubber properties brings together very interesting and prominent features, such as the giant thermomechanical effect, i.e., the spontaneous elongation/contraction related to the temperature changes. The results of various previously published studies and studies presented in this thesis show the possible physical and chemical parameters, which can be used in tuning the phase transition from the paranematic to the nematic phase and thus the thermomechanical response in LCEs. We show that by playing with the quantity of LCE building blocks like the crosslinkers density [29, 31, 56] or with the sample preparation conditions [56, 57] we can significantly influence the nature of the PN-N transition and thus the temperature dependence of the strain $\lambda(T)$

$$\lambda = \frac{l(T)}{l_0}, \quad (52)$$

where $l(T)$ denotes the temperature-dependent change of the LCE sample length and l_0 the length of the non-deformed sample, i.e., the sample in the isotropic phase. By controlling

the nature of the PN-N transition the evolution of the thermal expansion (l/l_0) can be tuned from the “on-off” or discontinuous to the continuous response (Figure 24).

In particular, it was shown that by varying the density of crosslinkers, the crosslinking temperature or the external stress field, the LCEs can be prepared in such a way that they show either subcritical or supercritical behavior, which is then reflected in the fast or slow thermomechanical response.

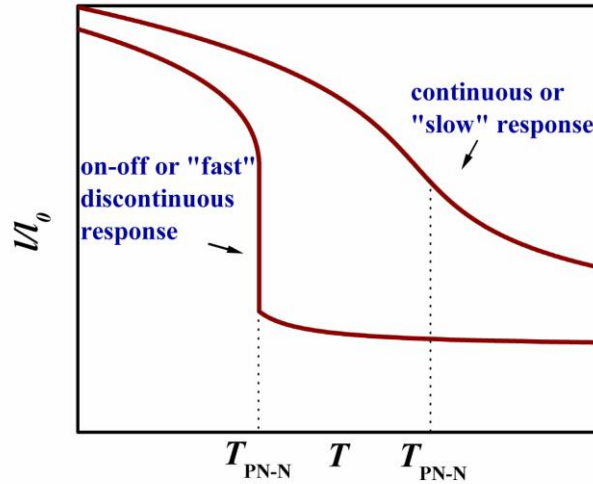


Figure 24: *Evolution of the thermal expansion (l/l_0).* The evolution is shown for a discontinuous and supercritical phase transition, corresponding to the “on-off” and the continuous thermoelastic response, respectively.

In order to see the impact of each parameter systematic studies were made to change only one parameter at a time. It was found that the applied mechanical stress affects the PN-N transition similar like the internal stress related to the crosslinking density. However, the impact of these parameters is not as strong as the impact of the crosslinking temperature parameter. In any case, all of these parameters are relevant tools for controlling the LCEs’ thermoelastic behavior.

3.5 Short summary of the main experimental results in the LCE studies

In this thesis we present the first experimental results, which show that the transition from the paranematic to the nematic phase and thus the type of the thermomechanical response in the MC-LCEs can be controlled besides the chemical parameter, i.e., the crosslinking density (shown by A. Lebar et al. for SC-LCEs and by G. Cordoyiannis et al. for MC-LCEs in Ref. [29] and [31]), also via two physical parameters such as the applied external mechanical field, which is imprinted during second crosslinking step, and the temperature at which this second crosslinking step was made.

For the future work, it will be interest to measure also the strain as a function of temperature for the MC-LCEs under three different already mentioned conditions.

4 Electrocaloric effect in organic and inorganic materials

Electrocaloric effect is defined as a reversible change in the temperature of an electrocaloric material due to the applied electric field under adiabatic conditions. As mentioned in the Introduction, it is a very attractive and potentially important phenomenon due to the broad range of possible applications, as for example in cooling and heating devices of the new generation, where the heating and cooling elements will be made without moving parts, and they will be more efficient with respect to energy consumption and more environmentally friendly.

The microscopic mechanism of the ECE is not yet fully established, but it is a direct consequence of the change of entropy S stimulated by an external electric field and resulting in an induced change of the ferroelectric dipolar state, from the less ordered into a more ordered one (Figure 25) and vice versa, when the electric field is removed [62, 63]. The entropy of a system can be considered as a sum of the entropy related to the electric ordering, i.e., the entropy of the dipolar subsystem and the entropy related to the temperature of a material or lattice-vibration or phonon entropy.

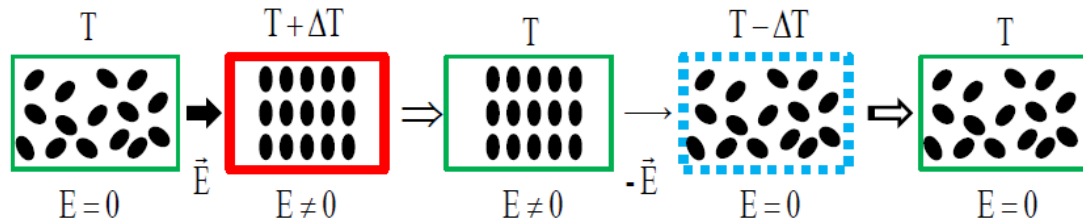


Figure 25: *Schematic representation of the electrocaloric cycle.* An applied electric field induces changes in the ferroelectric dipolar state, from the completely disordered to an ordered one, and vice versa [81].

An adiabatically applied electric field results in an increase of the material temperature due the lattice-vibration entropy compensation of the reduction of the dipolar-subsystem entropy. In contrast, the adiabatic removal of the electric field causes a cooling of the material, i.e., the temperature of the material decreases as a result of the decrease of the lattice-vibration entropy, which compensates for the increase of the dipolar-subsystem entropy. In both cases the total entropy of the whole system remains constant as it should during the adiabatic process. However, the two basic processes are important in the electrocaloric effect, the isothermal process that leads to an entropy change ΔS_{dip} of the dipolar subsystem (from point $S(E_1, T_1)$ to $S(E_2, T_1)$ in Figure 26) and the adiabatic process, which yields the change in temperature due to the change of the lattice entropy ΔS_{ph} compensating the ΔS_{dip} (from point $S(E_1, T_1)$ to $S(E_2, T_2)$ in Figure 26).

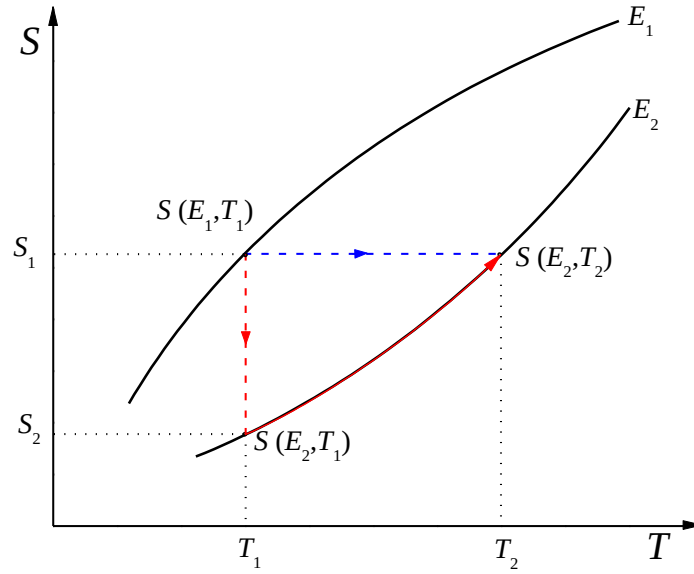


Figure 26: *Schematic representation of the entropy change during the electrocaloric cycle.* E_1 and E_2 denote the constant electric fields. The path from point $S(E_1, T_1)$ to $S(E_2, T_1)$ represents the isothermal process and the path from $S(E_1, T_1)$ to $S(E_2, T_2)$ adiabatic process.

The electrocaloric heating/cooling cycle is comparable with a corresponding heating/cooling cycle of a classic compressor, which can be found for example in nowadays refrigerators, where the pressure p of gas is changing (Figure 27) [85]. The adiabatic compression of the gas, which serves as a coolant medium, is equivalent to the isothermal polarization of a dielectric material during which entropy decreases and its subsequent compensation by the increase of the phonon entropy. In both systems the temperature increases. In the reversed process, the adiabatic expansion of a gas results in a decrease of the gas temperature as a consequence of a lower pressure at a constant total entropy. This is similar to the adiabatic depolarization, i.e., the removal of the electric field which results in an increase of the dipolar entropy that is compensated by a decrease of the lattice entropy, i.e., the temperature of the electrocaloric material is decreasing [193].

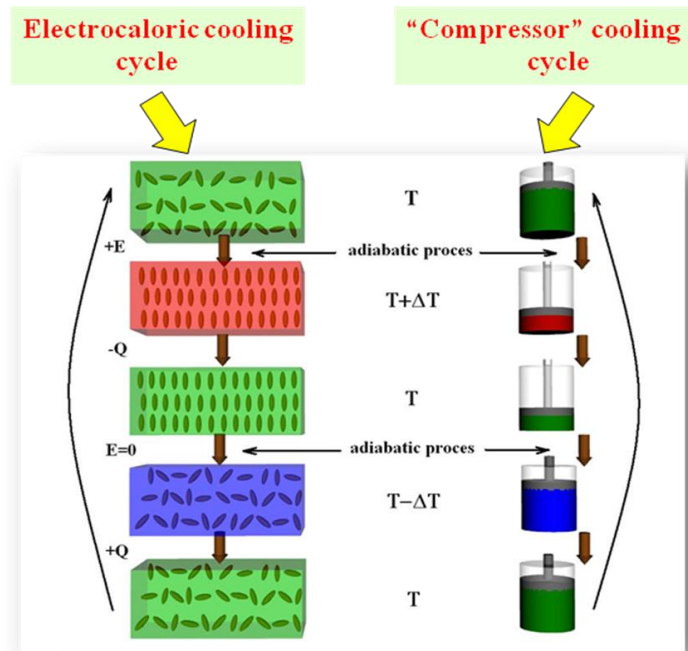


Figure 27: Schematic comparison of the electrocaloric and the classic heat engine cycle. The working media are a dielectric material in the EC cycle and a gas in the classic engine cycle [85].

So, in nowadays refrigerators the working media is a gas and its temperature change is achieved by changing the gas pressure. On the other hand, in the case of an electrocaloric material, its temperature change can be achieved by a change of the electric field. Thus there exists a possibility that some parts of nowadays refrigerators, as for example gas, tubes, condenser, etc. could be replaced by an electrocaloric device consisting of several electrocaloric elements between the heat exchanger and the cooling plate, which are separated by heat conductors or heat switches (Figure 28). Such a replacement could result in several advantages, like simpler design, there will be no moving parts, and the most important estimations show that a refrigerator with an electrocaloric device with no gas should be more energy efficient and environmentally friendlier.

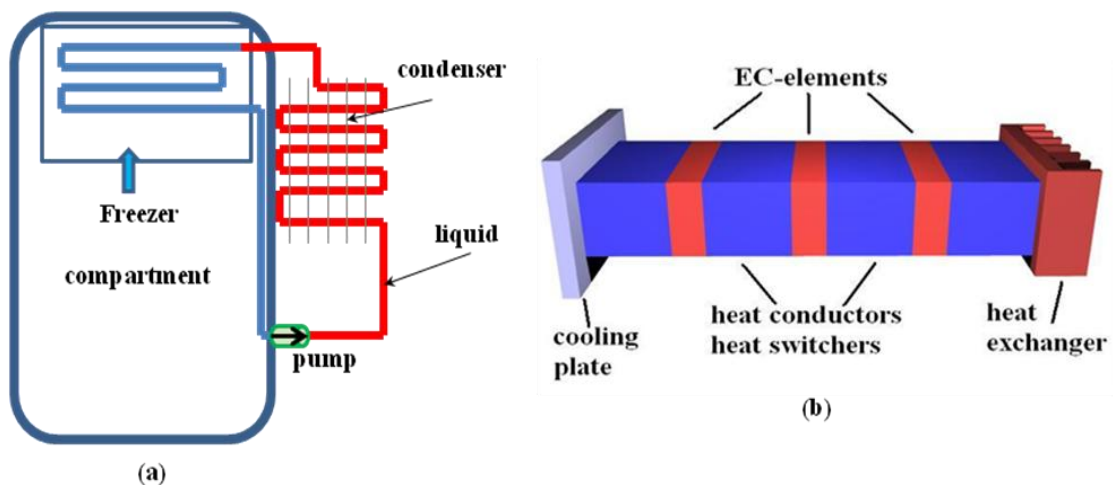


Figure 28: *Schematic representation of the classic and electrocaloric cooling device; (a) nowadays refrigerator consists of different parts; (b) the EC device consisting of several EC elements between a heat exchanger and a cooling plate, separated by heat conductors or heat switchers. Across such a device a gradient in the temperature can be achieved [85].*

The ECE, i.e., the heating or cooling of electrocaloric material due to the applied electric field under adiabatic conditions recently attracted considerable attention due to the first prediction of the giant electrocaloric response in some inorganic and organic materials [62-69]. Specifically, a giant ECE exceeding 12 K was observed in PZT thin films around 222°C [62]. A similarly large ECE was detected in the ferroelectric (P(VDF-TrFE)) copolymer around 70°C, and in the relaxor ferroelectric (P(VDF-TrFE-CFE)) terpolymer near room temperature [63]. These observations were based on indirect measurements of the electrical polarization $P(T, E)$ as a function of temperature and the electric field E . Using the well-known Maxwell relation $(\partial P / \partial T)_E = (\partial S / \partial E)_T$, the magnitude of the ECE, ΔT_{EC} , of the measured material with density ρ and the heat capacity C_p under the change of an electric field from E_1 to E_2 , has been determined from [62-64]

$$\Delta T_{EC} = -\frac{1}{\rho C_p} \int_{E_1}^{E_2} T \left(\frac{dP}{dT} \right)_E dE. \quad (53)$$

This formula is derived by using the Gibbs free energy G for a dielectric material, expressed as a function of the internal energy of the system U , temperature T , entropy S , stress X , strain x , electric field E and the electric displacement D [84]

$$G = U - TS - X_i x_i - E_i D_i. \quad (54)$$

The Maxwell relation can be derived for (S, T) and (D, E) [194]

$$\left(\frac{\partial S}{\partial E_i} \right)_{T, X} = \left(\frac{\partial D_i}{\partial T} \right)_{E, X} \quad (55)$$

or

$$-\left(\frac{\partial T}{\partial E} \right)_S = \frac{T}{c_E} \left(\frac{\partial D}{\partial T} \right) = \frac{T}{c_E} p_E. \quad (56)$$

Here c_E is the specific heat capacity and p_E is the pyroelectric coefficient at constant electric field. The entropy S , strain x_i and an electric displacement are expressed as

$$S = -\left(\frac{\partial G_1}{\partial T} \right)_{X, D}, \quad x_i = -\left(\frac{\partial G_1}{\partial X_i} \right)_{T, D}, \quad D_i = -\left(\frac{\partial G_1}{\partial E_i} \right)_{T, X}. \quad (57)$$

The differential of the Gibbs free energy (Eq. 54) is given by

$$dG = -SdT - x_i dX_i - D_i dE_i. \quad (58)$$

Thus the isothermal entropy change ΔS and the adiabatic temperature ΔT_{EC} for the ECE material with density ρ can be expressed as [194]

$$\Delta S = \int_{E_1}^{E_2} \left(\frac{\partial D}{\partial T} \right)_E dE, \quad (59)$$

$$\Delta T_{EC} = -\frac{T}{\rho c_E} \int_{E_1}^{E_2} \left(\frac{\partial D}{\partial T} \right)_E dE. \quad (60)$$

From Eqs. (55) and (56) it is evident that the pyroelectric coefficient p_E is proportional to the ECE. The expressions in Eqs. (55) and (60) show that in order to achieve a large ECE temperature change ΔT_{EC} , the dielectric material needs to possess a large pyroelectric coefficient over a broad temperature and electric field range. However, in the case of the ECE in a dielectric material both the isothermal entropy change ΔS and adiabatic temperature change ΔT_{EC} , are important parameters [195, 196].

The adiabatic temperature change ΔT_{EC} can also be derived by using the phenomenological theory [194]. This theory is able to illustrate the macroscopic phenomena in ferroelectric or ferromagnetic materials close to the phase transition temperature. In the case of the ECE this phase transition is related to the order-disorder transition, which induces changes in the entropy. The Gibbs free energy is now given in terms of the electric polarization [194]

$$G = \frac{1}{2} \alpha P^2 + \frac{1}{4} \xi P^4 + \frac{1}{6} \zeta P^6. \quad (61)$$

Here, $\alpha = \beta(T - T_C)$ and β , ξ , and ζ denote the temperature independent phenomenological coefficients. Using the relation $(\partial G / \partial T)_D = -\Delta S$, the entropy change is given by

$$\Delta S = -\frac{1}{2} \beta P^2 \quad (62)$$

and the adiabatic temperature change ΔT_{EC} is calculated from the relation $\Delta T_{EC} = (T \Delta S / c_E)$

$$\Delta T_{EC} = -\frac{1}{2c_E} \beta T P^2. \quad (63)$$

In the case of the second order ferroelectric-paraelectric phase transition, as for example in the case of the (PVDF-TrFE) 55/45 copolymer [63, 78, 82, 84], the Gibbs free energy as a function of the polarization can be written as

$$G = G_0 + \frac{1}{2} \beta (T - T_C) P^2 + \frac{1}{4} \xi P^4 - EP, \quad (64)$$

where G_0 is the free energy of the paraelectric phase, i.e., independent of the polarization, β and ξ are temperature independent phenomenological coefficients, T_C is the Curie temperature, E the electric field and P the polarization. The relation between the polarization P and the electric field E is given by the equation of state

$$E = \beta(T - T_C)P + \xi P^3. \quad (65)$$

If $E=0$ and $T < T_C$ then the polarization deduced from Eq. (65) is

$$P^2 = \beta(T_C - T)/\xi. \quad (66)$$

Further, if $E \neq 0$ then by differentiating Eq. (65) we obtain the reciprocal permittivity ε

$$\frac{\partial E}{\partial P} = \frac{1}{\varepsilon} = \beta(T - T_C) + 3\xi P^2 \quad \text{if} \quad T < T_C \quad (67)$$

and

$$\frac{\partial E}{\partial P} = \frac{1}{\varepsilon} = \beta(T - T_C) \quad \text{if} \quad T \geq T_C. \quad (68)$$

From Eqs. (66) and (68), i.e., the polarization versus temperature and the permittivity versus temperature relationships, the coefficients β and ξ could be determined from the experimental data.

It should be noted that the temperature of the ferroelectric-paraelectric phase transition is a function of the DC bias electric field [84].

In the case of the first order transition, Eq. (59) needs to take into account the discontinuous change of polarization at the phase transition

$$\Delta S = \int_0^E \left(\frac{\partial P}{\partial T} \right)_E dE - \Delta P \left(\frac{\partial E}{\partial T} \right). \quad (69)$$

However, as shown above, the coefficient β could be calculated from two equations Eqs. (62) and (68). It was also shown [78] that the secondary pyroelectric effect related to the sample dimensional changes in a polymer makes a significant contribution to the observed ECE. Thus the experimentally measured ΔS will be larger than calculated from Eq. (62). This means the coefficient β from the slope of curve $\Delta S(P^2)$ will be larger than β obtained from the dielectric data, i.e., from Eq. (68).

On the other hand, the ECE predictions of the indirect method in ferroelectric materials can only be tested by the direct method, i.e., so called electrocaloric thermometry (see details below). The direct ECE measurements have been performed by using a home-made high-resolution calorimeter, allowing us (i) precise measurements of the sample temperature variation ΔT_{EC} stimulated by the change in the applied bias electric field, and (ii) the stabilization of the bath temperature within 0.1 mK, which is very important in measurements of small ΔT_{EC} in thin samples on a thick ECE inactive substrates. More about high-resolution calorimeter and its capabilities can be found in Chapters 2 and 3.

The ECE effect was verified directly in various inorganic and organic ferroelectric materials, including bulk, thick and thin films of PMN, PMN-PT, PLZT, and P(VDF-TrFE) based terpolymers, copolymers, and various blends of copolymers and terpolymers. A detailed description of those results will be given in Section 4.2. The large observed magnitudes of ECE in these systems are consistent with recent indirect measurements in ferroelectric systems and the mismatch was observed between the direct and indirect methods in relaxor systems. The latter is a consequence of a fact that the Maxwell relations presented above can only be used for thermodynamic equilibrium and ergodic systems [75, 82, 84]. The important finding is also that the effective ECE responsiveness

$\Delta T_{EC}/E$ shows a characteristic peak near the liquid-vapor type critical point in bulk perovskite relaxor materials demonstrating its relevance for the enhancement of the ECE in those systems. The relevance of the critical point proximity for the enhancement of the giant ECE is in a way similar to the enhancement of the giant electromechanical response observed at the critical point [91].

4.1 Direct measurements of the electrocaloric effect

As already mentioned, here the direct measurements of the electrocaloric effect in various materials are presented; some of them like in thin films for instance were first direct measurements of the ECE. For this reason a high-resolution calorimeter with small modifications has been utilized to measure a sample temperature variation due to the ECE when an external field was applied. The sample temperature was measured by using a small bead thermistor (Figure 29). Fast electric as well as internal thermal response times allow the application of the zero-dimensional model in data analysis with sufficient accuracy. A rigorous data analysis and the applied zero-dimensional model are presented in paragraph 4.1.3.

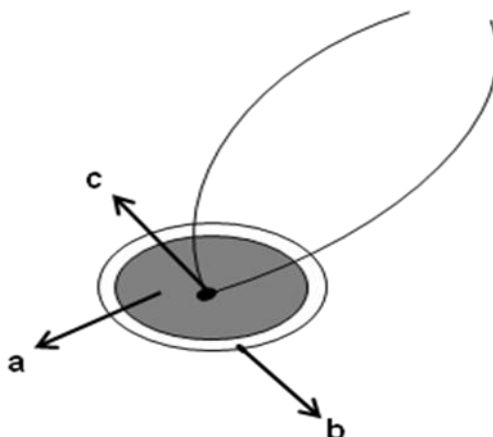


Figure 29: A sketch of the sample; (a) a part of the sample covered with electrode; (b) a sample without electrode, and (c) a small bead thermistor [76].

4.1.1 Preparations of samples

The electrocaloric effect was investigated by direct measurements in several organic and inorganic ferroelectric and relaxor ferroelectric materials produced and characterized by two research groups, the research group of Prof. Dr. Marija Kosec, from the Electronic Ceramics Department, Jožef Stefan Institute, Slovenia and the group of Prof. Dr. Qiming M. Zhang, from Pennsylvania State University, USA. Below, the preparation and some characteristics of each sample are briefly presented.

Specifically, in the case of organic samples the normal ferroelectric P(VDF-TrFE) 55/45 mol% copolymer and the relaxor ferroelectric P(VDF-TrFE-CFE) terpolymer were investigated to verify by employing the direct method [75, 78, 81, 82, 84] the results obtained by the indirect method [63]. Further, the relaxor ferroelectric P(VDF-TrFE-CFE)

terpolymer blend with 5% and 10% P(VDF-CTFE) copolymer [75, 77, 197] were used to check if the blending has an impact on the ECE in polymer materials. The third investigation was related to the impact of the irradiation on the ECE. For this reason the normal ferroelectric and the high-energy irradiated, i.e., the relaxor ferroelectric P(VDF-TrFE) 68/32 mol% copolymer were compared [74, 79].

In addition, inorganic bulk relaxor perovskite ferroelectric materials such as PMN, 0.70PMN-0.30 PT, 0.65PMN-0.35 PT [74, 76, 80, 83, 85] were investigated to check if the liquid-vapor type critical point has some influence on the electrocaloric response of bulk relaxor ferroelectrics. Furthermore, the 8/65/35 PLZT thick films [197] and self-standing (without substrate) 0.65PMN-0.35 PT thick films on a Pt layer (serving as an electrode) [198] were measured and, finally, the 8/65/35 PLZT relaxor thin films [74] were also investigated (Figure 30).

4.1.1.1 Organic materials

4.1.1.1.1 Normal ferroelectric P(VDF-TrFE) 55/45 mol% copolymer

The ferroelectric poly(vinylidene-fluoride/trifluoroethylene) 55/45 mol% copolymer films were produced using a solution-cast method by the group of Prof. Q. M. Zhang at Pennsylvania State University (as well as all other organic materials). The P(VDF-TrFE) 55/45 mol% copolymer powders were dissolved in N, N-dimethyl formamide and then stirred for around 5-12 hours at room temperature [63, 78]. Later, the polymer solution was filtered with 1 μm sized polytetrafluoroethylene or glass fiber membrane filter and then cast on clean glass plates. The glasses coated with copolymer were dried at 343 K for around 10 h in an oven. After this the films were peeled off from the glass plate and annealed at 135-140°C for over 10 h. The final thickness of films was 4-7 μm . Aluminum electrodes of 7 mm diameter were thermally evaporated on both surfaces of the copolymer films.

The dielectric properties as a function of temperature measured using a precision LCR meter (HP4284A) equipped with a temperature chamber (Delta 9023) [78] shows a ferroelectric-paraelectric transition at 340 K. Very little thermal hysteresis observed in the heating and cooling runs indicates that the ferroelectric-paraelectric transition is of second order, i.e., continuous. This was also confirmed by measuring the polarization as a function of temperature, which shows the continuous behavior at this transition [82, 84]. From the measurements of the electric displacement (D) – electric field (E) hysteresis loops at different temperatures [82, 84] it is shown that below the phase transition temperature, the polymer is in a ferroelectric state, i.e., a normal hysteresis loop is observed. At higher temperatures, the hysteresis loop becomes slim and a remanent polarization slowly diminishes. By direct measurements of the permittivity as a function of temperature in different DC bias fields [82, 84] it was shown that the FE-PE phase transition is a function of the DC bias field.

4.1.1.1.2 Relaxor ferroelectric P(VDF-TrFE-CFE) terpolymer

Samples of the poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) (P(VDF-TrFE-CFE)) 59.2/33.6/7.2 mol% terpolymer were prepared by the spin-cast method [63, 96, 98]. However, terpolymer was obtained from the normal ferroelectric copolymer by defect modification, i.e., through copolymerization with a bulky monomer CFE [63].

The typical thickness of terpolymer samples covered by aluminum electrodes of 7 mm diameter was between 3-6 μm . At first, the polymer resins were dissolved in

dimethylformamide spin coated on aluminum electroded glass substrates. Then in order to remove the excess solvent and to improve the crystallinity, the samples were annealed in vacuum at 100°C.

It was observed that P(VDF-TrFE-CFE) terpolymer shows the strong relaxor type dispersion in the complex dielectric constant with a broad maximum around room temperature [63, 96].

4.1.1.1.3 Relaxor ferroelectric P(VDF-TrFE-CFE) terpolymer blended with 5% and 10% P(VDF-CTFE) copolymer

P(VDF-TrFE-CFE) terpolymers were synthesized by a suspension polymerization process and the poly(vinylidene fluoride-chlorotrifluoroethylene) (P(VDF-CTFE)) copolymer was purchased from Solvay [199]. The blend films were prepared using the solution cast method in which N, N-dimethylformamide was used as a solvent. The terpolymers and copolymer were mixed together in a proper ratio. The final solution was dried on a glass slide at 343 K for 5 h. The terpolymers were unstretched and the blend films were uniaxially stretched to about five times the original film thickness to improve the breakdown field, so that the measurements can be carried out at high fields. The final thickness of samples was between 4 and 6 μm . Furthermore, these films were annealed at 373 K for 15 h in a vacuum oven to improve the crystallinity. At the end the films were electroded with thermally evaporated aluminum of 6 mm diameter [63, 75, 88, 98].

It was observed that in the case of P(VDF-TrFE-CFE) relaxor terpolymer on blending with a small amount of P(VDF-CTFE) 91/9 mol% copolymer, the polarization increases, and this may results in an increase of the ECE. The polarization can also be increased at high electric fields, i.e., higher than 2 MV/cm. Also it is known that blended films exhibit much higher elastic modulus than pure terpolymers and an enhanced breakdown electric field that makes them possible to extend the measurements to higher fields compared with the pure terpolymers [75, 84, 98, 200].

The measurements of the dielectric constant as a function of temperature for the pure terpolymer and the terpolymer blend with 5% wt of P(VDF-CTFE) copolymer show that the blend films still retain the typical relaxor dielectric behavior, i.e., the broad dielectric peak that moves toward higher temperatures with increasing measuring frequency, and the maximum dielectric values are reduced [75].

4.1.1.1.4 Ferroelectric P(VDF-TrFE) 68/32 mol% copolymer

The normal ferroelectric poly(vinylidene fluoride-trifluoroethylene) 68/32 mol% copolymer was investigated in our studies by the direct method using a high resolution calorimeter, and the high-energy electron irradiated one was also studied by Prof. Zhang's group via a direct method using an infrared photo detector.

It was shown that the P(VDF-TrFE) 68/32 is in principle a normal ferroelectric [201]. Its dielectric peak at the ferroelectric to paraelectric phase transition does not depend on frequency and it exhibits a thermal hysteresis between the heating and cooling, due to the first order phase transition with a latent heat more than 2.1×10^4 J/kg.

The high-energy electron irradiation converts the normal ferroelectric materials to relaxor ferroelectrics [97]. From dielectric measurements [74] it is evident that the dielectric constant of high-energy electron irradiated P(VDF-TrFE) 68/32 mol% copolymer exhibits a broad peak, which moves toward higher temperatures with increasing frequency. This is a typical fingerprint of relaxor ferroelectrics [97].

The P(VDF-TrFE) 68/32 mol% copolymer powders were purchased from Solvay and Cie from Belgium. The films were prepared by using the solution-cast method and then

five times uniaxially stretched. The thickness of those films was between 10 and 15 μm . The irradiation process was made in a nitrogen atmosphere at 110°C with 1.2 MeV electrons and 70 Mrads dose [97]. At the end the samples were coated with thermally evaporated aluminum electrodes of 7 mm diameter.

4.1.1.2 Inorganic materials

4.1.1.2.1 Relaxor ferroelectric bulk ceramic materials PMN, PMN-0.30 PT, PMN-0.35 PT

These ceramic materials were synthesized by using the mechanochemical synthesis and sintering [202]. All the below mentioned inorganic materials were prepared by the group of Prof. M. Kosec at the Jožef Stefan Institute. Specifically, bulk and thick films were prepared by Dr. Janez Holc and Dr. Hana Uršič and thin films were prepared by Dr. Barbara Malič. It was shown from X-ray diffraction analysis that all these materials were single phase perovskites [202]. The composition values are of the nominal chemical composition of the synthesis mixture, and they are less than 0.02 different from the values of the actual chemical composition [202]. The measured concentrations of the PMN, PMN-xPT materials were 94% and 97% of the theoretical values. All the samples were not hot-pressed and they were covered with gold electrodes and their thickness varied from 60 to 100 μm [202].

4.1.1.2.2 Relaxor ferroelectric 8/65/35 PLZT bulk and thick ceramic films

The thick film of 8/65/35 lead lanthanum zirconate titanate (PLZT) ceramics was prepared by printing and firing paste on an alumina substrate. The firing was made in a PbO rich atmosphere to obtain a nearly theoretically dense film [203, 204]. The samples were 28 μm thick and covered with the gold electrode of 6 mm diameter sputtered at the room temperature. As a bottom electrode, platinum paste was used.

The bulk 8/65/35 PLZT ceramic was synthesized using the mixed method [203, 205]. Pressed pallets were sintered at 1200°C for 2 h. The bulk samples were around 70 μm thick and covered with gold electrodes of 6 mm diameter.

4.1.1.2.3 Self-standing relaxor ferroelectric PMN-0.35PT thick films on Pt layer

The PMN-0.35PT thick film paste was prepared from an organic vehicle and a high energy milled powder fired at 700°C. At first platinum (Pt) paste was screen printed on the alumina substrate and fired at 1350°C for approximately 2 h. Later the thick films were screen printed and fired at 950°C for the next 2 h. On the top of the samples the gold electrodes were deposited by sputtering. At the end the thick films with a Pt layer were peeled off from the alumina substrates [202, 206, 207].

These thick films and the Pt electrode were used for further treatment. In the first step both components were screen printed and fired on the alumina substrate. Next, the alumina support was glued on the top of the PMN-0.35PT layer. In the third step the composite PMN-0.35PT/Pt conductor/top alumina support were removed from the alumina substrate. At the end the glue was dissolved in acetone and the PMN-0.35PT samples were ready for measurements [202, 206, 207].

4.1.1.2.4 Relaxor ferroelectric 8/65/35 PLZT thin films

The La-doped $\text{Pb}(\text{ZrTi})\text{O}_3$ relaxor ceramic thin films with the composition $(\text{Pb}_{0.88}\text{La}_{0.08})(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$ (8/65/35 PLZT) were fabricated using a sol-gel method [208]. Details

about this method, which contains different processing steps, can be found in Refs. [209-211]. The PLZT thin films were covered with 100 nm platinum (below) and 80 nm thick Cr/Au (top) electrodes and the thickness of the PLZT film was around 0.45 μm . The details of the layer composing the substrate are shown in Figure 31 showing the cross section of the thin film and substrate obtained by scanning electron microscopy (SEM). Below the Pt layer there is a 30 nm thick TiO_2 layer sitting on top of a 450 nm thick SiO_2 layer. All these layers were deposited on a 600 μm thick Si monocrystal. The measurements of the dielectric constant as a function of the temperature at different frequencies show significant broadening of the ferroelectric-paraelectric phase transition [74].

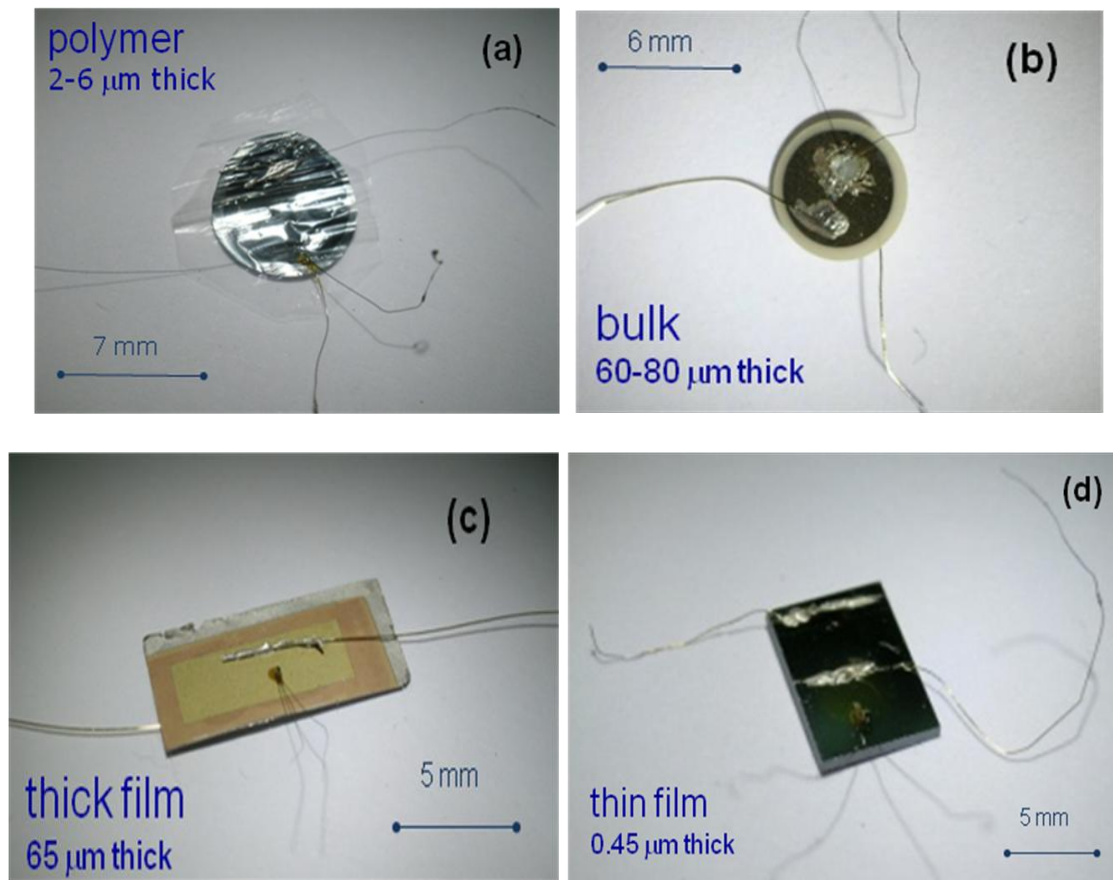


Figure 30: *Presentation of organic and inorganic materials produced by the two research groups mentioned above. The typical sample arrangements are shown for (a) polymer, (b) bulk material, (c) thick film and for (d) thin film. A small bead thermistor and the gold wires were directly attached to the samples [74, 74, 83, 198].*

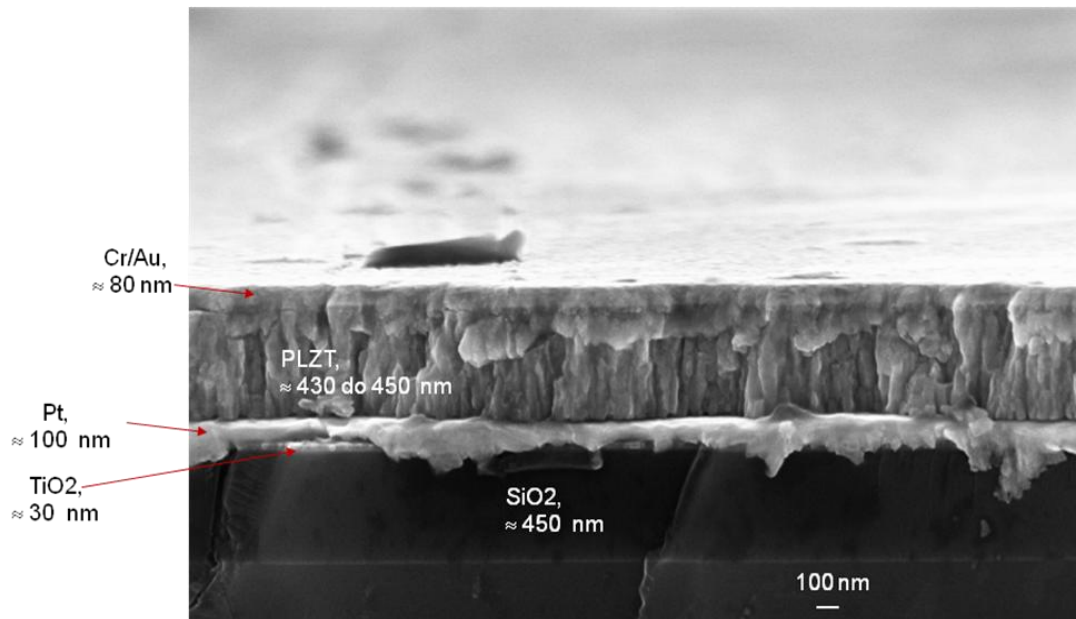


Figure 31: *The PLZT thin film configuration obtained by SEM.* The PLZT thin film is covered with Cr/Au (top) and Pt (below) electrode and TiO₂ and SiO₂ layers are below the Pt layer. All these layers are deposited on a Si monocrystal [74].

4.1.2 Experimental set-up

As mentioned above the ECE measurements in different samples were investigated by using the home-made high resolution calorimeter presented in Chapter 2, but with some small modifications. Thus instead of the Arbitrary Signal Generator a High Voltage Generator driven by the Arbitrary Signal Generator was used to generate the electric field step signal, which was applied to the sample.

A simple construction of the whole calorimeter setup is presented in Figure 32. As shown, the calorimeter set-up consists of the High Voltage Generator, Arbitrary Signal Generator, Digital multimeter (DMM), Temperature controller and a computer. The High Voltage Generator is driven and the DMM is triggered by the Arbitrary Signal Generator. The DMM measures the platinum thermometer (PRT) resistance and the resistance of the microbead thermistor attached to the sample. The data are then collected from the DMM by a computer, which via a Temperature controller also controls the surrounding bath temperature.

The bath temperature is measured by a thermistor mounted in the copper (Cu) block. The flexible heater attached around the Cu block enables precise temperature stabilization. The shape, length, and the amplitude of the electric pulses are controlled by the computer via the programmable Arbitrary Signal Generator.

More details about the calorimeter set-up can be found in Refs. [99] and [100].

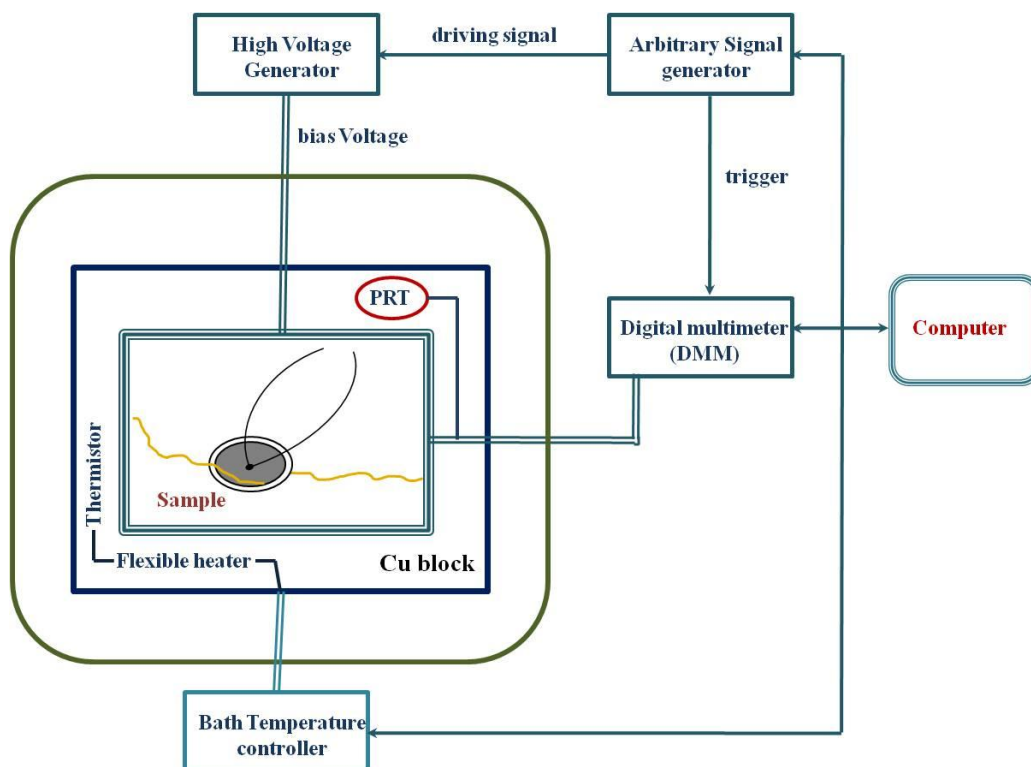


Figure 32: A simple schematic presentation of the ECE measurement set-up. In contrast to the ac calorimetry, here instead of the heat power an external field is applied to the sample.

4.1.3 Data analysis by using a zero-dimensional model

In order to explain the results of the direct measurements of the ECE obtained by using the high resolution calorimeter, the physical zero-dimensional model was used due to the fact that the internal thermal diffusion times of the samples are sufficiently short. The basics of such a model have already been presented in Chapter 2 and here it is expanded in order to take carefully into account different subsystems (such as the parts of the sample without electrodes, attached wires, inactive substrates etc.) and the corresponding heat flow dynamics among them [76].

The whole system consists of a sample with attached thermistor coupled with a bath via the thermal resistance and it is divided into subsystems related to a part of a sample with electrodes, to that without electrodes and to the thermistor (Figure 33). Each subsystem has its own heat capacity C_p , which are known quantities. Due to the small mass of the thermistor and the good coupling between the sample and the thermistor the relatively fast internal thermal response times are achieved in bulk and thick films in comparison to the external thermal time scale related to the coupling to the bath. Consequently, the system in Figure 33 can be solved by using a two-step simplification.

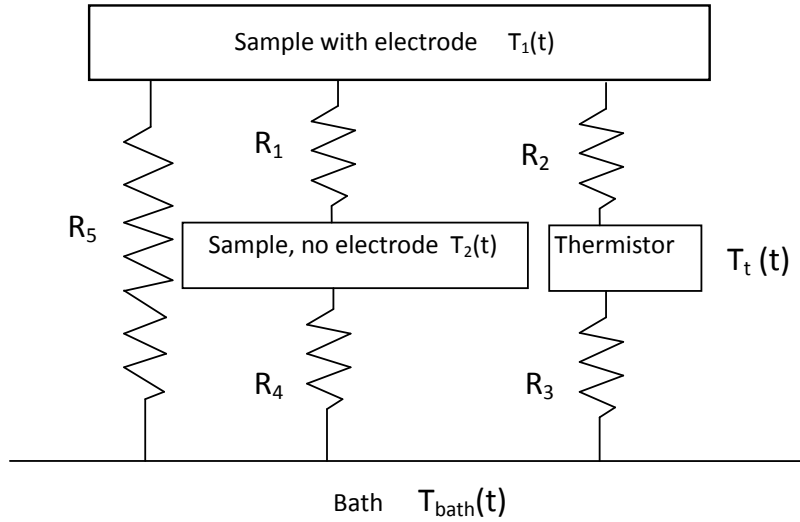


Figure 33: Schematic representation of the typical sample thermal subsystems and their mutual coupling. Each subsystem has its own heat capacity C_p and the couplings are represented by the thermal resistances R_i , $i=1, \dots, 5$ [76].

In the case of the system shown in Figure 33, an analytical solution is not easy to obtain. A system of three differential equations needs to be solved. Following the equation

$$P = \frac{dQ}{dt} = C_p \frac{dT}{dt} \quad (70)$$

the differential equations for the system are

$$\frac{(T_1 - T_2)(t)}{R_1} - \frac{(T_2(t) - T_b)}{R_4} = C_{p, vbe} \frac{dT_2(t)}{dt} \quad (71)$$

$$\frac{(T_1 - T_t)(t)}{R_2} - \frac{(T_t(t) - T_b)}{R_3} = C_{p, t} \frac{dT_t(t)}{dt} \quad (72)$$

$$-\frac{(T_1 - T_2)(t)}{R_1} - \frac{(T_1 - T_t)(t)}{R_2} - \frac{(T_1(t) - T_b)}{R_5} = C_{p, ve} \frac{dT_1(t)}{dt} . \quad (73)$$

Here the T_1 , T_2 , T_b and T_t denote temperatures of the part of the sample with the electrode, the part of the sample without electrodes, the bath temperature and the thermistor temperature, respectively. The symbols R_i , $i=1, \dots, 5$, are related to thermal resistivities between different parts shown in Figure 33, and the $C_{p, ve}$, $C_{p, vbe}$, $C_{p, t}$ are heat capacities of the part of the sample covered with the electrode, of the part of the sample without the electrode and of the thermistor, respectively.

As mentioned above, the above system can be solved in two steps. First the system of differential equations for the subsystem in Figure 34(a) is solved and then differential equations for the second subsystem (Figure 34(b)) are solved with the boundary

conditions determined from the first subsystem.

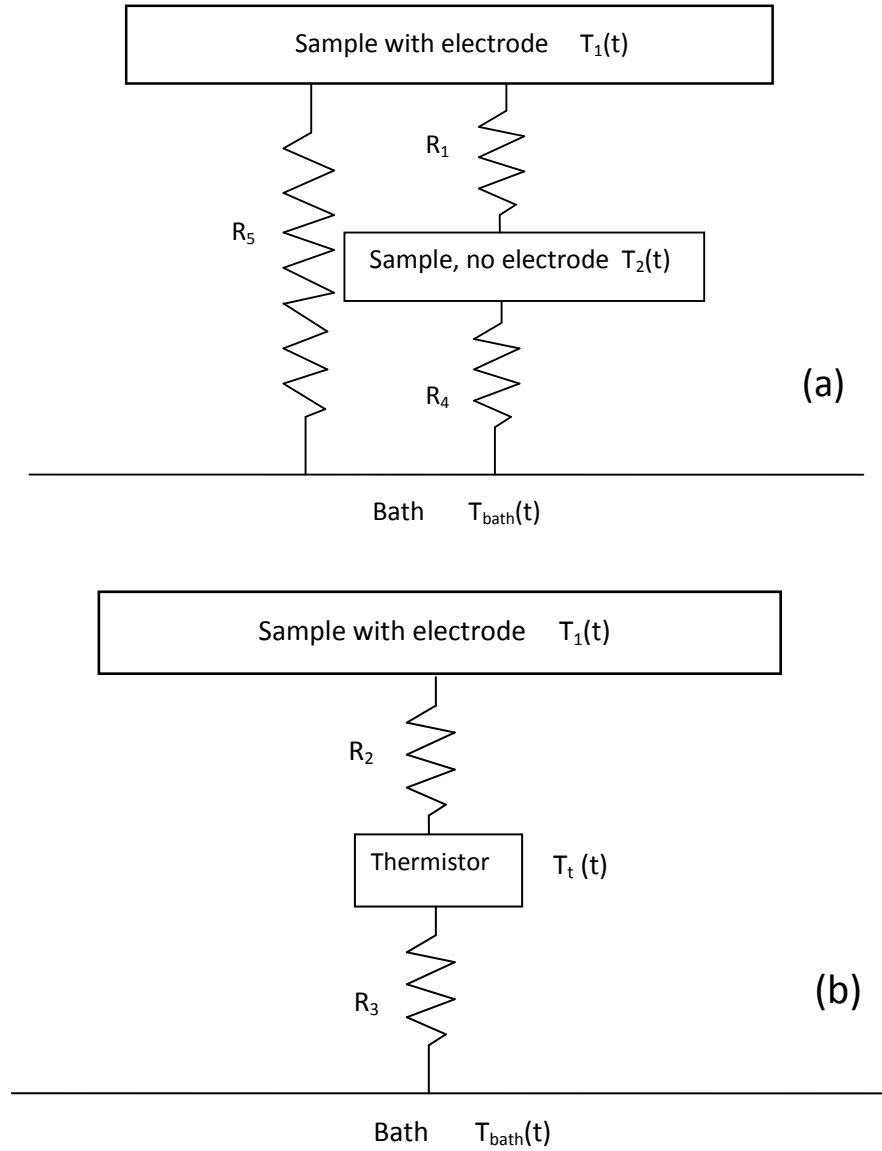


Figure 34: *Schematic representation of two systems, which are solved in a two-step procedure. In the first subsystem (a) the part of the sample with the electrode comes into equilibrium with the part of the sample without the electrodes. Then, in the second step (b) the whole block together with the small thermistor comes into equilibrium with the surrounding bath [76].*

From the system of differential equations for subsystem (a) the expression for the temperature $T_1(t)$ is obtained. This solution is then used in the second step for a subsystem (b). The differential equation for this second subsystem in Figure 34(b) is given by the expression in Eq. (73). After some mathematical calculations and assuming a step electrical signal the final solution $T(t)$ is obtained [76]

$$T_t(t) = T_{\text{bath}} + [(1 - A - C)\Delta T_{\text{res}} + (B + D)\Delta T_{\text{EC}}]e^{-t/\tau_1} + (A\Delta T_{\text{res}} - B\Delta T_{\text{EC}})e^{-t/\tau_2} + (C\Delta T_{\text{res}} - D\Delta T_{\text{EC}})e^{-t/\tau_3} \quad (74)$$

with $T_t(0) = T_{\text{bath}} + \Delta T_{\text{res}}$ and the constants A , B , C and D defined as

$$\begin{aligned} A &= \frac{\tau_{21}\tau_{32}\left(\frac{R_1C_{p,\text{vbe}}}{\tau_{32}} - 1\right)}{(R_1C_{p,\text{vbe}} + \tau_3)R_2C_{p,t}} \\ B &= A\left(1 + \frac{\tau_3}{R_1C_{p,\text{vbe}}}\right) \\ C &= \frac{\tau_{31}\tau_{32}}{\left(\frac{R_1C_{p,\text{vbe}}}{\tau_3} + 1\right)R_2C_{p,t}\tau_2} \\ D &= C \frac{\tau_2\left(1 + \frac{\tau_3}{R_1C_{p,\text{vbe}}}\right)}{\tau_3} \end{aligned} \quad (75)$$

where $\tau_{ij} = \frac{\tau_i\tau_j}{\tau_i - \tau_j}$. ΔT_{res} represents the additional Joule heating of the sample due to the

finite electric conductivity. It can be determined very precisely from the difference $\Delta T_{\text{res}} = T_t(t_F) - T_t(0)$ between the initial temperature level at $t=0$ (field not turned on yet) and the temperature level reached at some large time t_F exceeding the external thermal time in which the sample reaches the equilibrium with the external bath and in which the electric field still remains to be turned on. Analogously, it can also be determined from the data measured when the field is switched off by considering the difference $\Delta T_{\text{res}} = T_t(t_F) - T_t(\infty)$. Here, $T_t(\infty)$ represents the temperature level at very long times after the electric field is switched off. Let us note that ΔT_{res} was found to be negligibly small in most bulk and thick film samples. For example, as shown in Figure 35 $T_t(t_F) - T_t(\infty) \approx 0$ indicates no resistive heating of the sample. Only in thin films at higher fields the resistive Joule heating became important to be included in the data analysis.

Here ΔT_{res} , $C_{p,\text{vbe}}$, $C_{p,t}$, R_1 and T_{bath} are already determined, known quantities, while R_2 , τ_i , ΔT_{EC} are fit parameters. R_1 is defined from the heat-transfer equation at a specific geometry of the sample. Such a method of data analysis works fine in describing the $T_t(t)$ as shown by the solid line representing the fit to the measured data in Figure 35. Here, the fit parameters can be established very precisely due to a large number of precisely measured data points. In fact, it turned out that such a rigorous analysis is, in most cases, unnecessary due to the rather fast internal thermal timescales and a further simplified procedure of data analysis can be employed. This even further simplified method will be presented below in the case of the thin films data analysis.

In the case of thin films with a thickness around a few hundred nm the situation is much simpler due to the very fast internal thermal response times, typically of the order of few milliseconds up to tens of milliseconds. This implies a very fast transfer of the heat

through the whole sample, including the substrate and the electrodes, thus allowing a very fast internal equilibration of the system. Such a thermally equilibrated system now slowly loses the heat on a much longer time scale to the surrounding bath. In this case only the external relaxation of the temperature of the whole internally equilibrated system is first considered

$$\Delta T(t) = T_{\text{bath}} + \Delta T e^{-t/\tau}. \quad (76)$$

The final ECE temperature change ΔT_{EC} of the subsystem covered with the electrodes is then determined from

$$\Delta T_{\text{EC}} = \Delta T \frac{\sum C_p^i}{C_p^{\text{EC}}}. \quad (77)$$

Here C_p^i typically stands for the heat capacities of the attached small thermistor, supporting wires, electrodes, and part of the sample without electrodes, i.e., all the subsystems participating in the fast internal equilibration. C_p^{EC} denotes the heat capacity of the sample covered with electrodes in which the ECE takes place. The typical error of estimation of ΔT_{EC} in thin films was around a few percent up to ten percent, mostly related to the uncertainty in the determination of thicknesses of different layers. In the case of bulk and thick film samples, this error was much smaller, below one percent.

The entropy change ΔS was determined from

$$T \frac{\Delta S}{m} = c_p \Delta T_{\text{EC}}, \quad (78)$$

where T is the temperature at which the ECE was measured and c_p is the sample's specific heat capacity.

As mentioned above, a typical step-like electrical signal with various amplitudes was applied in the experiments on bulk samples and thick films. The duration of the pulses was chosen so that the sample could get into thermal equilibrium with the surrounding baths while the field remains turned on. The temperature of the system was measured in the vicinity of the positive and negative ramps as a function of time (Figure 35). Open circles denote directly measured data points and the solid line through the data points presents the fit to Eq. (76). The determined ΔT_{EC} from the fits was typically around few percent to 30 % larger than the observed maximum temperature deviation from the bath temperature. This difference is related to losses to the bath during the internal equilibration between the different components of the system presented in Figure 33.

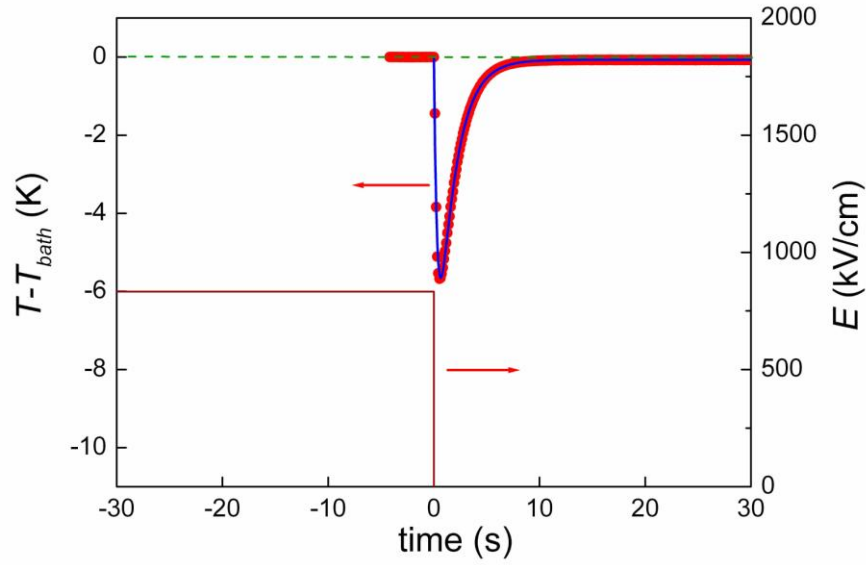


Figure 35: Measured EC data (open circles), the fit (solid line) and the schematic representation of the electric field pulse duration [75].

One example of a determination of the ECE in thin films is presented in Figure 36. ΔT was obtained by fitting the exponentially decaying wings related to heat losses to the surrounding bath (fitting curves represented by the red solid line in Figure 36). The final value of the ECE temperature change ΔT_{EC} was calculated by using Eq. (77).

In order to reduce the damage of the sample and to measure the ECE at higher electric fields, short step pulses between ~ 1 and 5 s were used (Figure 37). In such a case the ΔT_{EC} was calculated by using the calibration of short pulse data to data obtained by standard step pulses (around 250s long) at a lower magnitude of the electric field.

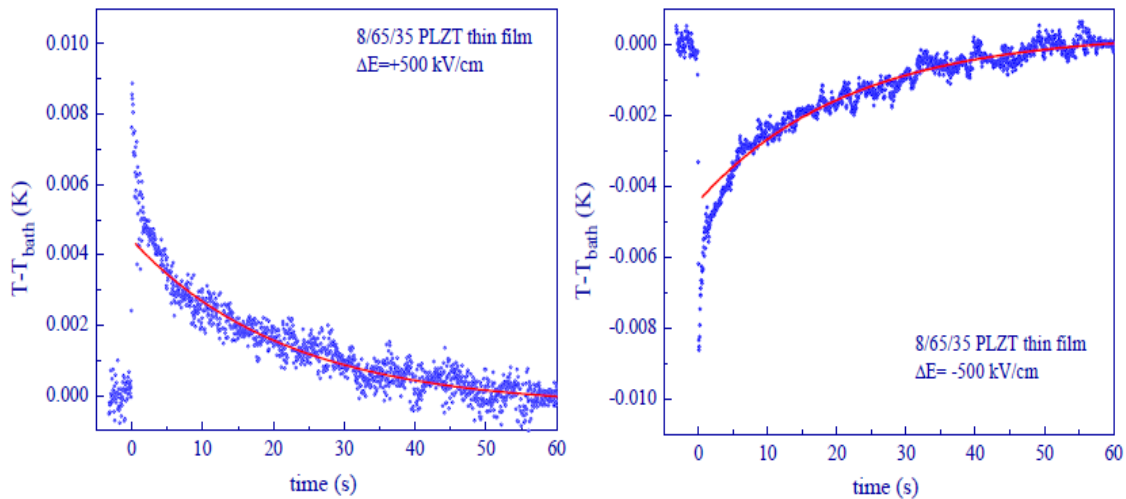


Figure 36: An example of the determination of the ECE in thin film samples. The red lines present the fitting curves. The initial fast changing data within first few seconds is a remnant of the internal sample equilibration taking place at a much faster time scale. In this case most of the sample heat is already lost to the substrate at a much shorter time scale and only the equilibration of the systems with and without electrodes is still taking place on a time scale of a second.

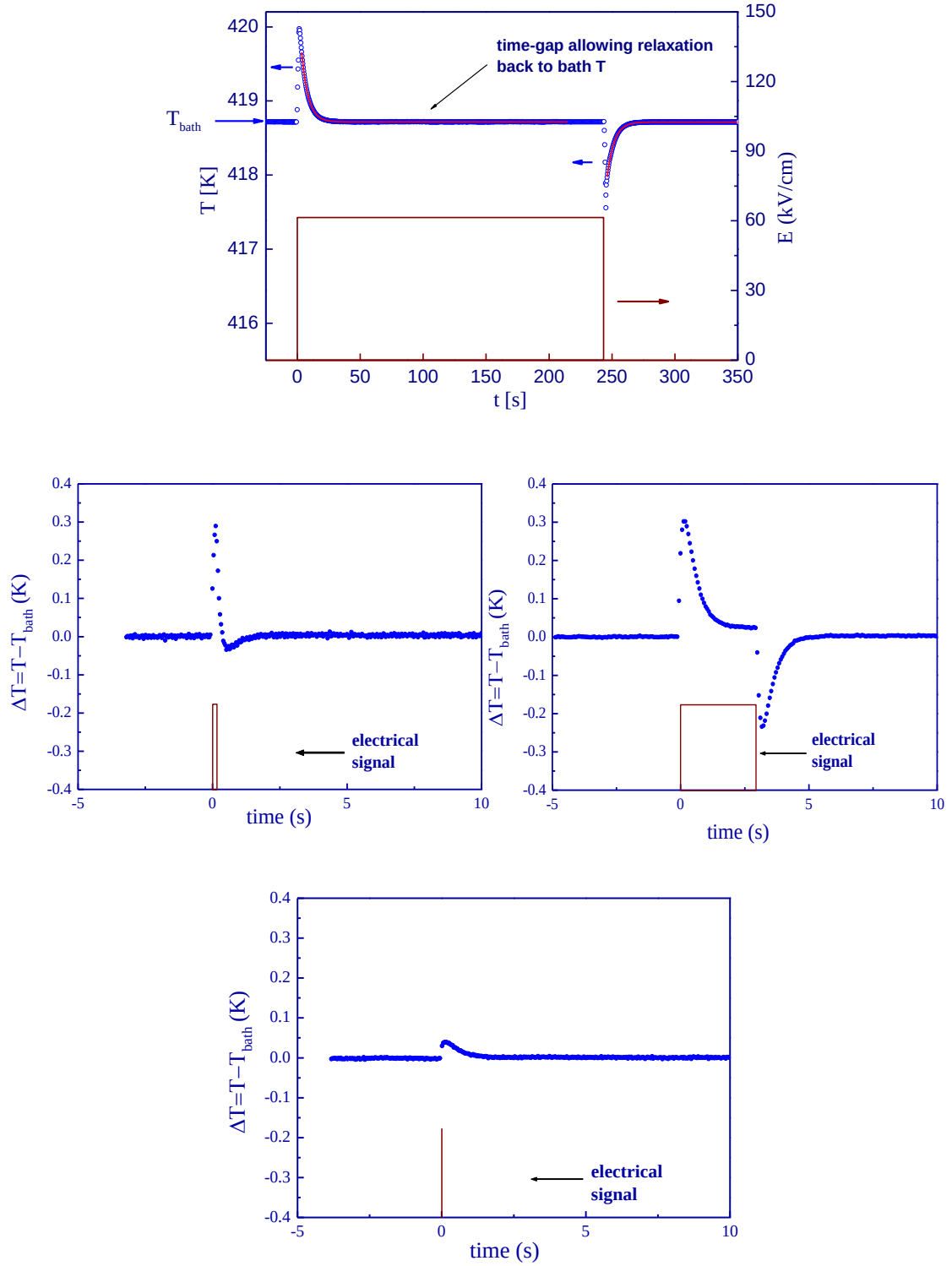


Figure 37: Different pulses of the electric field used during the ECE measurements. Standard step pulses are around 250 s long and the short pulses are between 0.1 and 5 s long.

4.2 Experimental results of the ECE measurements

In this section all our experimental results on samples mentioned above are presented. For simplicity the term specific entropy change Δs , defined as $\Delta s = \Delta S/m$, will be used instead of the term entropy change per mass.

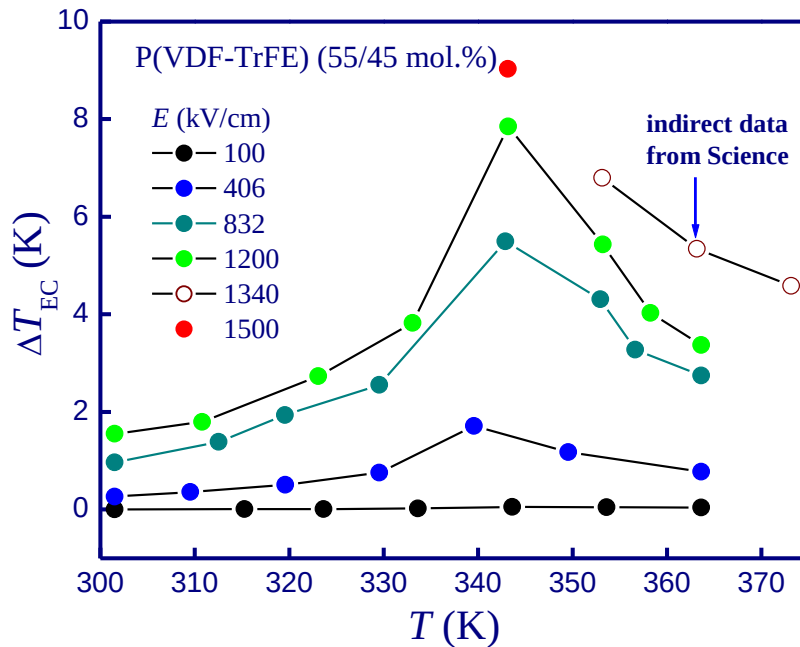
4.2.1 Organic materials

4.2.1.1 Comparison between direct and indirect measurements of the ECE in ferroelectric and relaxor ferroelectric polymers

4.2.1.1.1 P(VDF-TrFE) 55/45 mol% copolymer

The directly measured ECE temperature ΔT_{EC} and the specific entropy Δs changes as a function of the temperature between 300 and 365 K for unstretched P(VDF-TrFE) 55/45 mol% copolymer are presented in Figure 38 [82, 84]. The electrocaloric effect reaches a maximum value at a temperature of around 343 K. The dielectric measurements performed by Zhang's group showed that the FE-PE transition is continuous and it takes place at 343 K [78, 82, 84]. The ECE data presented in Figure 38 show that a significant enhancement of the ECE temperature change takes place in the vicinity of the ferroelectric-paraelectric phase transition.

The maximum temperature change ΔT_{EC} is around 10 K and the specific entropy change Δs around 30 J/kgK at the magnitude of the electric field of $E=1.5$ MV/cm. The temperature change as a function of the electric field $\Delta T_{EC}(E)$ is presented in Figure 39.



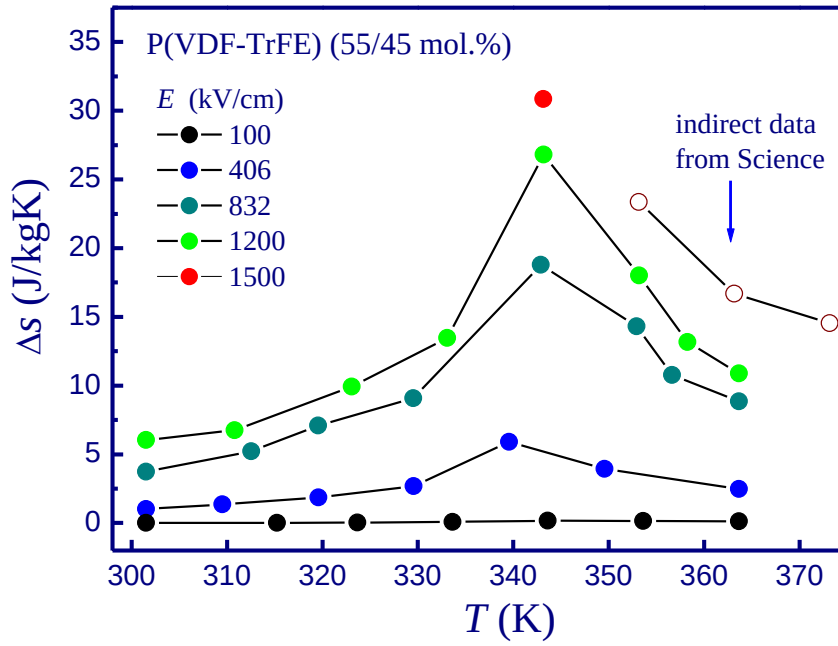


Figure 38: ΔT_{EC} and Δs in *P(VDF-TrFE)* 55/45 mol% copolymer as functions of temperature at several values of the electrical field amplitude E [82, 84].

In previous studies of the ECE response investigated by indirect measurements the ECE temperature change ΔT_{EC} was more than 12 K and the specific entropy change Δs of around 60 J/kgK was observed at the temperature 353 K under the electric field $E=2.09$ MV/cm [63].

To conclude, the presented results demonstrate a good agreement between the ECE data measured directly and the ECE data deduced from the Maxwell relations, which were published in Ref. [63] This shows that the Maxwell relations can be used to deduce the ECE in ferroelectrics at temperatures above the FE-PE phase transition [78].

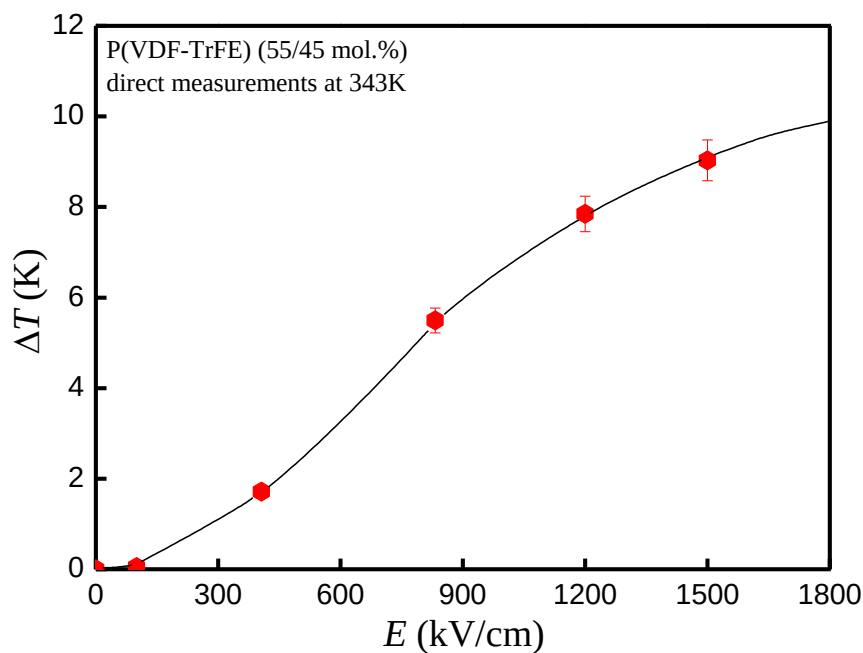


Figure 39: Electrical field variation of the ECE temperature change in *P*(VDF-TrFE) 55/45 mol% copolymer measured at the a constant temperature of 343 K.

As is shown below, an agreement between the direct and indirect measurements of the ECE does not exist in the case of relaxor ferroelectric polymers.

4.2.1.1.2 *P*(VDF-TrFE-CFE) terpolymer

As mentioned above this relaxor ferroelectric terpolymer was obtained from the normal ferroelectric *P*(VDF-TrFE) copolymer by adding a bulky monomer CFE [63]. It was shown that these relaxor ferroelectric polymers exhibit a large electric-field induced polarization near room temperature, indicating a potential for a giant ECE [63, 96].

The electrocaloric temperature change ΔT_{EC} was measured directly as a function of the temperature for different applied electric fields, ranging from around 80 to 750 KV/cm. The results presented in Figure 40 show that with increasing temperature T the value of the electrocaloric response decreases above the smeared peak and the weak temperature dependence of the ECE is observed. The largest temperature change ΔT_{EC} is observed at room temperature around 289 K for all measured electric fields. Therefore, the field dependence of the ΔT_{EC} was investigated at a constant temperature $T = 289$ K (Figure 41). It is shown that the significant ECE, around 4 K, can be achieved at the relatively modest field amplitude of around 750 kV/cm [81].

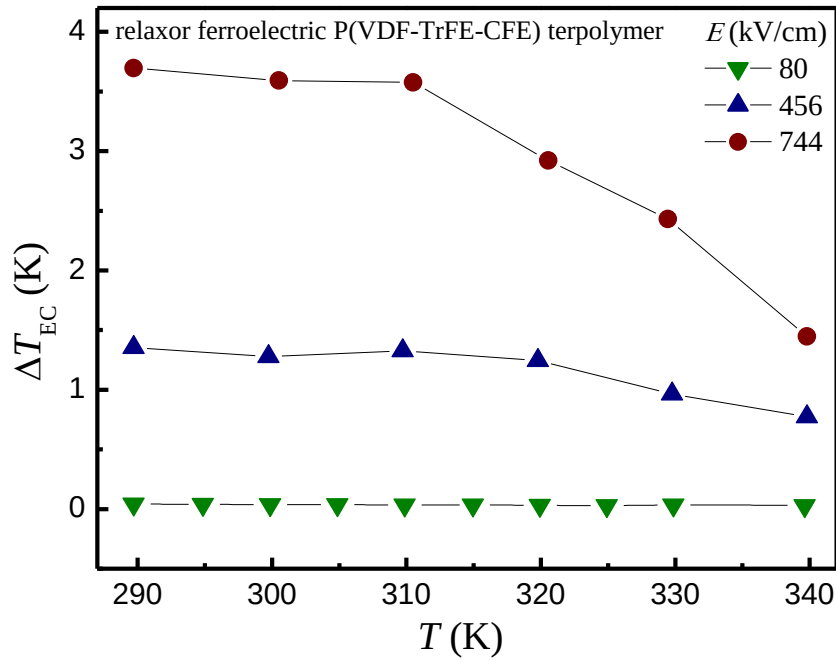


Figure 40: The ECE temperature change ΔT_{EC} as a function of the temperature for different electric fields measured for the relaxor ferroelectric terpolymer P(VDF-TrFE-CFE) [81, 82, 84].

It is known that in relaxor ferroelectrics several polarization mechanisms that contribute to the electrocaloric effect exist. It was shown that the polar nanoregions and the field-induced dipolar reorientations contribute to the entropy ΔS for various electric fields [96].

The specific ECE entropy change Δs as a function of the temperature for three different electric fields is presented in Figure 42. Figure 43 shows Δs as a function of the electric field at a constant temperature $T=289$ K. The change of entropy is around 15 J/kgK at electric field strength of 744 kV/cm.

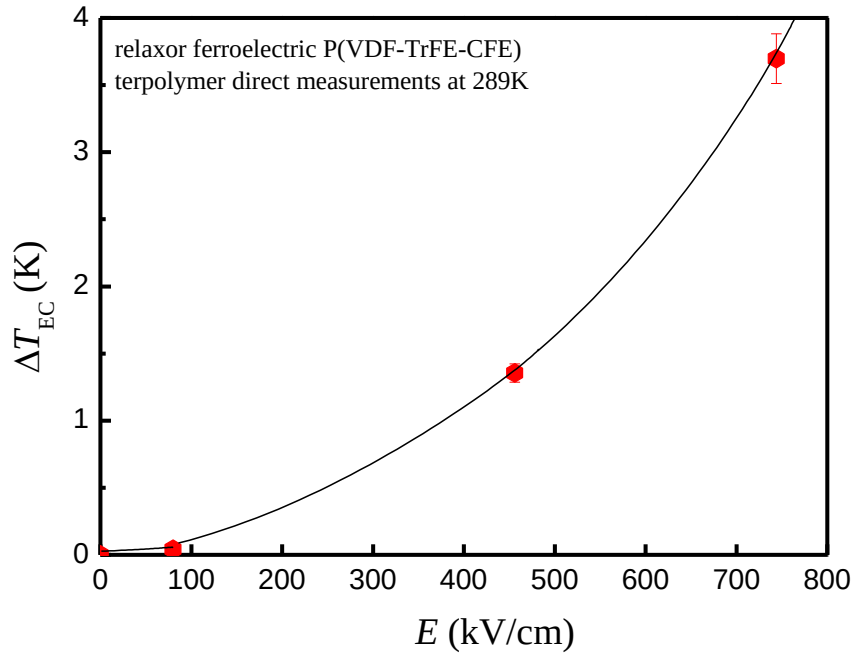


Figure 41: *Electric field variation of the ECE temperature change ΔT_{EC} measured at a constant temperature of 289 K for P(VDF-TrFE-CFE) terpolymer [81].*

In contrast to the data obtained by employing an indirect method (B. Neese, et al. [63]), the direct ECE data show different behavior [81, 84]. The directly measured ECE data show a decrease of ΔT_{EC} with increasing temperature, in contrast to increasing ΔT_{EC} obtained by the indirect measurements. In addition, by comparing the data at the same field amplitude the ECE obtained in direct measurements is systematically larger than that obtained from the Maxwell relation [63]. It turned out that the main difference is reflected in a significantly different β , which is determined to be typically smaller in the case of the indirect method [75], thus reducing the estimated change of entropy ΔS from Eq. (62).

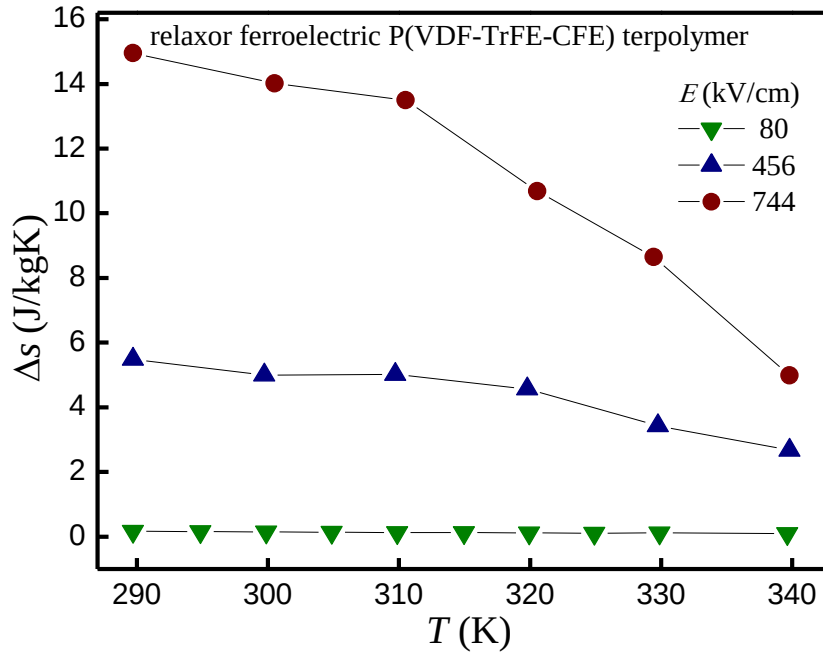


Figure 42: The entropy density change Δs of the ECE in the P(VDF-TrFE-CFE) terpolymer as a function of the temperature for various electric fields [81, 82, 84].

Consequently, it can be concluded that the Maxwell relation is not a suitable choice for the electrocaloric characterization of the organic as well as inorganic relaxor ferroelectrics [75, 82, 84]. This ascertainment is perhaps a consequence of the non-ergodic behavior of relaxor ferroelectric polymers, even at temperatures above the dielectric constant maximum, but the Maxwell relations (Eqs. 59 and 60) are valid only for ergodic, i.e., systems in thermodynamic equilibrium [84].

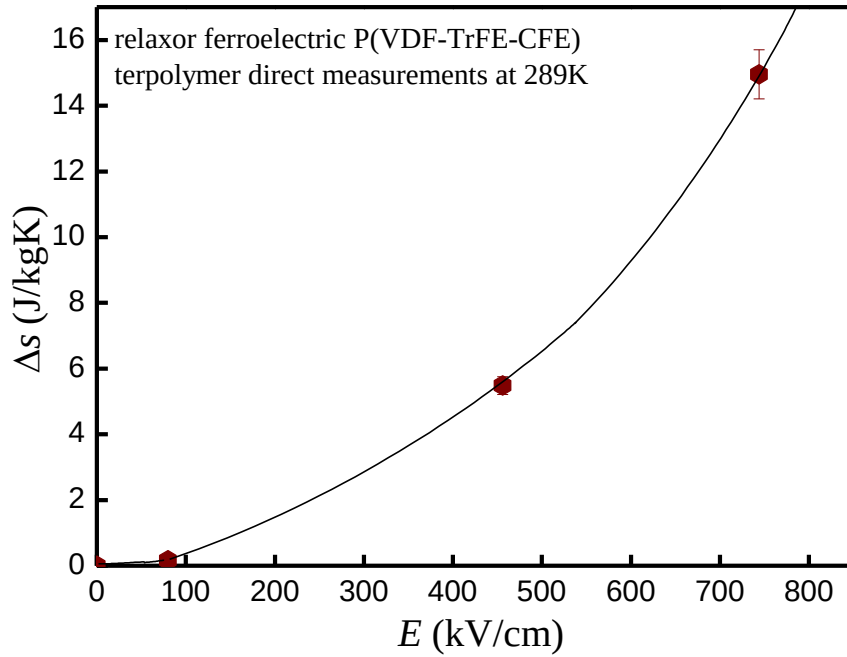


Figure 43: Δs as a function of the electric field amplitude measured at a constant temperature of 289 K for P(VDF-TrFE-CFE) terpolymer [81].

4.2.1.2 Impact of blending on ECE response

4.2.1.2.1 P(VDF-TrFE-CFE) terpolymer blended with 5% and 10% P(VDF-CTFE) copolymer

It was already mentioned that in the case of blending the P(VDF-TrFE-CFE) relaxor terpolymer with a small amount of P(VDF-CTFE) 91/9 mol% copolymer the polarization increases, thus resulting in an increase of the ECE [63]. In addition, the blended films exhibit a high elastic modulus and enhanced breakdown electric fields that make them possible to extend the measurement of the ECE to higher fields [75, 84, 98, 200].

In both 5% and 10% blended systems the electrocaloric temperature change ΔT_{EC} was measured as a function of the temperature in the range between 300 and 330 K at various electric fields (Figures 44a and 44b) and as a function of the amplitude of the electric field at a constant temperature 318 K (Figures 45a and 45b) [75, 77]. It is shown that the largest ECE around $\Delta T_{EC}=12$ K was observed near room temperature at the field amplitude $E=1.698$ MV/cm in 5% blends. In terpolymer blended with 10% copolymer the electrocaloric effect of around $\Delta T_{EC}=6$ K was found at the slightly smaller electric field of 1.2 MV/cm. Such high magnitudes of the ECE in polymer blends are achieved due to the high electric break down field in these materials and the increased polarization. Regarding the entropy changes ΔS , the polar nanoregions and the field-induced dipolar reorientations contribute to ΔS [96].

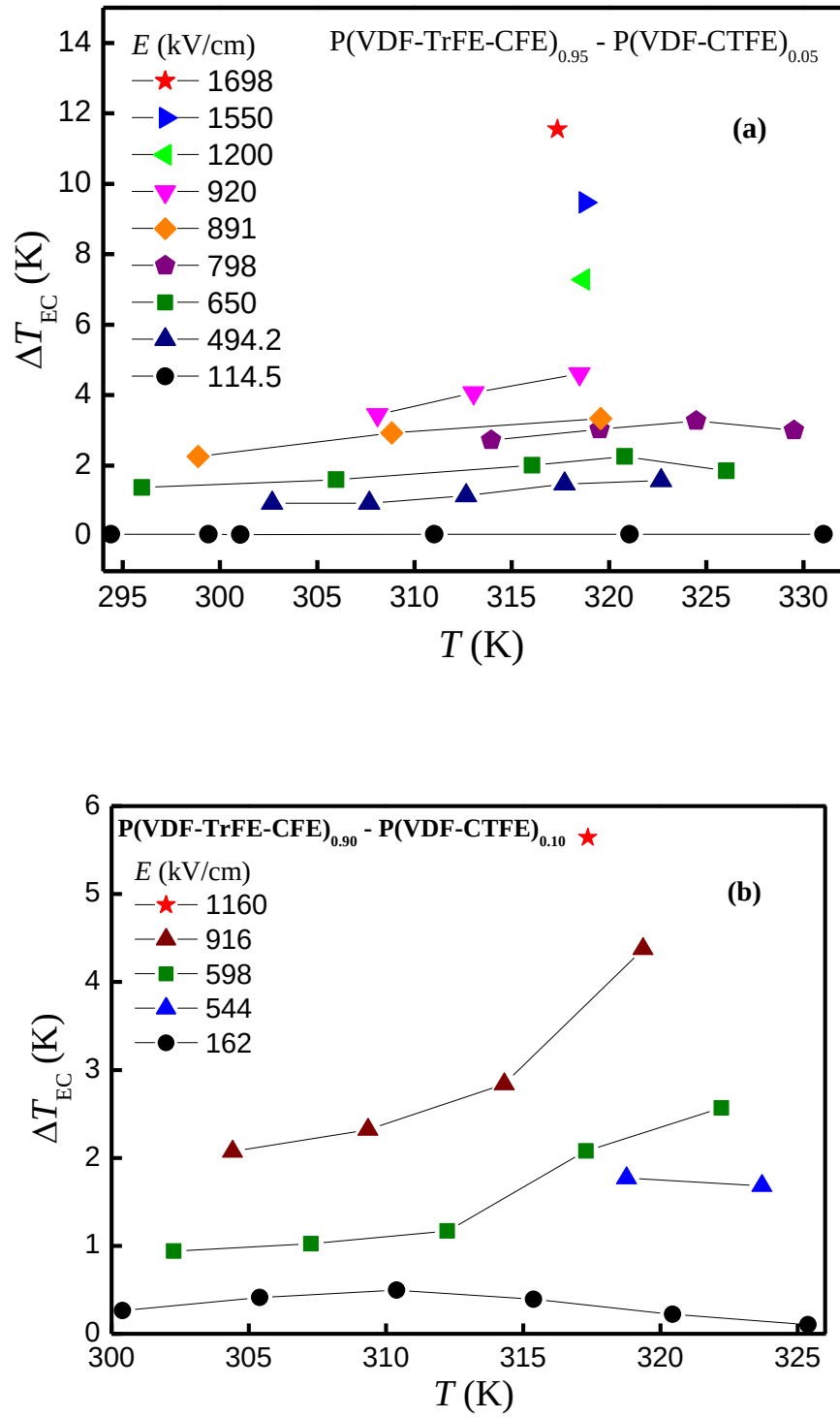


Figure 44: The ECE temperature changes ΔT_{EC} in $P(\text{VDF-TrFE-CFE})$ relaxor terpolymers blend with (a) 5% and (b) 10% $P(\text{VDF-CTFE})$ copolymers as functions of the temperature for various values of the electric field amplitude [75, 77].

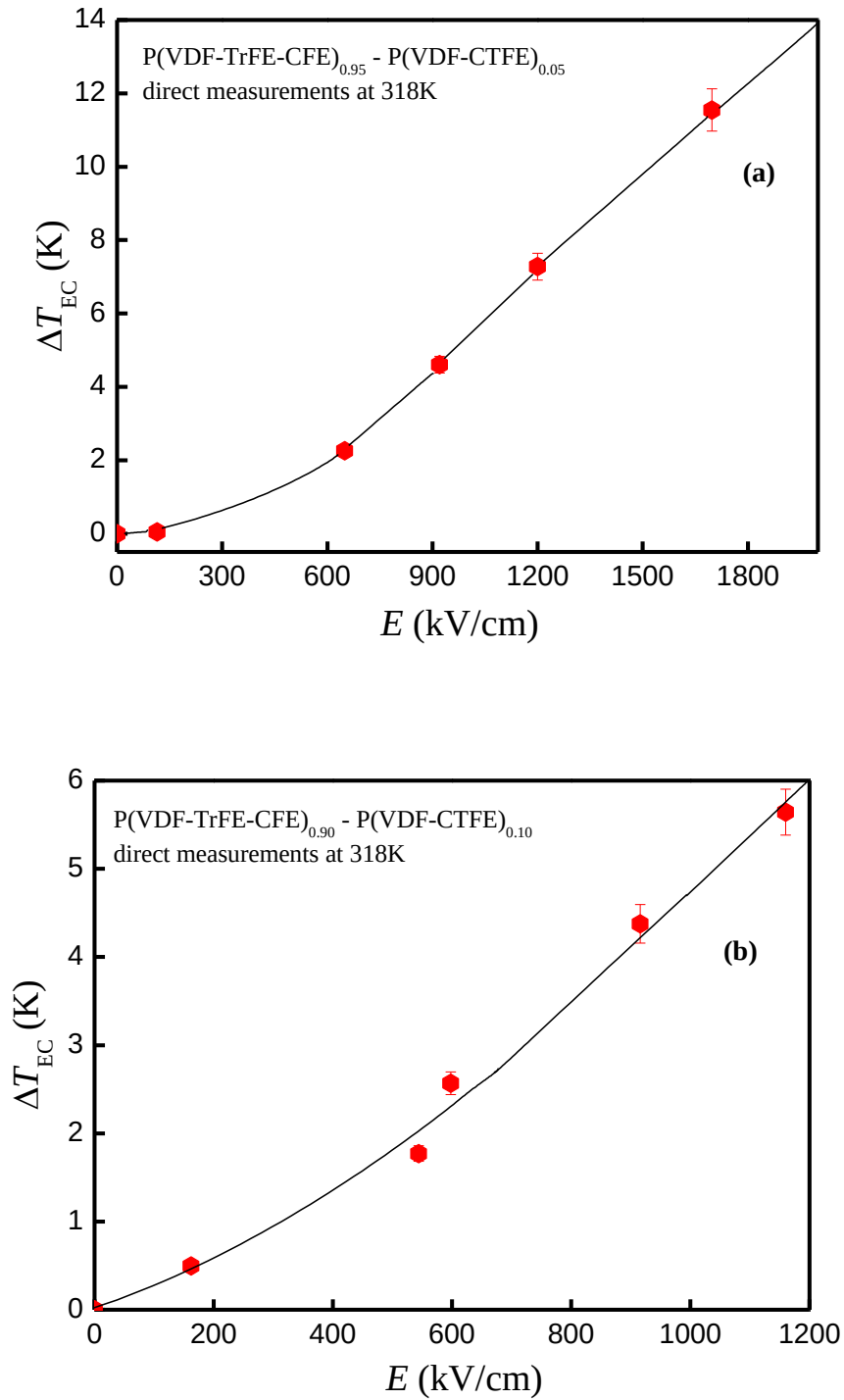


Figure 45: Electric field variation of the ECE temperature change ΔT_{EC} measured at a constant temperature of 318 K for $P(VDF-TrFE-CFE)$ relaxor terpolymers blend with (a) 5% and (b) 10% $P(VDF-CTFE)$ copolymers [75, 77].

The variation of the specific entropy Δs as a function of the temperature at different values of the electric field amplitude and as a function of the amplitude of the applied electric field at a constant temperature of 318 K are presented in Figure 46 for 5% terpolymer-copolymer blends and in Figure 47 for 10% blends. The specific entropy

change Δs for the $P(\text{VDF-TrFE-CFE})$ relaxor terpolymer blends with 5% $P(\text{VDF-CTFE})$ copolymer is around 50 J/kgK at an electric field value $E=1.7$ MV/cm [75], and around 25 J/kgK at the field strength of 1.2 MV/cm [77] in the case of 10% blend.

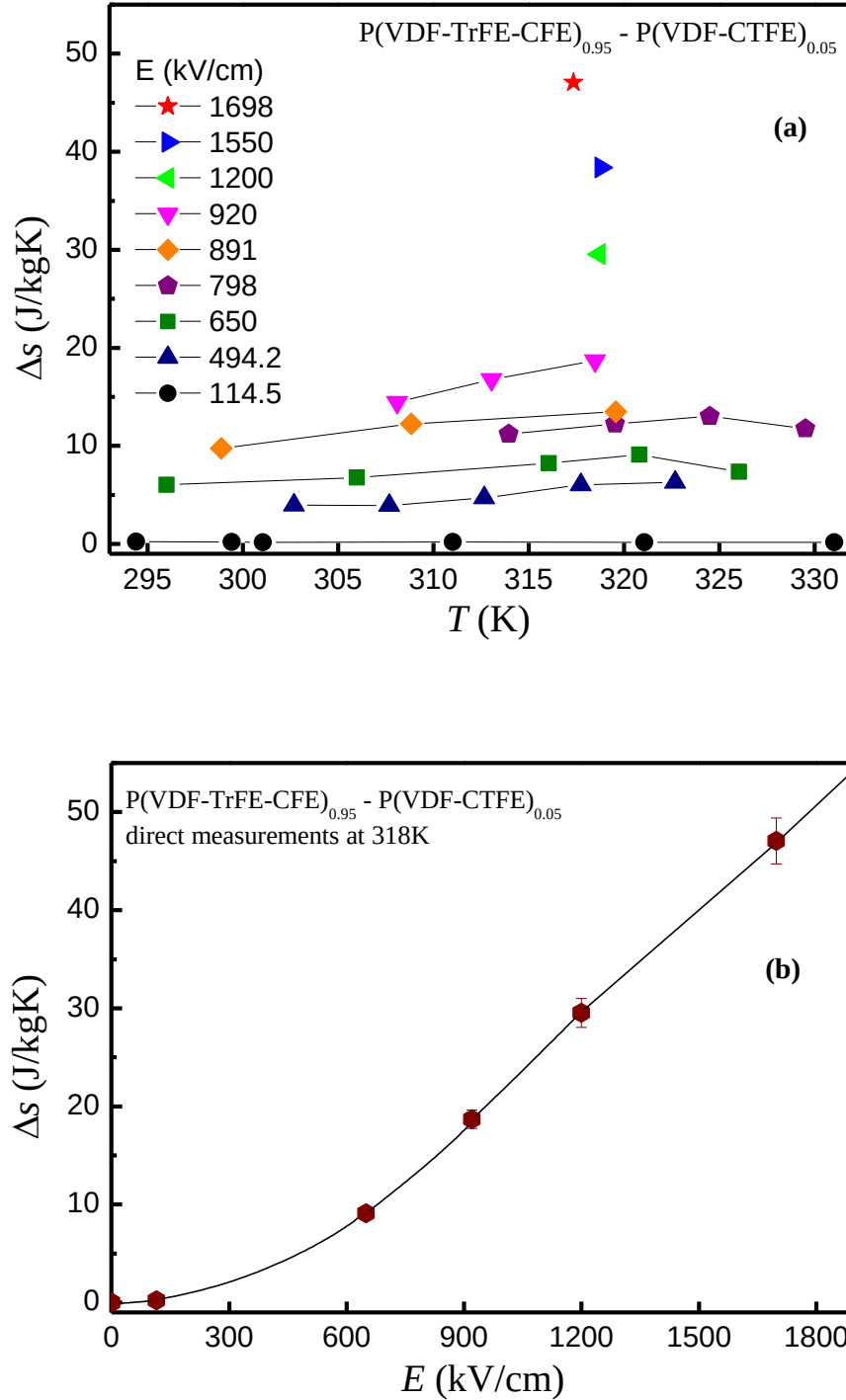


Figure 46: The entropy density change Δs of the ECE (a) as a function of the temperature for various electric fields and (b) as a function of the electric field amplitude measured at a constant temperature of 318 K for $P(\text{VDF-TrFE-CFE})_{0.95} - P(\text{VDF-CTFE})_{0.05}$.

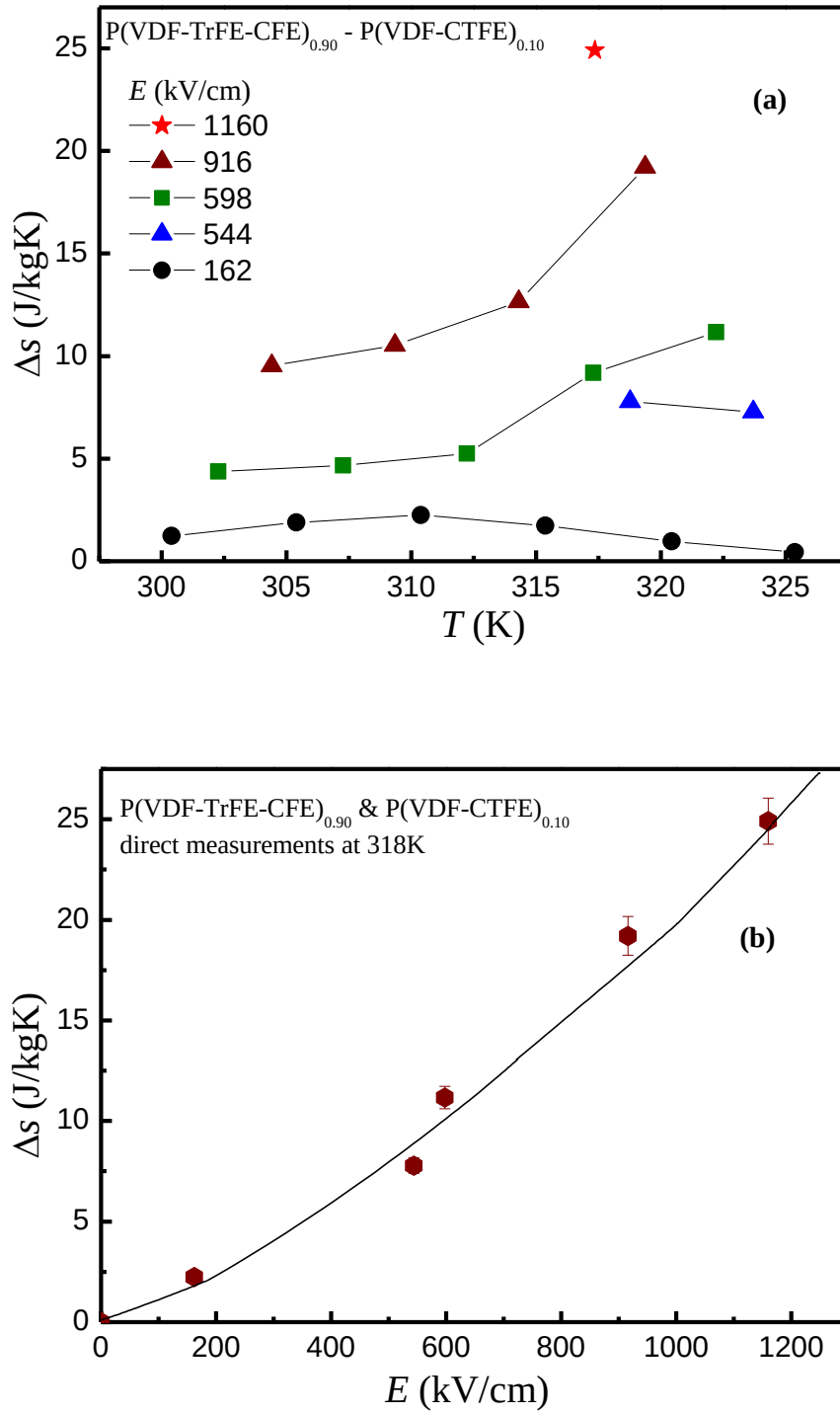


Figure 47: The entropy density change Δs of the ECE (a) as a function of the temperature for various electric fields and (b) as a function of the electric field amplitude measured at a constant temperature of 318 K for $P(\text{VDF-TrFE-CFE})_{0.90}-P(\text{VDF-CTFE})_{0.10}$ [77].

The ECE responsivity $\Delta T_{\text{EC}}/E$ measured at 318 K exhibits a maximum at $E=1.7$ MV/cm in the case of 5% terpolymer-copolymer blends, and in 10% blends at $E=1.2$ MV/cm [197]. The ECE responsivity $\Delta T_{\text{EC}}/E$ as a function of the electric field is presented in Figure 48 for 5% terpolymer-copolymer blends.

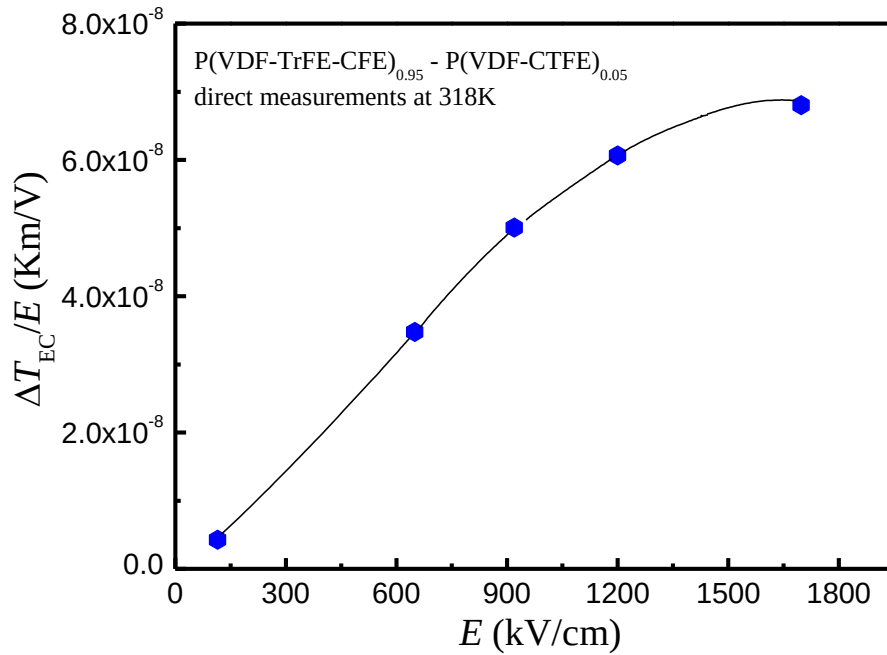


Figure 48: The ECE responsivity $\Delta T_{EC}/E$ as a function of the electric field change measured at 318 K for $P(\text{VDF-TrFE-CFE})_{0.95}\text{-}P(\text{VDF-CTFE})_{0.05}$ [197].

To conclude it was shown that the maximum temperature change ΔT_{EC} is significantly larger in the terpolymer blended with the copolymer in comparison to the pure terpolymer. Therefore, the direct measurements confirm that the blending increases the ECE response.

4.2.1.3 Impact of the high-energy irradiation on the ECE response

The normal ferroelectric $P(\text{VDF-TrFE})$ 68/32 mol% copolymer can be converted into a relaxor ferroelectric copolymer by high-energy irradiation [197]. Here, the comparison of the ECE is given for the copolymer and the irradiated copolymer. The ECE was investigated by direct measurements employing the high resolution calorimeter in the ferroelectric copolymer and the ECE response of the irradiated copolymer was also studied by the direct method employing the IR photodetector by Zhang's group. As shown below, the irradiation increases the ECE response.

The ECE temperature change ΔT_{EC} and the specific electrocaloric entropy change Δs as functions of the temperature between 310 and 380 K at three different selected amplitudes of the electric field are shown in Figure 49. The maximum of the ECE response before breakdown $\Delta T_{EC}=2.5$ K at the electric field $E=700$ kV/cm is achieved at a temperature of around 370 K, corresponding to the ferroelectric transition temperature in this material. The specific entropy change Δs is around 8 J/kgK at an electric field of $E=700$ kV/cm [79].

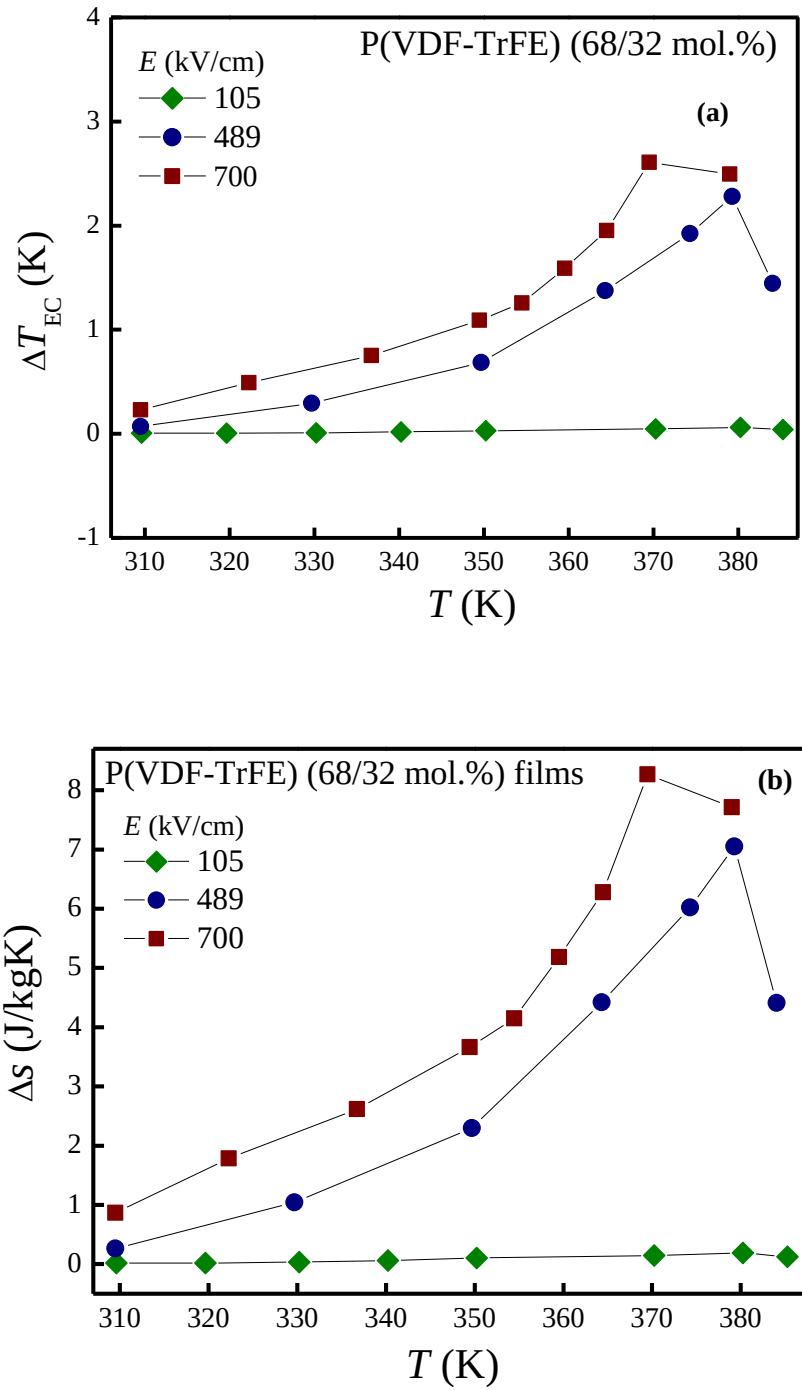


Figure 49: (a) ΔT_{EC} and (b) Δs in P(VDF-TrFE) 68/32 mol% copolymer as functions of temperature at several values of the electrical field amplitude E [79].

The ΔT_{EC} as a function of the electric field E is presented in Figure 50. It is shown that ΔT_{EC} monotonously increases with the increasing amplitude of the electric field, and it exceeds 2.5 K at relatively small amplitude of the electric field. This indicates that a considerable electrocaloric effect indeed exists in P(VDF-TrFE) 68/32 mol% copolymer thin films. In Figure 51 the ECE responsivity $\Delta T_{EC}/E$ as a function of the electric field is presented. It is shown that this quantity exhibits the maximum at a relatively high electric

field exceeding $E \sim 500$ kV/cm [79]. This indicates that in these polymer films the high EC responsivity can still be achieved at high electric fields.

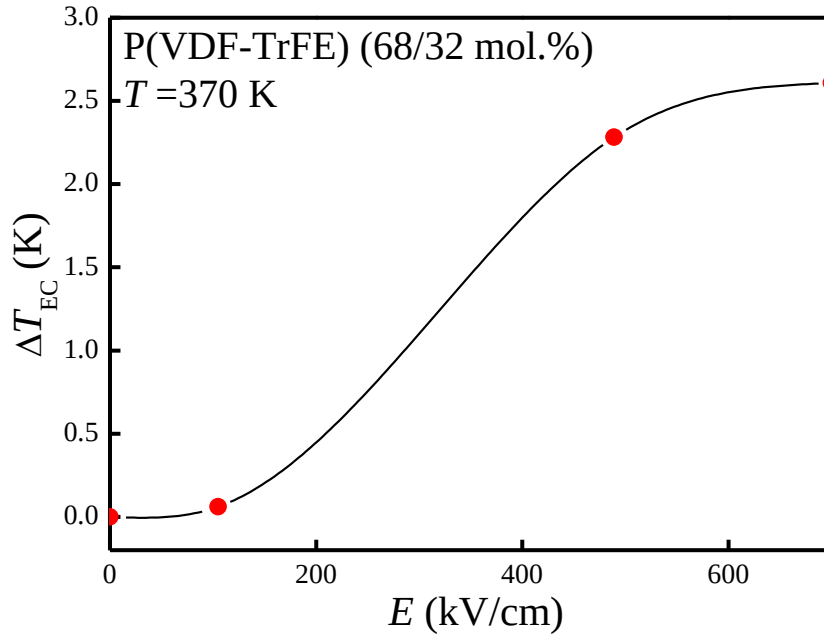


Figure 50: ΔT_{EC} as a function of the electric field amplitude measured at a constant temperature of 370 K for P(VDF-TrFE) 68/32 mol% copolymer [79].

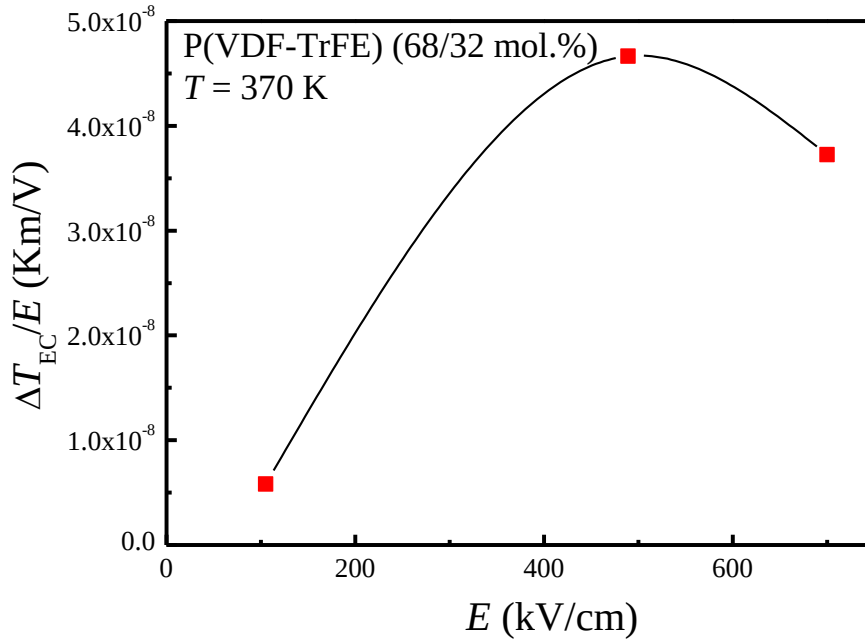


Figure 51: The ECE responsivity $\Delta T_{EC}/E$ as a function of the electric field amplitude measured at 370 K for P(VDF-TrFE) 68/32 mol% copolymer films [79].

The idea of enhancing the ECE by irradiation was developed by Prof. Zhang's group, which made direct measurements of the ECE response in the irradiated P(VDF-TrFE) 68/32% copolymer. The ECE in this sample was measured at several temperatures around room temperature, and it was observed that the maximum temperature change ΔT_{EC} is achieved at 306 K [74]. At this temperature at the highest measuring electric field of $E=1.60$ MV/cm, the $\Delta T_{EC} \sim 20$ K was achieved and the isothermal specific entropy change was $\Delta s \sim 95$ Jkg⁻¹K⁻¹. These results are presented in a joint publication [74].

The comparison between the ECE temperature change in ferroelectric copolymer and in irradiated, i.e., relaxor ferroelectric P(VDF-TrFE) 68/32 mol% copolymer is presented in Figure 52 for the overlapping electric field range.

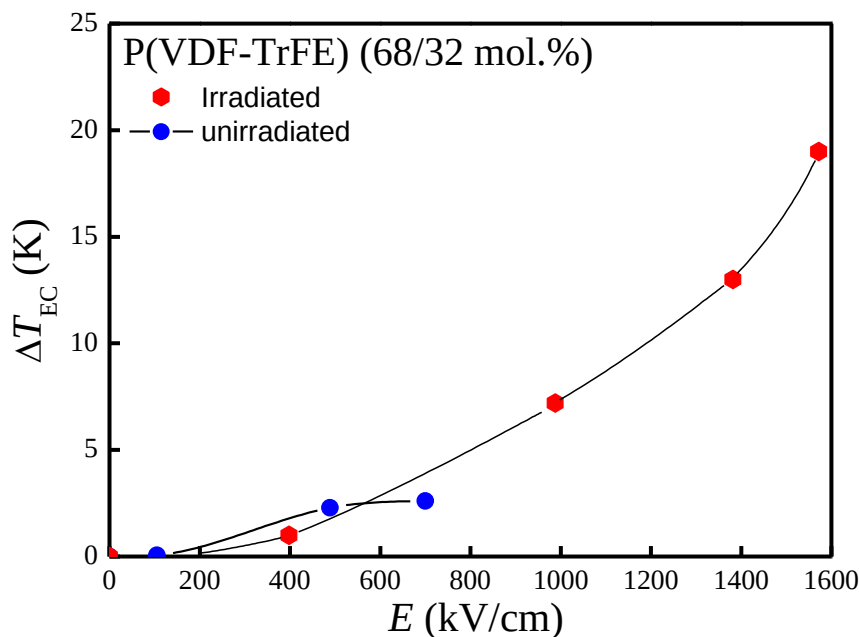


Figure 52: The comparison between the ECE temperature change ΔT_{EC} as a function of the electric field in ferroelectric copolymer [79] and in irradiated relaxor ferroelectric P(VDF-TrFE) 68/32 mol% copolymer [74].

4.2.2 Inorganic materials

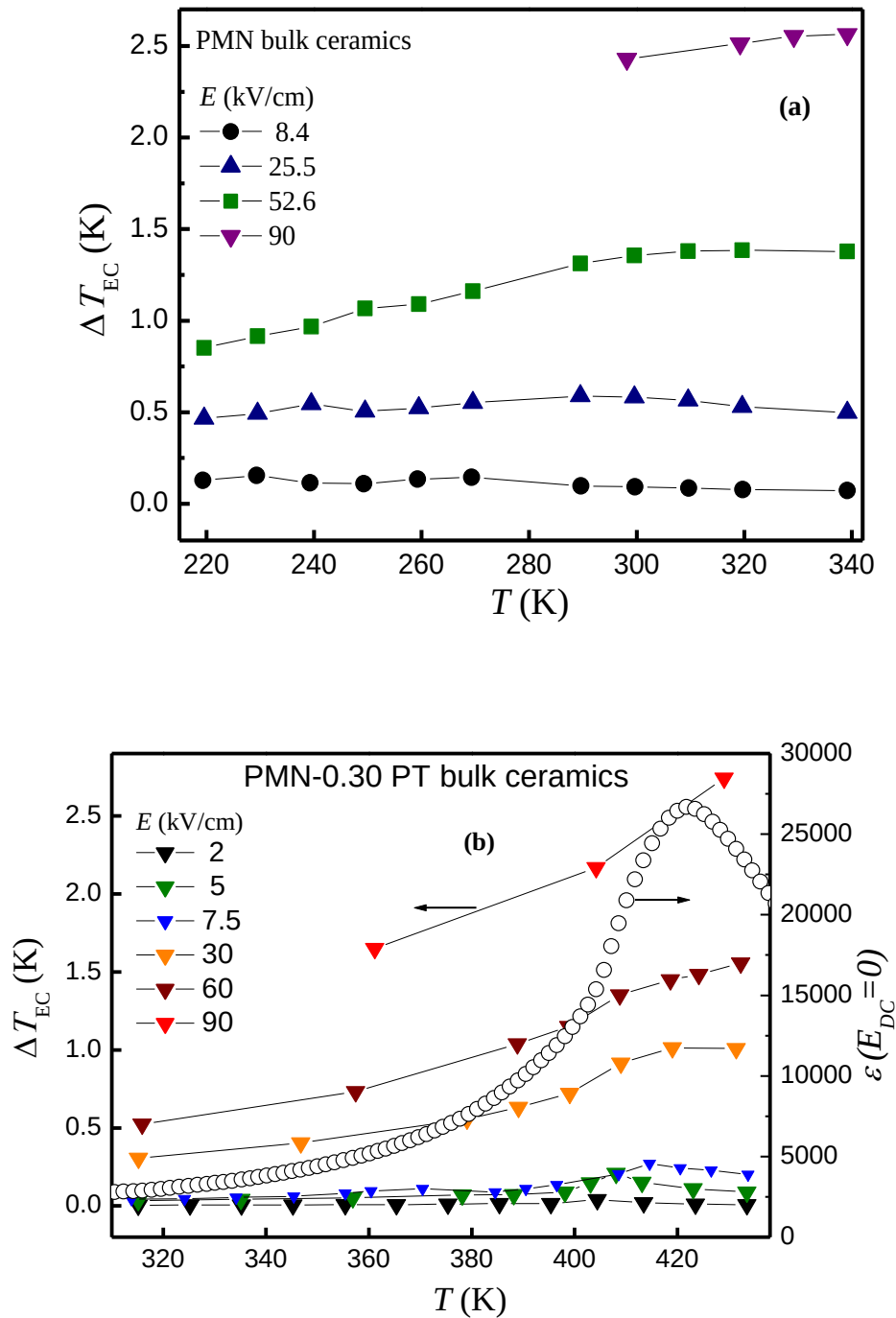
4.2.2.1 ECE in the vicinity of the critical point

4.2.2.1.1 PMN, PMN-0.30 PT, PMN-0.35 PT and 8/65/35 PLZT bulk materials

For all the investigated materials it was shown that the largest electrocaloric effect is observed near the electric field-induced ferroelectric phase transition [74, 76, 80, 83, 85]. On the other hand, not long ago it was also reported that in bulk PMN ceramics the giant electromechanical response is observed near the liquid-vapor type critical point (CP) [91].

Due to the low break down field in the bulk materials, the maximum achieved amplitude of the electric pulse was approximately 90 kV/cm. Nevertheless, as shown below, in comparison to previously published data [62, 63], the relatively high ΔT_{EC}

indicates the existence of a giant ECE in these materials. An amplitude of ΔT_{EC} directly measured for all samples in a broad temperature range shows that bulk ceramics exhibit a weak temperature variation of the ECE near room temperature (Figure 53) [76, 80, 83, 198]. The dielectric measurements in bulk PMN-0.30PT and in 8/65/35 PLZT show that the broad ECE maximum is achieved near the phase transition (Figure 54) [83], which takes place on the low temperature slope of the dielectric peak [91]. Note that even in a pure PMN system the ferroelectric transition is induced at the electric field strengths employed in the EC experiment. Moreover, it was observed that at higher electric fields, the maximum of the ΔT_{EC} is shifted towards higher temperatures following the field induced shift of the ferroelectric transition [91].



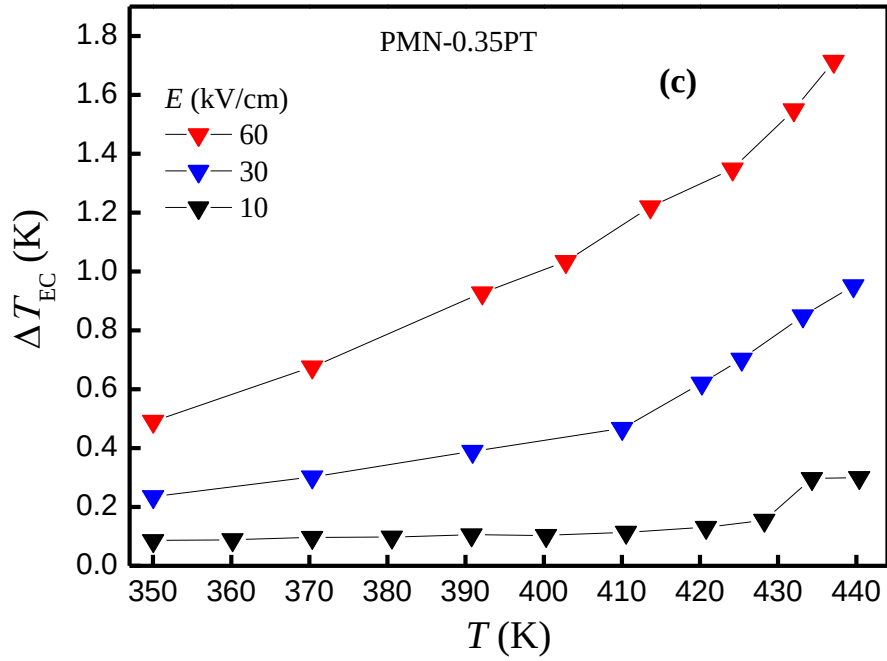


Figure 53: The ECE temperature change ΔT_{EC} as a function of the temperature for different electric fields measured for bulk relaxor perovskite ferroelectric materials (a) PMN, (b) PMN-0.30PT and (c) PMN-0.35PT [76, 80, 83, 198]. Open circles in the graph for 0.70PMN-0.30PT denote the dielectric constant measured at a small electric field.

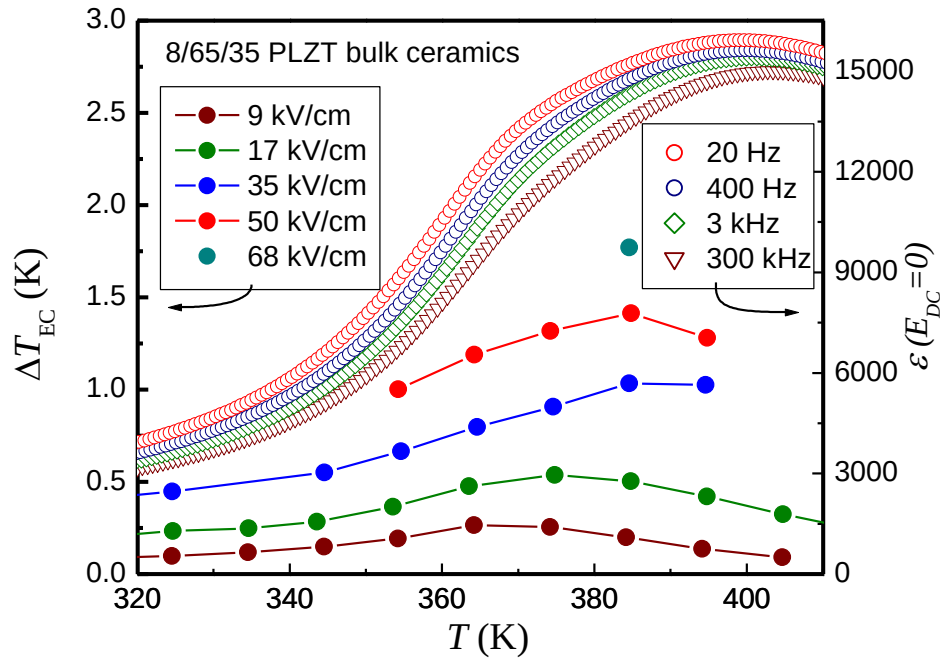
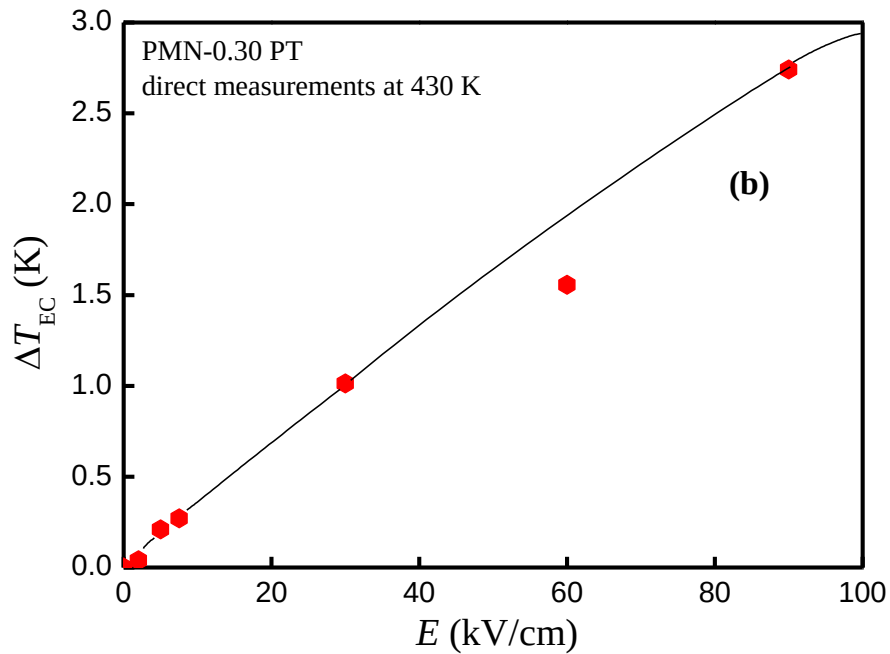
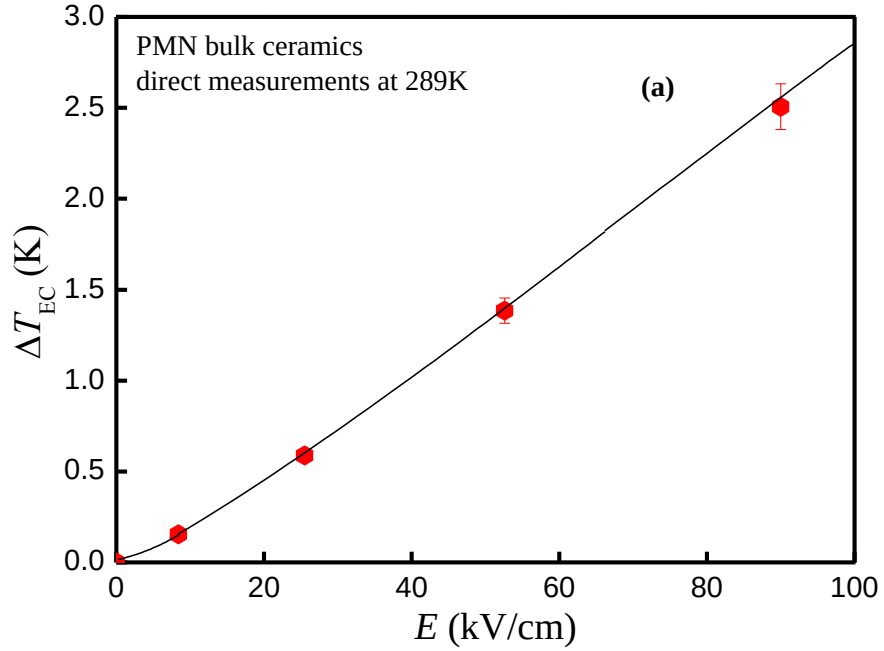


Figure 54: The ECE temperature change ΔT_{EC} as a function of the temperature for different electric fields in 8/65/35 PLZT bulk ceramics. Open circles denote the dielectric constant measured at a small field and at different frequencies [83].

The ΔT_{EC} as a function of the electric field amplitude at a constant temperature is presented in Figure 55. For all the materials the largest effect between 2 and 3 K was observed at field amplitude between 60 kV/cm and 90 kV/cm [76, 80, 83].



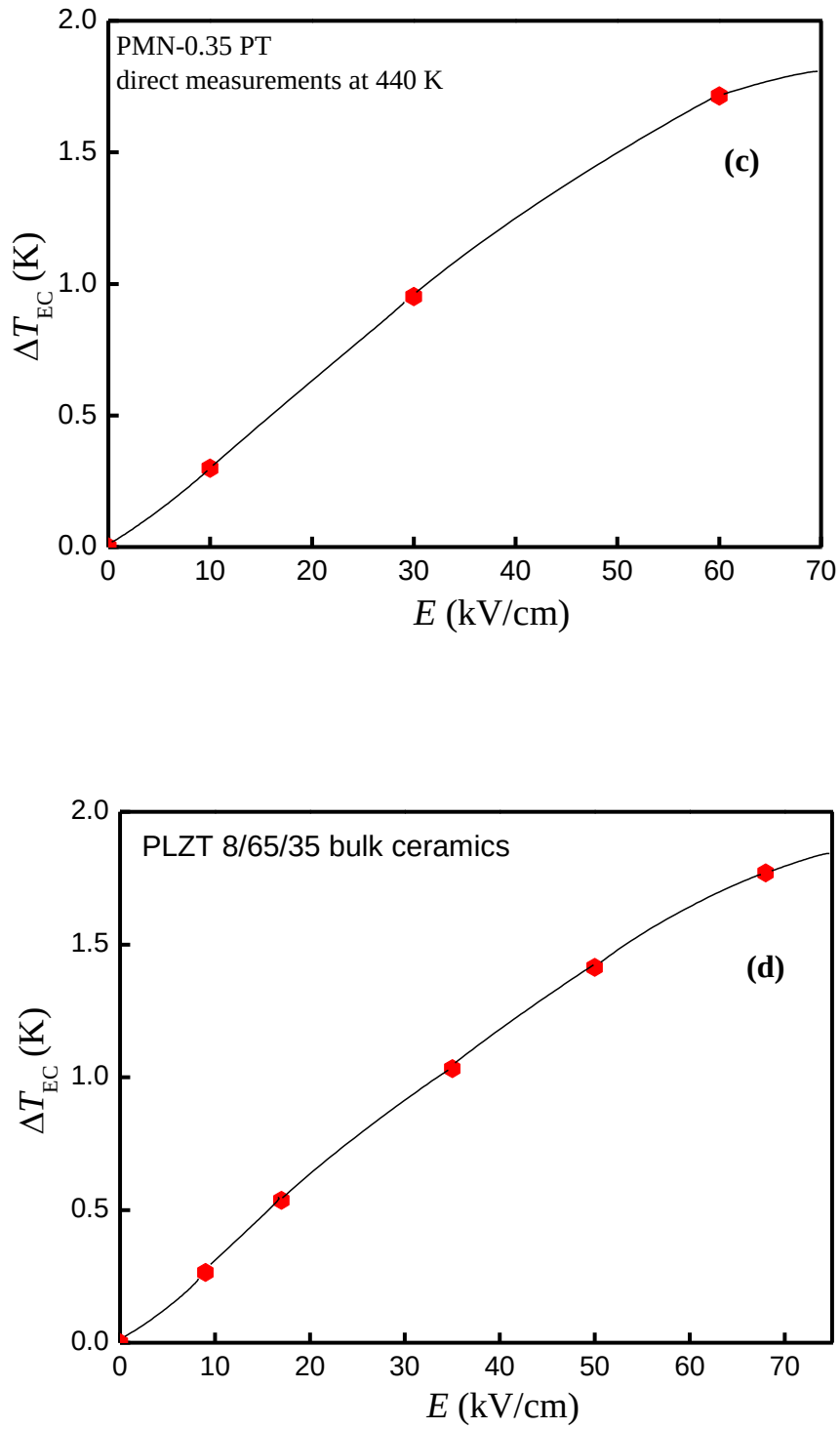
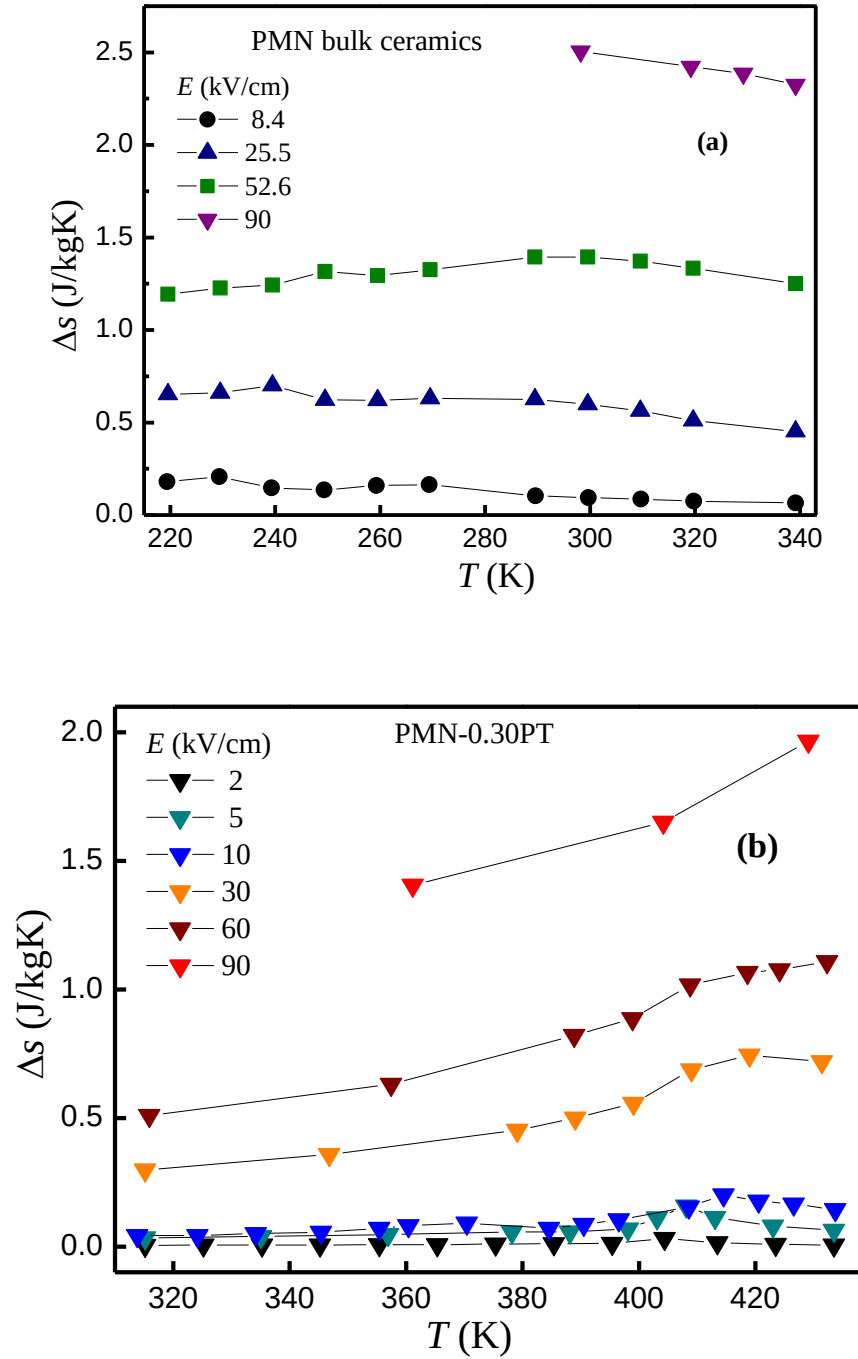


Figure 55: EC temperature change ΔT_{EC} as a function of the electric field amplitude measured at a constant temperature for bulk ceramic materials (a) PMN, (b) PMN-0.30PT, (c) PMN-0.35 PT and (d) 8/65/35 PLZT [76, 80, 83, 197, 198].

The changes of the specific entropy Δs as a function of the temperature for various electric fields E are presented in Figure 56. It is shown that the maximum change of the specific entropy Δs is around 2.5 J/kgK in pure PMN and 2 J/kgK in PMN-0.30PT bulk

ceramics at electric field amplitude of 90 kV/cm. In PMN-0.35PT ceramics the largest measured entropy change is around 1.2 J/kgK at an electric field of 60 kV/cm [76, 80, 83, 178].



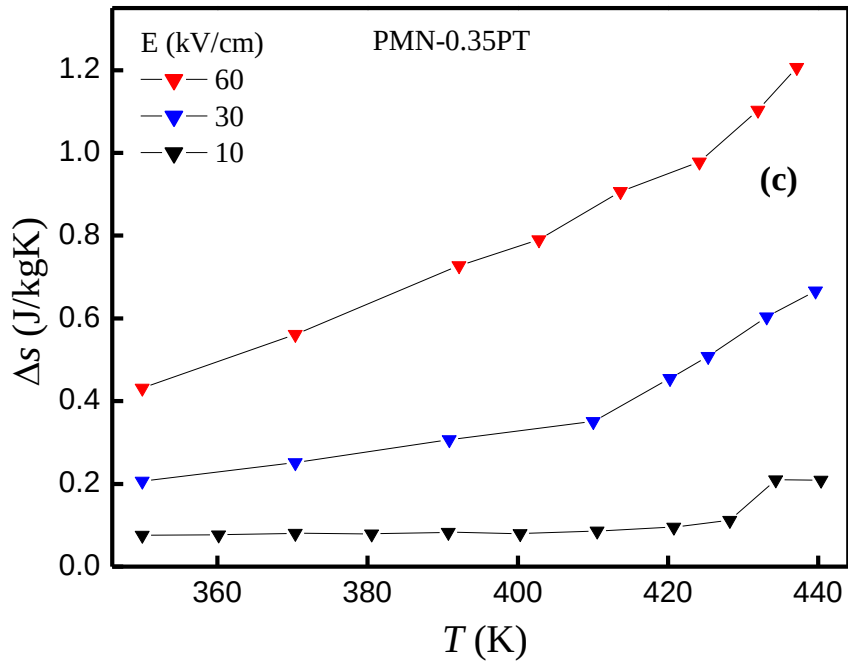


Figure 56: The specific entropy changes Δs as a function of the temperature for various electric fields for bulk ceramic materials (a) PMN, (b) PMN-0.30PT and (c) PMN-0.35PT [76, 80, 83, 198].

4.2.2.1.2 EC responsivity near the critical point: experiments and theory

As mentioned above, the ECE studies in bulk ceramic materials were investigated near the critical point (T_{CP} , E_{CP}). For all the samples it is shown that ΔT_{EC} monotonously increases at T_{CP} with increasing field above E_{CP} . Instead of ΔT_{EC} it is more interesting to focus on the EC responsivity $\Delta T_{EC}/E$, i.e., the ratio between the ECE temperature change and the amplitude of the electric field.

The responsivity $\Delta T_{EC}/E$ as a function of the electric field is presented in Figure 57. It was measured for PMN, PMN-0.30PT and 8/65/35 PLZT at the critical point (T_{CP} , E_{CP}), i.e., at the critical temperature T_{CP} and under the fields below and above the critical field E_{CP} [83]. The critical points, i.e., the point (T_{CP} , E_{CP}) in the E - T phase diagram were determined for the above materials by various techniques such as heat capacity studies and polarization measurements as a function of the temperature and the bias electric field [91, 103, 212]. The red solid line in Figure 57 represents the ECE response obtained from the mean-field calculations based on the spherical random bond random field (SRBRF) model introduced by Raša Pirc [83, 107, 108]. It is shown that the experimentally determined ECE behavior in the vicinity of the CP (obtained by direct measurements) is in good qualitative agreement with the theoretical predictions.

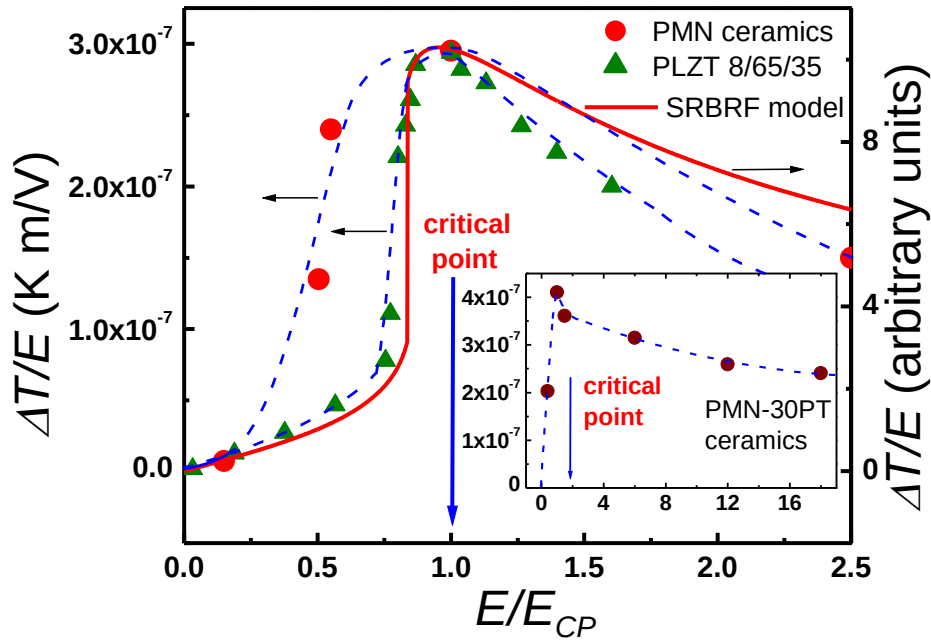


Figure 57: The EC responsivity $\Delta T_{EC}/E$ as a function of the electric field for PMN, PMN-0.30PT and 8/65/35 PLZT ceramics in the vicinity of the critical point (T_{CP} , E_{CP}), i.e., measured at the critical temperature T_{CP} under the fields below and above the critical field E_{CP} [83]. Red solid line represents the ECE response obtained from the mean-field calculations based on the spherical random bond random field (SRBRF) model [83, 107, 108].

For an explanation of the ECE behavior in the vicinity of the critical point the entropy as a function of the applied electric field and the temperature is considered. Under the adiabatic change of the electric field from E_1 to E_2 , the temperature changes from T_1 to T_2 and $S(E_1, T_1) = S(E_2, T_2)$, i.e., $\Delta S(E, T) = 0$ (see Figure S vs T in previous chapter, i.e., Figure 26). In general the entropy of the relaxor material can be written as a sum of the entropy of the dipolar subsystem $S_{dip}(E, T)$ and the phonon contribution $S_{ph}(T)$

$$S(E, T) = S_{dip}(E, T) + S_{ph}(T). \quad (79)$$

The first part S_{dip} is related to the contribution of the elementary dipolar entities in the system [107], i.e., in the case of the relaxors the current view is that it corresponds to the polar nanoregions (PNRs) [69], i.e., aggregates of the polarized unit cells.

$S_{dip}(E, T)$ is a function of both the temperature and the electric field. The second part, $S_{ph}(T)$ is weakly field dependent and thus this dependence can be ignored. $S_{ph}(T)$ is then given by [83]

$$\Delta S_{ph}(T) = S_{ph}(T_2) - S_{ph}(T_1) = \int_{T_1}^{T_2} \frac{C_{ph}(T)}{T} dT \cong \frac{C_{ph}}{T_1} \Delta T, \quad (80)$$

where $\Delta T = T_2 - T_1$ and ΔT is much smaller as than T_1 .

Next using the condition $S_{dip} + S_{ph} = 0$, the ECE temperature change ΔT_{EC} can be calculated from the expression

$$\Delta T_{\text{EC}} = \frac{T_1}{C_{\text{ph}}} [S_{\text{dip}}(E_1, T_1) - S_{\text{dip}}(E_2, T_1 + \Delta T_{\text{EC}})]. \quad (81)$$

This is a self-consistent equation [108]. The question here is, how to obtain the $S_{\text{dip}}(E, T)$? The standard way is to choose the Landau free energy for a scalar order parameter P , where $P=P(E, T)$ is expressed as [83, 108]

$$F = F_0 + \frac{1}{2}aP^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 + \dots - EP. \quad (82)$$

In order to describe the field-induced first order phase transition it was assumed that $a=a(T)$ and the parameters $b<0$ and $c>0$ are temperature-independent constants.

In normal ferroelectrics $a \propto T - T_C$, where T_C is the Currie-Weiss temperature and in relaxors $a(T) = (\epsilon_0 \chi)^{-1}$, where χ is the linear field-cooled dielectric susceptibility that is nonzero at all temperatures [83]. According to the SRBRF model, in a relaxor ferroelectric the coefficient $a(T)$ remains positive at all temperatures and for $E=0$ there is no phase transition. More details can be found in Ref. [108]. An explicit expression for $\chi(T)$ has been derived from the SRBRF model of relaxor ferroelectrics that is based on the concept of the PNRs [83, 107, 108]

$$\chi = \frac{\Theta(1-q)}{T - T_C(1-q)}. \quad (83)$$

This expression is consistent with the empirical expression for the susceptibility [83]. Here, Θ denotes an effective Curie constant and $q=q(T)$ is the spherical dipolar glass order parameter. More details are explained in Refs. [107, 108].

The dipolar entropy $S_{\text{dip}} = (-\partial F / \partial T)_E$ is given by

$$S_{\text{dip}} = S_0 + S_1(P). \quad (84)$$

Here, the first term S_0 is the configurational entropy of the dipolar entities at zero electric field and it does not contribute to the ΔS_{dip} . The second term $S_1(P)$ depends on the polarization P , which is a sum of the average dipole moments per unit volume. From Eq. (82) it follows

$$S_1(P) = -\frac{1}{2}a_1P^2 - \frac{1}{4}b_1P^4 - \frac{1}{6}c_1P^6 + \dots, \quad (85)$$

where $a_1=da/dT$, $b_1=db/dT$, $c_1=dc/dT$, etc. As mentioned above the parameters b , c , etc. are temperature independent, it follows that $b_1=c_1=\dots=0$. In the relaxors the term $S_1(P=0)$ vanishes because $P=0$ for $E=0$ [83, 108]. From Eqs. (81), (84) and (85) it follows

$$\Delta T_{\text{EC}} = \frac{1}{2} \frac{T}{C_{\text{ph}}} a_1(T + \Delta T_{\text{EC}}) P^2(E, T + \Delta T_{\text{EC}}). \quad (86)$$

This is a self-consistent equation for ΔT_{EC} as a function of the initial temperature $T=T_1$ and the final electric field $E=E_2$. This equation can be solved by iteration [108]. Here, the C_{ph} is the lattice heat capacity, assumed to be a nonsingular and a weak function of the temperature in the interval (T_1, T_2) . Because it is possible to evaluate the dipolar entropy change ΔS_{dip} directly from Eq. (85), the dipolar specific heat C_{dip} is not needed explicitly

[83, 108].

The ΔT_{EC} near the critical point (T_{CP} , E_{CP}) has been calculated from Eq. (86) with $a_1(T)$ derived from $a(T)$. The dimensionless parameters b and c were chosen as $b=-1/3$ and $c=|b|$ [83, 108]. The resulting ECE responsivity $\Delta T_{EC}/E$ has a maximum in the vicinity of the critical point, as shown in Figure 57. In fact, the red solid line in Figure 57 represents a cross-section of the plane shown in Figure 58 for $t=T/T_C=1$.

Therefore, the theoretical behavior of $\Delta T_{EC}/E$ is in a good qualitative agreement with the experimental results as presented in Figure 57 for the PMN, PMN-0.30PT and 8/65/35 PLZT ceramics.

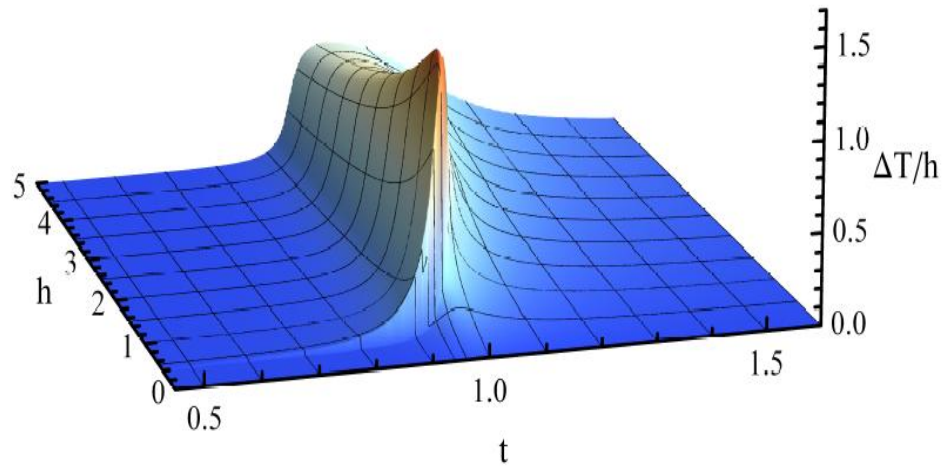


Figure 58: EC responsivity $\Delta T/h$ as a function of the electric field and the temperature as calculated from the SRBRF model; h denotes a reduced electric field $h=E/E_{CP}$ and t denotes the reduced temperature $t=T/T_{CP}$. The maximum is achieved at $E \sim E_{CP}$ and $T \sim T_{CP}$ [83].

4.2.2.2 ECE in thick films

4.2.2.2.1 8/65/35 PLZT thick films on an alumina substrate

Similar to the bulk materials the thick films exhibit rather low break down fields of ~ 80 kV/cm. Consequently, it is not possible to apply very large electric fields in EC experiments. But even for such relatively modest field amplitude, i.e., about 70 kV/cm, ΔT_{EC} reaches a value of around 1.8 K in thick films of 8/65/35 PLZT ceramics (Figure 59) [197]. The ECE response was investigated here in the temperature range between 350 and 395 K. The maximum is achieved at a temperature of around 380 K, i.e., near the FE-PE phase transition.

Figure 60 presents measurements of ΔT_{EC} and the ECE change of the specific entropy density Δs as a function of the electric field at a constant temperature of 374 K in thick 8/65/35 PLZT films. The specific entropy change Δs for the thick film is 1.5 J/kgK at a field strength of 68 kV/cm. The ECE responsivity $\Delta T_{EC}/E$ exhibits a maximum at $E \sim 20$ kV/cm and $T=374$ K [197], i.e., in the vicinity of the critical point. Generally, the results of the ECE obtained in thick films of 8/65/35 PLZT ceramics resemble those obtained in bulk 8/65/35 PLZT ceramics.

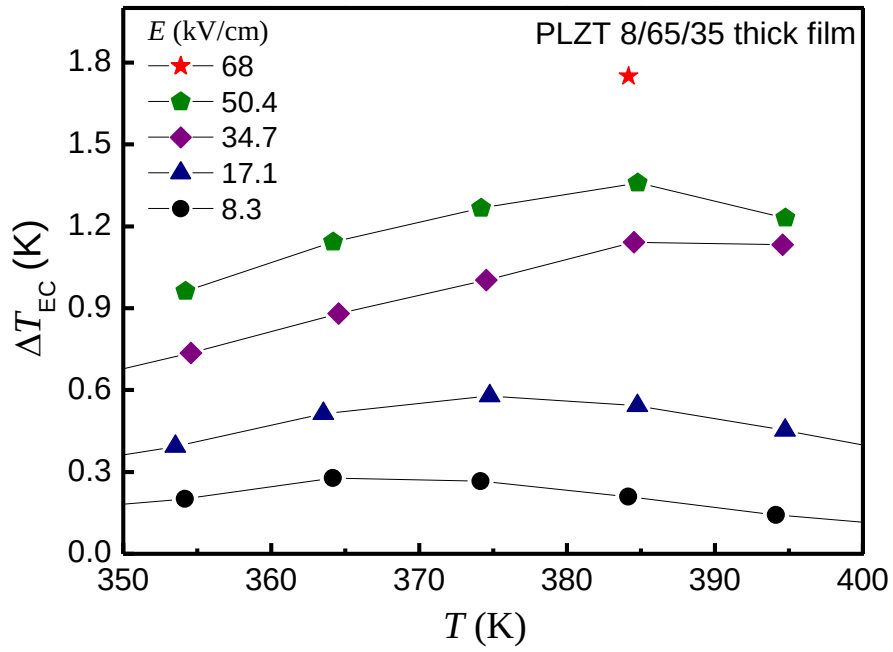


Figure 59: The ECE temperature change ΔT_{EC} in thick films of 8/65/35 PLZT ceramics as a function of temperature for different values of the electric field amplitude [197].

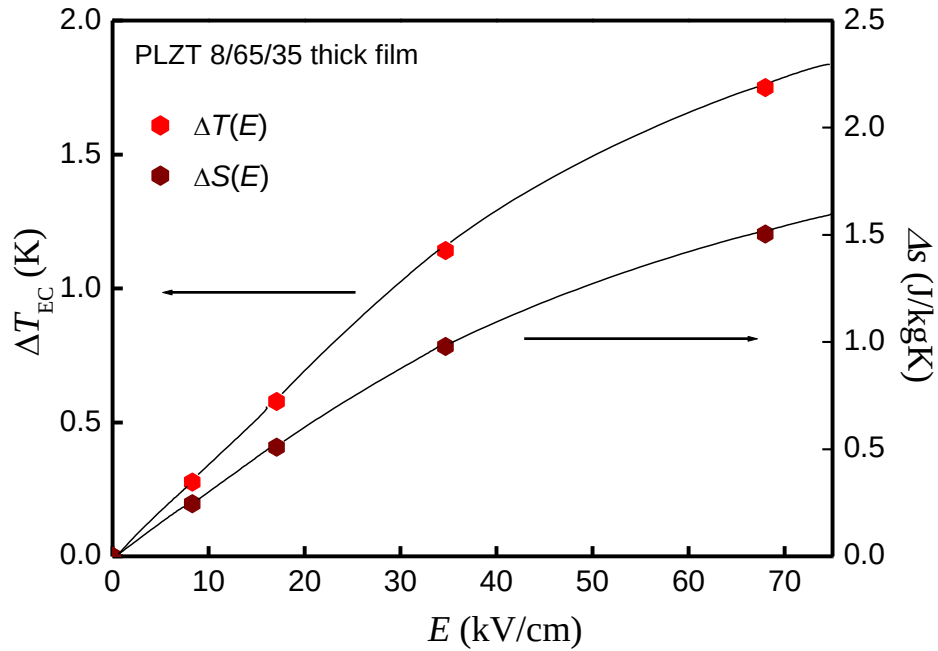


Figure 60: Electric field variation of the ECE temperature change ΔT_{EC} and the specific entropy change Δs for thick films of 8/65/35 PLZT ceramics measured at a constant temperature of 374 K [197].

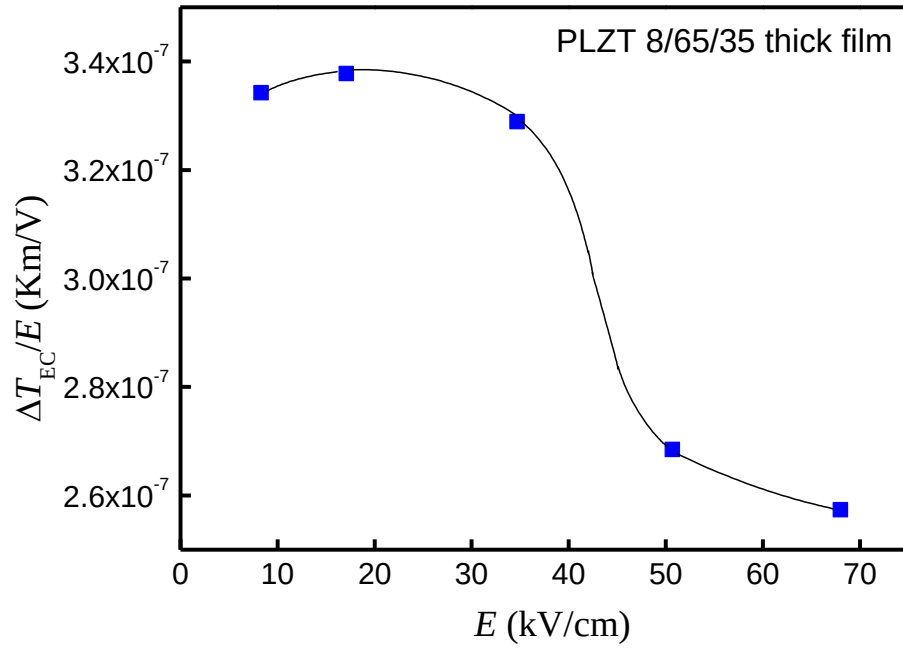


Figure 61: The ECE responsivity $\Delta T_{EC}/E$ as a function of the electric field amplitude measured at 374 K for 8/65/35 PLZT thick film ceramics [197].

4.2.2.2.2 Self-standing PMN-0.35PT thick films on Pt layer

Like in the case of PMN-0.35PT bulk materials, in PMN-0.35PT thick films on a 10 μm Pt layer it was not possible to use very large electric fields due to the relatively low break down field of about 80-90 kV/cm. However, still a large $\Delta T_{EC} \approx 2$ K comparable to that observed in bulk materials was observed for a relatively small amplitude of the electric field $E = 80$ kV/cm, at temperature 427 K. The ΔT_{EC} as well as the specific entropy change Δs as a function of the electric field are presented in Figure 62 [198].

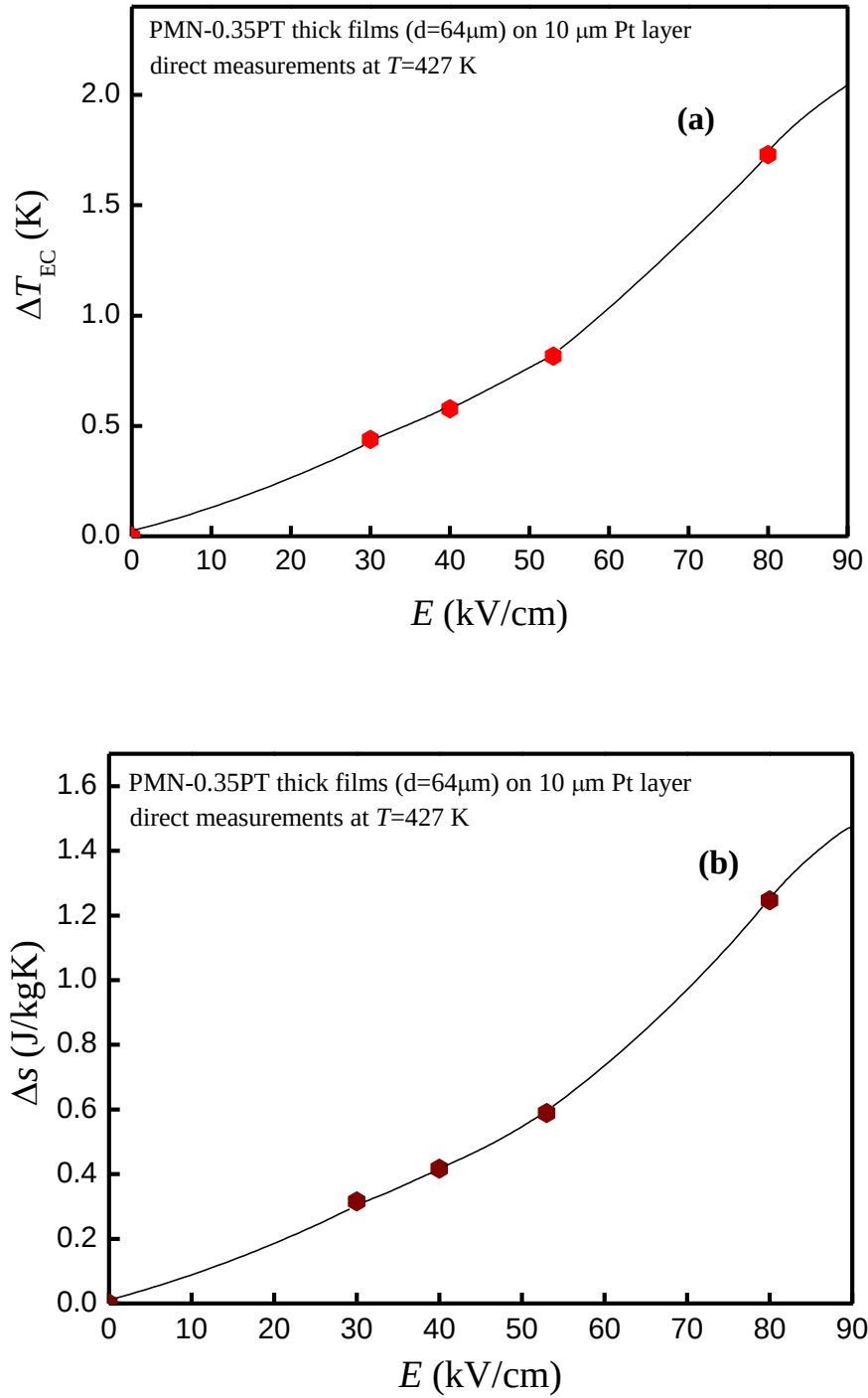


Figure 62: Electric field variation of (a) the ECE temperature change ΔT_{EC} and (b) the specific entropy change Δs for PMN-0.35PT thick films on a Pt layer measured at a constant temperature of 427 K [198].

These results show that slightly different procedure for the thick film's preparation does not have a significant impact on the magnitude of the ECE. We will see in the next section that the story is considerably different in the case of thin ceramic films.

4.2.2.3 ECE in thin ceramic films

4.2.2.3.1 Relaxor ferroelectric 8/65/35 PLZT thin ceramic films

It was found by dielectric experiments that the dielectric constant shows a rather smooth variation of the temperature in thin ceramic films. As a consequence the ECE in thin films is nearly constant in a broad temperature range, more than 100 K, near room temperature [74]. Therefore, the ECE temperature changes ΔT_{EC} as a function of the applied electric field close to room temperature at around 318 K were measured by applying the technique described in Section 4.1. The ΔT_{EC} data are presented in Figure 63. It was found that the so-far largest reported ΔT_{EC} exceeding 40 K at 1.25 MV/cm [74] can be induced in this material. The entropy change as a function of the electric field is presented in Figure 64. The thin film exhibits a specific entropy change $\Delta s \sim 50$ J/kgK at 1.25 MV/cm. It should be noted though that the thin films used in this study suffered for significant Joule heating, which above 500 kV/cm became comparable to or even exceeded the EC temperature change.

Maybe in these thin films at higher electric fields the Joule heating also due to a leakage current plays some role. It was found out that the leakage current strongly depends on the magnitude of the electric field with the typical values 1 nA at $E=200$ kV/cm and several tens of nA for the field above 700 kV/cm.

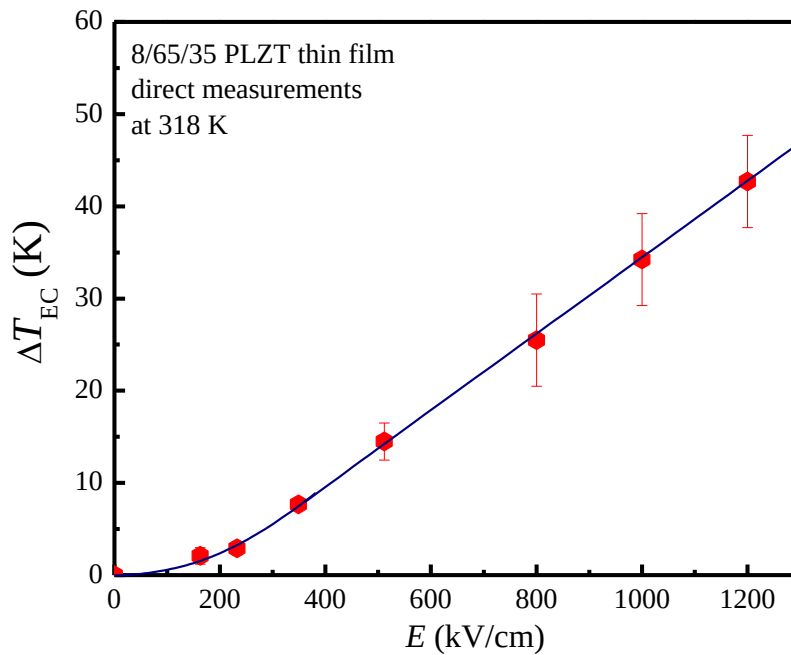


Figure 63: The ECE temperature change ΔT_{EC} as a function of the applied electric field measured close to room temperature at around 318 K in 8/65/35 PLZT thin ceramic film [74].

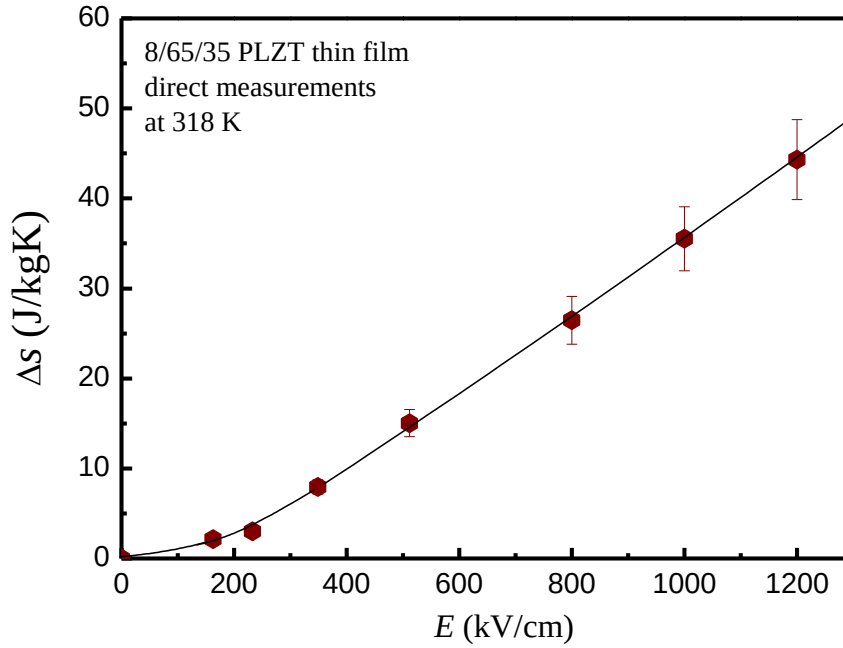


Figure 64: The ECE specific entropy change Δs as a function of the applied electric field amplitude measured close to room temperature at around 318 K in 8/65/35 PLZT thin ceramic film.

From the plot of the responsivity $\Delta T_{EC}/E$ as a function of the electric field amplitude it is evident that the maximum value is not achieved even for highest applied field (Figure 65). This indicates that the $\Delta T_{EC}/E$ maximum value is shifted toward higher electric fields, i.e., the range of fields that are interesting for applications. The second reason for using thin films is the field behavior of the electric polarization. The polarization in the PLZT thin films exceeds 1 C/m^2 for fields above 1 MV/cm . This is around three times larger than in the bulk PLZT where the saturation value of P is around 0.4 C/m^2 . Moreover, the Curie constant Θ was found to be smaller in thin films [74]. Having in mind that the ΔT_{EC} is directly proportional to the square of P (see Eq. (86)) with the proportionality factor inversely proportional to the Curie constant the ECE can be significantly enhanced in thin films.

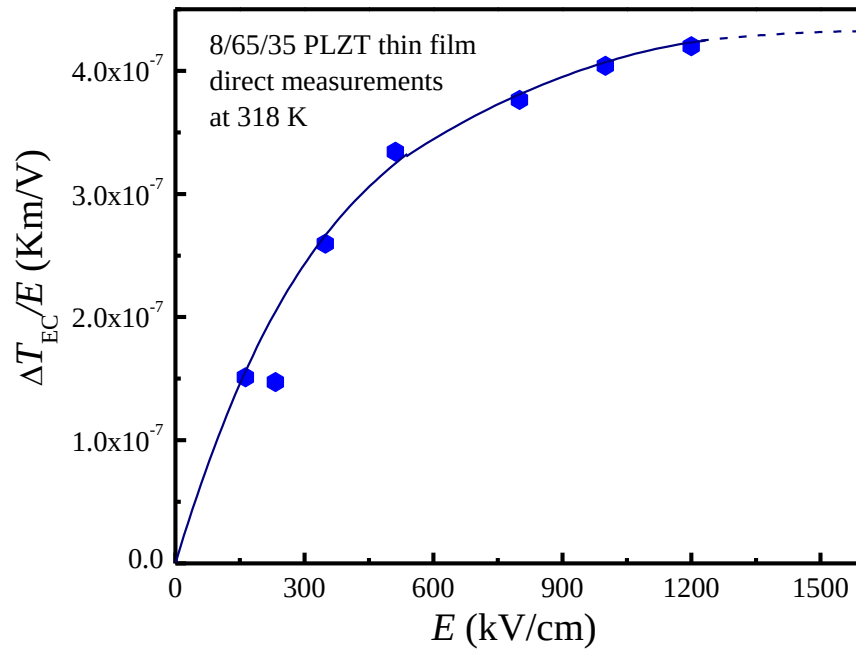


Figure 65: The EC responsivity $\Delta T_{EC}/E$ as a function of the electric field amplitude measured at 318 K for 8/65/35 PLZT thin ceramic film.

4.2.3 Summary of ECE experimental data obtained from direct measurements

Table 2: Comparison of the EC and MC properties of various electrocaloric and magnetocaloric materials [74].

Material	T (°C) ⁱ	Applied field ⁱⁱ	Δs (J/(kgK))	ΔT (K)	$\Delta T \cdot \Delta s$	Method ⁱⁱⁱ
ORGANIC						
P(VDF-TrFE)	70	1500	30	10	300	Direct
55/45	80	2009	60.8	12.6	768	Deduced [63]
P(VDF-TrFE-CFE)	16	750	15	4	60	Direct
	55	3007	60	12.4	744	Deduced [63]
Blends						
5%	45	1700	50	12	600	Direct
10%	45	1200	25	6	150	Direct
P(VDF-TrFE)						
Unirradiated	97	700	8.2	2.5	21	Direct
Irradiated	33	160	95	20	1900	Direct
INORGANIC						
bulk materials						
PMN	16	90	2.5	2.4	6	Direct
0.70PMN-0.30 PT	157	90	2.0	2.7	5.4	Direct
0.65PMN-0.35 PT	167	60	1.2	1.7	2	Direct
8/65/35 PLZT	110	68	1.5	1.8	2.7	Direct
thick films						
8/65/35 PLZT	110	68	1.5	1.75	2.6	Direct
0.65PMN-0.35 PT	154	80	1.2	1.73	1.7	Direct
(on 10 μ m Pt layer)						
thin films						
PLZT 8/65/35	45	120	50	40	2000	Direct
thin film						
data from literature						
PbZr _{0.95} Ti _{0.05} O ₃	226	48	7.9	12	95	Deduced [62]
thin film						
0.93PMN-0.07PT	25	72.3	9.7	9	87.3	Deduced [213]
thin film						
0.65PMN-0.35PT	140	75	33.4	31	1036	Deduced [214]
thin film						
Gd ₅ (Si ₂ Ge ₂)	-3	10	23.9	21	502	Direct [215]
Mn(As _{1-x} Sb _x)	7	5	30	13	390	Direct [216]

ⁱT is the temperature where the ECE or magnetocaloric effect (MCE) maximum was observed. ⁱⁱFor MCE, the magnetic field unit is Tesla (T). For ECE, the unit for electric field is kV/cm. ⁱⁱⁱDeduced method means the ECE values are deduced from the Maxwell relations ^(62, 63, 213-216)

The parameter that measures the quality of different cooling materials is $\Delta T\Delta s$, which is similar to the refrigerant capacity given by [195, 217]

$$RC = \Delta T_{HC}\Delta s, \quad (87)$$

where $\Delta T_{HC}=T_H-T_C$ is the difference between the heating and cooling ends of the cooling cycle. Some data of the ECE materials investigated in our studies and some from literature in comparison with MCE materials are presented in Table 2 [74]. It is shown that the irradiated P(VDF-TrFe) relaxor copolymer exhibits the refrigerant capacity $\Delta T\Delta s \sim 1900$ J/K, and the relaxor PLZT 8/65/35 thin film around $\Delta T\Delta s \sim 2000$ J/K. These values are more than two times higher than any previously reported values for electrocaloric and magnetocaloric materials and they indicate the relaxor ferroelectrics to be the best candidates for use in applications where large ECE is required.

4.3 Short summary of the ECE measurements

The direct measurements of the ECE have been investigated by using a high-resolution calorimeter for the various organic and inorganic ferroelectric and relaxor ferroelectric materials. The data were analysed by using the simple temperature ansatz based on the zero-dimensional model. It is shown that the largest EC effect can be observed in the relaxor ferroelectric thin films. A large EC effect is also observed in the bulk and thick films, where due to the low breakdown electric field it is not possible to use very large electric fields. The results obtained in ferroelectric polymers also show a good agreement between the indirect (presented in Ref. [63]) and direct measurements of the ECE. However, in the relaxor ferroelectrics such an agreement was not observed. Further, it is shown that the blending and the high-energy irradiation in the case of polymers increase the ECE.

As observed for all the samples, the EC temperature change as a function of the electric field $\Delta T_{EC}(E)$ monotonously increases even when crossing the critical point. In contrast the EC responsivity $\Delta T_{EC}/E$ exhibits a maximum near the critical point in bulk perovskite relaxor ferroelectrics. This is in a good agreement with the theoretical predictions [83]. No such maximum was achieved in thin films. This indicates that the maximum of the EC responsivity in thin films is shifted to larger electric fields, which are more useful for applications.

5 Magnetoelectric effect in soft composite materials

In recent time the intensity of research activities in the field of magnetoelectrics has increased dramatically. The reason for such an increase of activities can be found in the significant potential of these materials in novel multifunctional devices, especially in electronic applications and also in the chance to make a real and important contribution to the data storage industry [109].

Magnetoelectric materials are an important subgroup of multiferroics. They simultaneously exhibit ferroelectricity and ferromagnetism. This means, in these systems it is possible to manipulate the polarization via a magnetic field, and also the magnetization via the electric field [109]. Previous studies showed that the single-phase or single-composite magnetoelectrics, where the coupling between electric and magnetic properties is direct, are very rare in nature and they show a relatively weak magnetoelectric effect, not useful for a proper practical application [64, 109]. For this reason the focus has been shifted to composites, i.e., two or more phase-composite magnetoelectric materials. In such systems the coupling between the magnetic and electric properties is indirect, but usually much stronger than in single-phase magnetoelectrics. This ascertainment leads to the fact that an alternative way of engineering new optimal magnetoelectrics, i.e., magnetoelectric materials for technological applications, is to create indirect coupling between the ferroelectric and ferromagnetic materials. Until now, the main focus rests on solid single or composite magnetoelectrics, and despite several efforts no magnetoelectric effect was reported in soft materials.

In recent years efforts to produce new nanoparticles (NPs) exhibiting extraordinary properties were made. The reason for these efforts lies in fact that mixtures of different NPs and other conventional materials lead to the special materials with new properties that cannot be found in either of the individual components [110]. Promising candidates for such a conventional material are liquid crystals (LCs). As already discussed in previous sections these are very interesting soft materials with a long range orientational order and responsiveness to different external perturbations, as for example external magnetic or electric fields. Such external perturbations can very well align NPs via the ordering of the LC molecules [118-120]. As already noted in the Introduction, the LCs consist of anisotropic molecules that become ordered in a proper temperature range in the case of thermotropic LCs or for appropriate concentrations of liquid crystal (LC) molecules in lyotropic LCs. Our research of soft magnetoelectrics will be based on thermotropic ferroelectric LCs formed by rod-like molecules. As discussed in the Introduction, due to the chiral molecules the structural ordering exhibits a helical structure, and due to symmetry reasons the electrical polarization, $\vec{P} \propto \vec{n} \times \vec{v}$, appears [218-220]. As a result the ferroelectric SmC* phase is established. Such a phase has significant importance in our study. We will focus on LC–NPs mixtures exhibiting the SmC* phase.

Let us spend a few more words on the ferroelectric LCs. According to the theoretical predictions of R. Meyer, combining the chirality and the smectic C order we get a twist or helical pitch and ferroelectricity [219]. Indeed, in 1975 R. Meyer with his co-workers experimentally confirmed the ferroelectricity in LCs [220]. They found that the chiral

smectic C* phase is a ferroelectric phase. Here the molecules exhibit positional order inside the layer structure, and in each layer they are tilted by the same angle with respect to the layer normal. The chirality induces a finite twist from one layer to the next, producing a spiral twisting of the molecular axis along the layer normal. Each layer possesses the spontaneous polarization $\vec{P}$ perpendicular to the molecular tilt. A linear coupling between the electric polarization and the tilt is allowed due to the symmetry of the SmC* phase. Here, the ferroelectricity in the SmC* phase is a consequence of the linear coupling of the electric polarization with the tilt angle of the molecules. The latter is the primary order parameter that controls the phase transition, and the polarization is the secondary order parameter. Under the applied external electric field $\vec{E}$ parallel to the smectic layers, the linear coupling between the spontaneous polarization and the electric field distorts the arrangement of molecules (Figure 66). They become more and more aligned perpendicular to the electric field and, at the critical electric field E_C , the tilted smectic phase becomes homogeneous and uniformly polarized.

Cooling from the SmA to the SmC* phase causes a loss of some symmetry elements. By using the Landau theory, it was shown that the order parameters of this transition are the two component combinations of the molecular tilt and electric polarization. And also it was found that the SmA-SmC* phase transition is of the second order [218-220].

In the following section the theoretical estimation and experimental observation of the magnetoelectric effect in soft composite materials prepared as a mixture of ferroelectric liquid crystal and ferromagnetic NPs will be presented and the evidence that new soft magnetoelectrics could be engineered from such mixtures will be discussed.

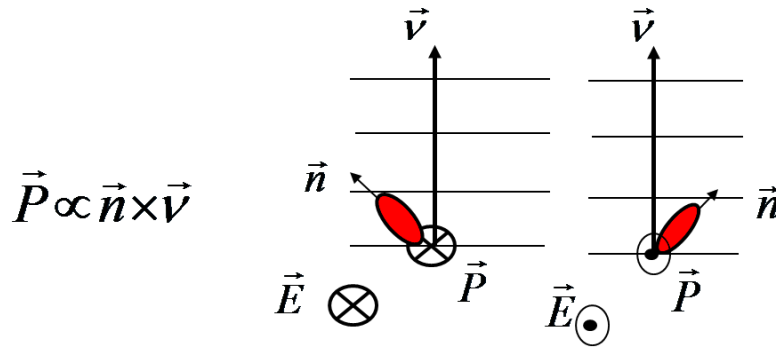


Figure 66: *Schematic representation of the SmC* phase.* Due to symmetry reasons the electric polarization appears and the applied external field distorts the arrangement of the molecules.

5.1 Theoretical estimation of the linear magnetoelectric coefficient α

In this section the estimation of the linear magnetoelectric coupling coefficient α for mixtures of magnetic nanoparticles and the ferroelectric liquid crystal as introduced by Samo Kralj in Ref. [221] is presented.

The linear magnetic coefficient is defined by

$$\alpha = \frac{\partial^2 f}{\partial E \partial H}, \quad (88)$$

at $E=0$ and $H=0$. Here f stands for the free energy density, E is the external electric field,

and H the external magnetic field.

The focus will be on the temperature behavior just below the SmA-SmC* phase transition temperature T_{AC^*} . The geometry of the problem is shown in Figure 67. The LC body is confined within a plan-parallel cell of thickness d . The confining cell plates are placed at $y=0$ and $y=d$ of the Cartesian coordinate system (x, y, z) . The corresponding unit vectors pointing along these coordinates are $(\bar{e}_x, \bar{e}_y, \bar{e}_z)$. The smectic layers are stacked along the z -axis, i.e., a local layer normal $\bar{v}$ is parallel to $\bar{e}_z$. Let assume that the plates enforce isotropic tangential anchoring (all the orientations within a (x, z) plane are equivalent).

The electric and magnetic external field are applied along the y and z -axis, respectively. Therefore, $\vec{E} = E\bar{e}_y$ and $\vec{H} = H\bar{e}_z$. At the mesoscopic level the orientational ordering is given by the nematic director field $\bar{n}$ which is parametrized as

$$\bar{n} = \bar{e}_x \sin \theta \cos \varphi + \bar{e}_y \sin \theta \sin \varphi + \bar{e}_z \cos \theta. \quad (89)$$

In the SmA phase $\theta=0$ and $\varphi=0$ for $E=0$. If the electric field is applied the LC molecules become tilted along the x -axis because of the electroclinic effects (there $\theta>0$ and $\varphi=0$ for $E>0$). The tilt is accompanied by the onset of the electric polarization $\vec{P}$ along $\vec{E}$. Due to symmetry reasons it holds

$$\vec{P} = \bar{n} \times \bar{v}. \quad (90)$$

Furthermore, let assume that ferromagnetic nanoparticles with a volume concentration ϕ are homogeneously dispersed within the LC body. Each of them carries a magnetic dipole moment $\bar{m}$, yielding magnetization $\vec{M} = \phi \bar{m}_{\text{eff}}$, where $\bar{m}_{\text{eff}}$ points along the average dipole orientation. We assume that $\bar{m}$ tends to align perpendicular to $\bar{n}$, hence magnetization $\vec{M} = \phi \bar{m} \theta$.

For the given geometry it is sensible to assume that the system exhibits roughly spatial homogeneity. The most essential free energy density f terms in the SmA phase are given by

$$f \approx \frac{A_0(T - T_{AC^*})\theta^2}{2} + \frac{P^2}{2\chi} - PE - t\theta P - m\phi H\theta. \quad (91)$$

The variational parameters of the system are the continuum fields θ and P . The quantities A_0 , χ and t are material dependent constants. The first and the second term in Eq. (91) enforce the SmA ordering, i.e., $\theta=0$ and $P=0$. The third term reflects the tendency of the parallel alignment of $\vec{P}$ and $\vec{E}$. The fourth one enforces the electroclinic effect, and the last term describes the linear coupling between $\vec{M}$ and $\vec{H}$. It takes into account that $\bar{m}_{\text{eff}}$ tends to be aligned perpendicular to $\bar{n}$.

Minimization of f (Eq. (91)) with respect to P yields the relation between P and θ :

$$P = (E + t\theta)\chi. \quad (92)$$

By inserting Eq. (92) into Eq. (91) the free energy can be expressed only in terms of θ :

$$f \approx \frac{A_0(T - T_{AC^*}^{\text{eff}})\theta^2}{2} - \frac{\chi E^2}{2} - \theta(\phi H m + E t \chi), \quad (93)$$

where

$$T_{AC^*}^{(eff)} = T_{AC^*} + \frac{t^2 \chi}{A_0}. \quad (94)$$

Minimization of f (Eq. (91)) with respect to θ yields

$$\theta = \frac{\phi m H + t \chi E}{A_0 (T - T_{AC^*}^{eff})}. \quad (95)$$

Note that $\theta=0$ in the absence of the external fields. Insert Eq. (95) into Eq. (93) and taking into account Eq. (88), it follows

$$\alpha = -\frac{\phi m t \chi}{A_0 (T - T_{AC^*}^{eff})}. \quad (96)$$

Therefore, α is linearly proportional to ϕ and m and inversely to $(T - T_{AC^*}^{eff})$. The magnetoelectric coefficient is expected to be maximal at the SmA-SmC* phase transition.

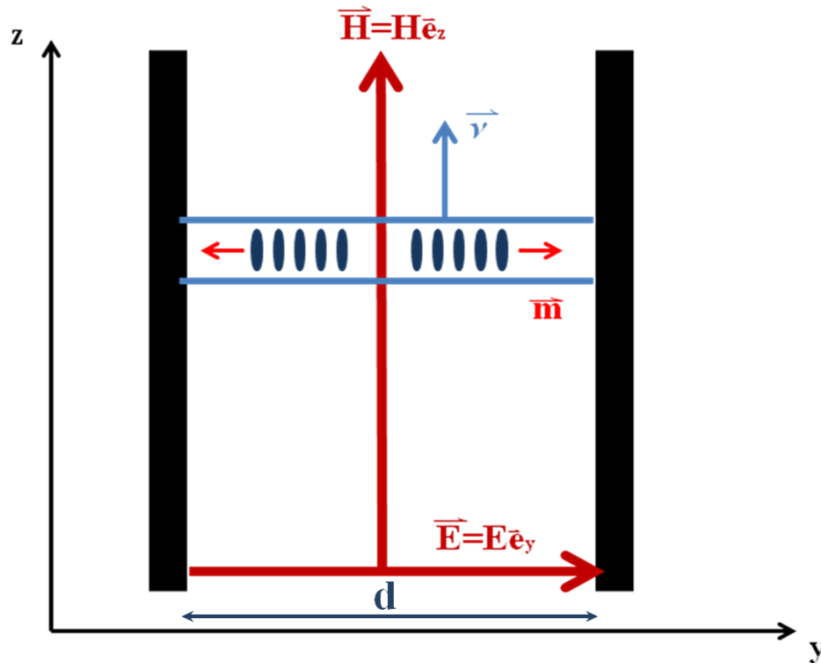


Figure 67: Schematic representation of the LCs-NPs mixtures confined within a planparallel cell with thickness d . $\vec{v}$ denotes a layer normal and $\vec{m}$ is the magnetization of the nanoparticles. The external electric field $\vec{E}$ and magnetic field $\vec{H}$ are perpendicular [221].

Further, by inserting Eq. (95) into expression $\vec{M} = \phi \vec{m} \theta$ it follows

$$M = M_0 + \alpha E, \quad (97)$$

where $M_0 = \phi m \frac{\phi m H}{A_0 (T - T_{AC}^{\text{eff}})}$. Thus

$$\Delta M = M - M_0 = \alpha E. \quad (98)$$

According to Eq. (98) we expect a linear magnetoelectric effect.

From the presented theory it is shown that in the mixtures of the ferroelectric liquid crystal and the magnetic nanoparticles the coupling between the LC polarization and NPs magnetization exists. This theoretical prediction will be tested experimentally in the next section.

5.2 Preparation and characterization of soft LC and magnetic NPs mixtures

Two similar systems of different ferroelectric liquid crystals (FLCs) and the same ferromagnetic nanoparticles (NPs) were investigated. The chosen magnetic NPs were weakly anisotropic maghemite ($\gamma\text{-Fe}_2\text{O}_3$) particles with a typical diameter around 20 nm (Figure 68). These NPs were prepared by Dr. Sašo Gyergyek from the Materials Synthesis Department, JSI, under the supervision of Prof. Dr. Miha Drofenik. The size of the NPs was estimated from transmission electron microscopy (TEM) images of at least 500 NPs (Figure 69). The particles were covered with the oleic acid in order to form a stable suspension in toluene, and they have been prepared in the following way. At first oleic acid coated, hydrophobic particles were synthesized by the co-precipitation of Fe(II) and Fe(III) cations by ammonia. Next, the synthesized suspension of NPs was treated hydrothermally at 200 °C for approximately 3 hours to promote particle growth from, on average, 11 nm to the final size around 20 nm. The hydrophobic NPs were precipitated by adding HNO_3 and soaked in oleic acid. At the end the excess oleic acid was removed by washing NPs with acetone. And then finally the particles were dispersed in toluene. More about the preparation of magnetic nanoparticles can be found in Ref. [178].

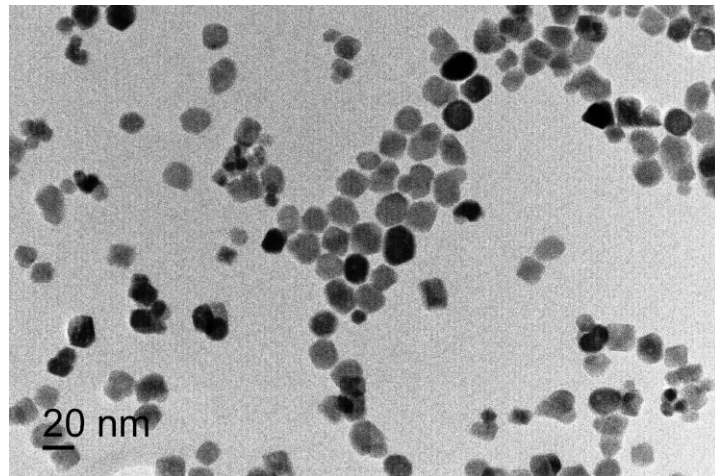


Figure 68: *TEM image of maghemite ($\gamma - \text{Fe}_2\text{O}_3$) magnetic nanoparticles. NPs were weakly anisotropic, covered with oleic acid and dispersed in toluene [172].*

Further, the quality of the synthesized NPs was checked by using a superconducting quantum interference device (SQUID), i.e., the SQUID susceptometry method. It was observed that the blocking temperature of the particles is well above 380 K [172-174]. This means that NPs act as permanent magnets in the temperature range of our interest.

For the liquid crystal samples two ferroelectric compounds were chosen, SCE9 and Felix 015/100. Both liquid crystals (LCs) exhibit a broad ferroelectric smectic C* phase (SmC*) near room temperature and they have large values of spontaneous polarization exceeding $200 \mu\text{C}/\text{m}^2$. The sequence of all the phases in both LCs with decreasing temperature from the isotropic phase is as follows: isotropic (I), nematic (N), smectic A (SmA) and SmC* phase. The phase transitions from one phase to another take place at the following temperatures: $T_{\text{IN}} \approx 392\text{K}$, $T_{\text{NA}} \approx 360\text{K}$ and $T_{\text{AC}^*} \approx 334\text{K}$ in SCE9, and at $T_{\text{IN}} \approx 357\text{K}$, $T_{\text{NA}} \approx 356\text{K}$ and $T_{\text{AC}^*} \approx 343\text{K}$ in Felix 015/100. Both LCs are diamagnetic, i.e., they do not contribute significantly to the magnetization of mixtures. This was checked by measuring the magnetization of both liquid crystals in a broad temperature range of interest.

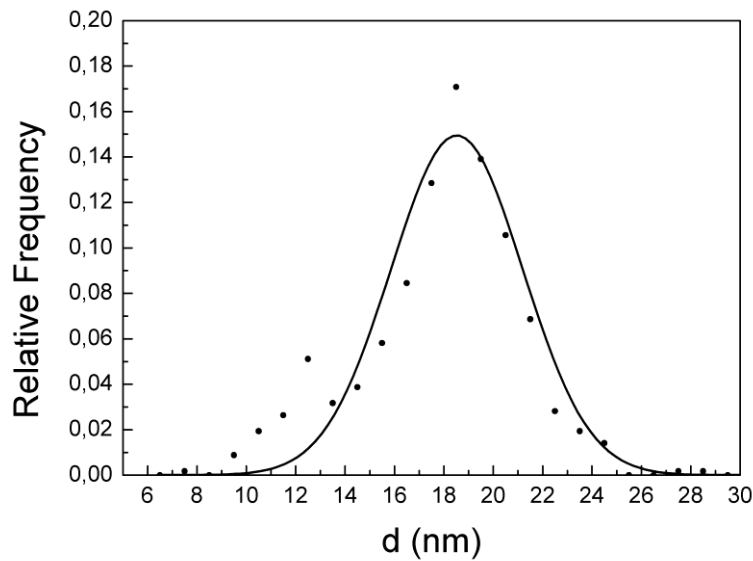


Figure 69: *The NPs size distribution estimated from the TEM image. The empirical NPs size-distribution function (solid circles) is fitted with a Gaussian distribution function (solid line) [222].*

After the characterization of both components, i.e., magnetic NPs and LC, the LC-NPs mixture concentrations of $x = 0.10$ and $x = 0.14$ were prepared by using the simple method presented below. Here, x was calculated by using the formula $x = m_{\text{NP}} / (m_{\text{NP}} + m_{\text{LC}})$, where m_{NP} denotes the mass of NPs and m_{LC} is the mass of the liquid crystal. The mixture preparation procedure was made in the following way. The LC was dissolved in the toluene together with the magnetic NPs. Such a solution was then mixed in the isotropic phase, i.e., at 393 K in the case of SCE9 LC and at 383 K for Felix

015/100, for approximately 2 hours to allow all the solvent to evaporate and to achieve a homogeneous dispersion, which was stable for several months.

It is important to mention that the temperature of the mixture preparation was always kept higher than the blocking temperature of the magnetic nanoparticles. This was to make sure that the NPs did not act as permanent magnets. This prevented the aggregation of the NPs. After the whole solvent was evaporated, the mixture was quenched from the isotropic to the SmC* phase to prevent the phase separation that can happen during the slow cooling through intermediate phases between the isotropic and nematic phases.

To check the stability of the prepared mixture, the small angle X-rays scattering measurements (SAXS) were made on the synchrotron in Trieste [223] on six month old mixtures. It is shown that the particle sizes are rather narrowly distributed around 17.7 nm, with a standard deviation of less than 6 nm (Figure 70). This finding is in a good agreement with the particle size distribution obtained from the transmission electron microscopy (TEM) mentioned before. This demonstrates that the LC-NPs mixture is stable, practically without forming aggregates and very uniform even after six months [173].

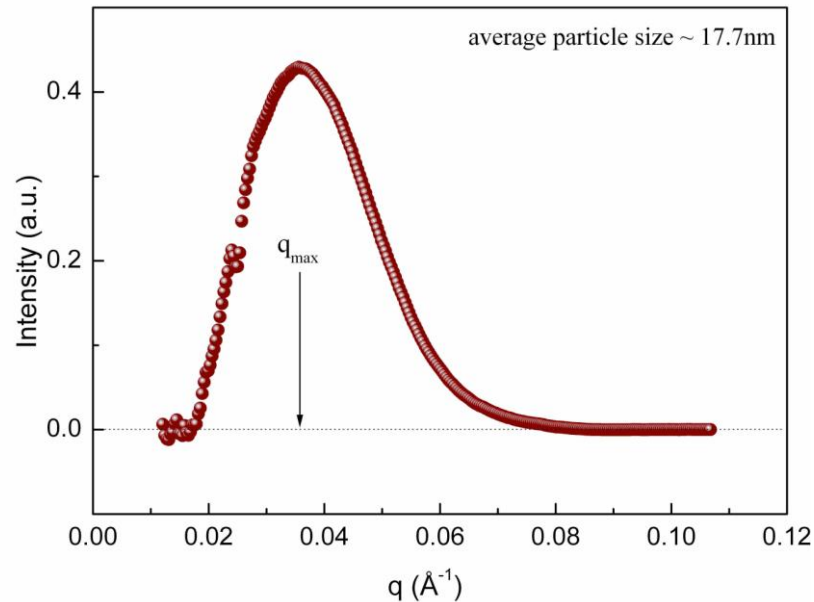


Figure 70: *X-rays scattering intensity as a function of the wave vector q . The relatively narrow distribution between 11 and 25 nm indicates that the mixture remains stable and practically without aggregates even after six months [173].*

After preparation, the stable LC-NPs mixtures were characterized by using three different methods: dielectric spectroscopy, SQUID magnetic susceptometry, and high-resolution calorimetry. For each of these techniques a corresponding sample cell filled with the LC-NPs mixture was prepared.

In the case of the dielectric measurements a cell composed of two glass plates covered with ITO electrodes was used (Figure 71(a)). The cell thickness was 120 μm . The cell was filled with the LC-NPs mixture and sealed with Torr Seal glue. For the magnetic measurements the mixture was put into a small thin glass tube (Figure 71(b)), and for calorimetric studies the sample was placed in a home-made silver cell (Figure 71(c)), thermally linked to a temperature stabilized bath through supportive wires and air. Details about dielectric spectroscopy and calorimetric methods are given in the 2nd Chapter of this thesis. Details about SQUID susceptometry can be found elsewhere [176].

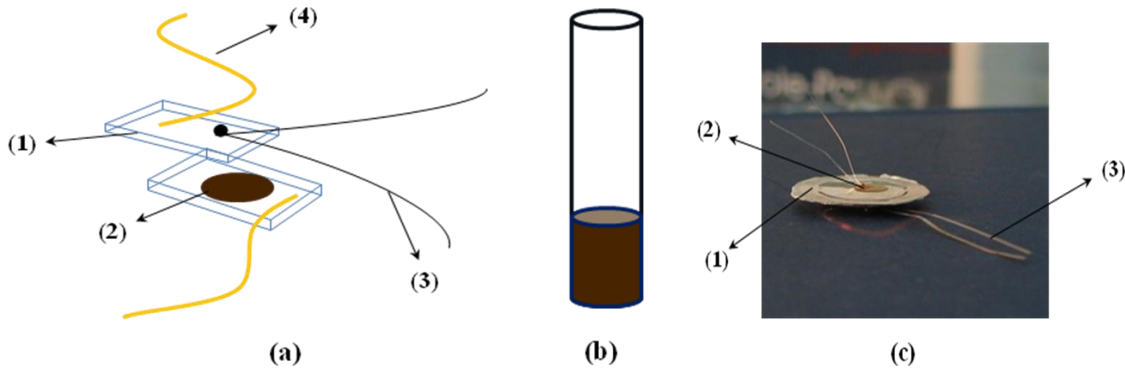


Figure 71: The sample arrangements for (a) dielectric measurements ((1) glass plates; (2) mixture; (3) thermistor; (4) gold wire), (b) SQUID measurements and (c) calorimetry measurements ((1) a silver cell; (2) thermistor; (3) heater).

The dielectric measurements were made by using a HP4284A Precision LCR meter. The frequency-dependent dielectric constant of the SCE9 LC and the magnetic NPs mixture with a concentration of $x = 0.10$ was measured between 400 Hz and 300 kHz in the temperature range from 300 K to 360 K, with a cooling rate of 400 mK/h. The excitation voltage was 1 V. The dielectric spectroscopy results are presented in Figure 72. The purpose of the dielectric measurements is to check the impact of the NPs on the dynamical properties of the director field as well as to estimate their disordering impact. It is shown that both the soft and Goldstone mode anomalies are similarly suppressed and smeared as in the case of aerosil mixtures [137, 138, 149]. Moreover, it has been observed (Figure 72b) that the electric field strongly suppressed the Goldstone mode that it is still present in the 10% mixture as a result of the unwinding of the helical structure. The dielectric results show that the helical structure, though partially unwound, is still present and that it can be distorted by an external field. That is important for our purpose of controlling the magnetization with the electric field via the director field distortions. Namely, if the NPs would rigidly pin down the director field as it is in the case in aerosil mixtures at higher concentrations it would be impossible to cause any changes in the director field by the external field.

The next procedure is to check whether the changes in the director field can be observed in the NPs magnetization, as suggested by the above-described theory. This would signal that there exists coupling between the director field and the NPs. The simplest way is to cool down the mixture through the SmC* transition at which the collective change of the director field, i.e., the tilt θ , appears. Here, the magnetic experiments supported by the calorimetric measurements were applied as discussed below.

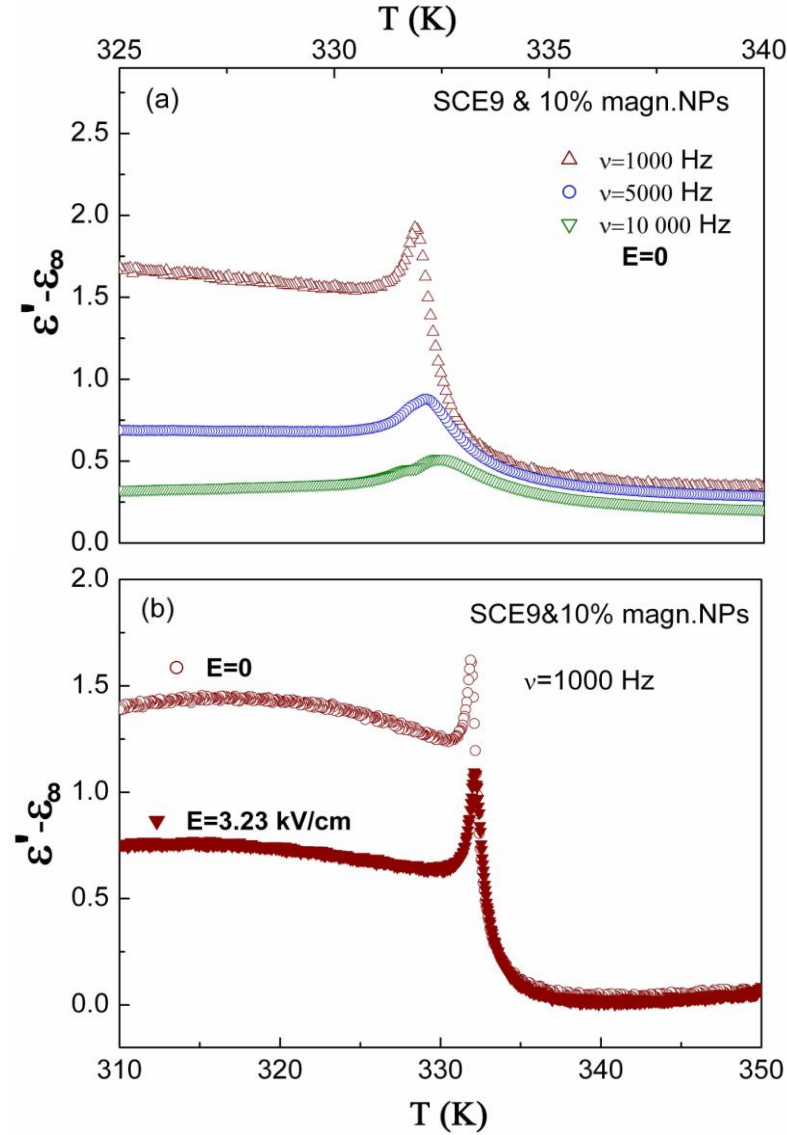


Figure 72: Temperature dependence of the real part ϵ' of the complex dielectric constant observed in SCE9 LC compound mixed with magnetic NPs. The temperature dependent real part of the dielectric constant ϵ' is presented for (a) three different frequencies, and (b) for two different electric fields. A constant background value $\epsilon_{\infty} = 4.5$ was subtracted from all the data [172].

5.3 Coupling between the molecular director field and magnetic nanoparticles in a soft magnetoelectric

As mentioned above, it is our task to verify whether there is a coupling between the director field and the magnetic NPs, i.e., whether the above theoretical prediction $\vec{M} = \phi \vec{m} \theta$ is valid.

In this case we focused on the collective change of the director field, i.e., the onset of the molecular tilt at the ferroelectric SmC* phase transition. If there is a coupling between the LC director field and the magnetic NPs, the change of the magnetization should be observed below the ferroelectric phase transition temperature T_{AC^*} following closely the

temperature change in θ , i.e., the temperature evolution in the magnetization change should reflect the change of the tilt which plays a role of the primary order parameter.

For this purpose the magnetic susceptibility and high resolution calorimetry measurements were performed in the temperature interval around the SmA-SmC* phase transition for both bulk LCs SCE9 and Felix 015/100. The magnetic properties were measured with a commercial SQUID-based magnetometer with a 5T magnet (Quantum Design MPMSXL-5) by Dr. Marko Jagodič from the Institute of Mathematics, Physics and Mechanics, Ljubljana, under the supervision of Prof. Dr. Zvonko Jagličić. The first measurements were made on a 10% mixture of the SCE9 LC and ferromagnetic maghemite ($\gamma\text{-Fe}_2\text{O}_3$) NPs [174]. The sample was first heated above the SmA-SmC* phase transition (334K), i.e., to 350 K in a zero magnetic field. At 350 K a constant magnetic field of $\mu_0 H = 10$ mT was applied and the magnetic susceptibility χ was measured from 350 K to 320 K, and back to 350 K with a rate of 0.15 K/min. Next the measurement was repeated again by cooling the sample back to 320 K with a slightly faster cooling rate of 1 K/min. The results of this experiment are presented in Figure 73. The temperature profiles of the excess magnetic susceptibility show a visible anomalous response below the expected ferroelectric transition temperature T_{AC^*} . Here the excess magnetic susceptibility $\Delta\chi$ was obtained by subtracting the extrapolated linear temperature dependence of the magnetic susceptibility $\chi_{\text{background}}$ observed in the SmA phase.

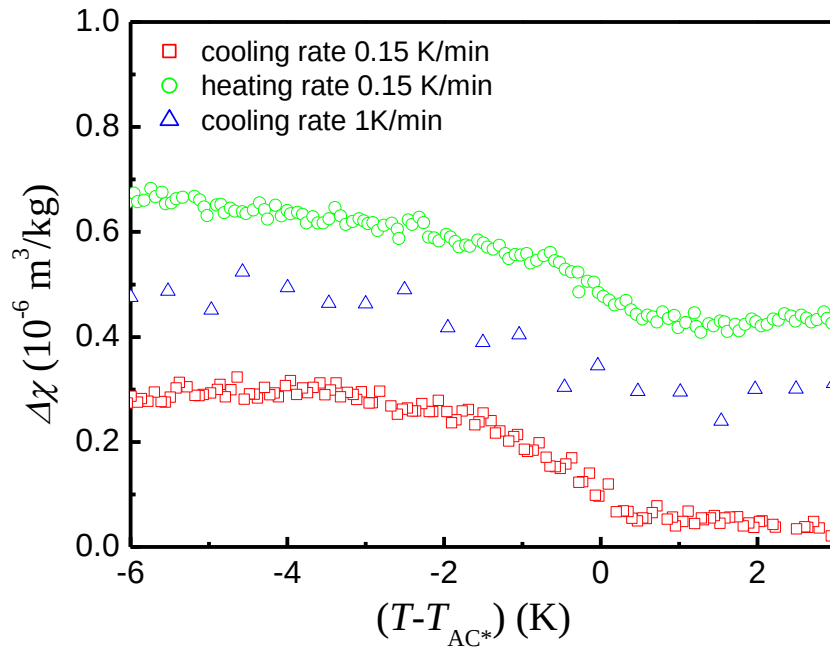


Figure 73: Excess magnetic susceptibility $\Delta\chi$ of SCE9 LC mixtures with magnetic NPs of diameter 17 nm with $x = 0.10$. $\Delta\chi = \chi - \chi_{\text{background}}$, where $\chi_{\text{background}}$ represents the linear temperature dependence of magnetic susceptibility in SmA phase extrapolated to low temperatures. For clarity, the $\Delta\chi$ data obtained during the heating (open circles) and cooling (open triangles) were shifted by $0.4 \cdot 10^{-6} \text{ m}^3/\text{kg}$ and $0.3 \cdot 10^{-6} \text{ m}^3/\text{kg}$. The SmA-SmC* transition temperature $T_{AC^*} = 332 \text{ K}$ [174].

Later on we prepared a 14% mixture of SCE9 LC and maghemite NPs [173]. Here a sample was first heated to about 320 K in a zero magnetic field. Then the external magnetic field of $\mu_0 H = 10$ mT was applied and the temperature dependence of the magnetic susceptibility was measured from 320 K to 400 K with a heating rate of 0.15 K/min. As expected, the temperature profiles of the excess magnetic susceptibility $\Delta\chi$ for both samples are proportional to the increase of the tilt angle below the T_{AC^*} (see Figure 74) indicating that the change in $\Delta\chi$ temperature dependence below T_{AC^*} is indeed a consequence of the coupling between the NPs magnetic moments and the LC director field, which exists even at higher NPs concentrations (Figure 74). It is also shown that magnetic NPs (MNPs) have an impact on the LC ordering. As we can see, the SmA-SmC* phase transition temperature in bulk SCE9 LC is at 334 K, but in LC-MNPs mixtures, depending on the NPs' concentration, it is shifted by 2-4 K to lower temperatures.

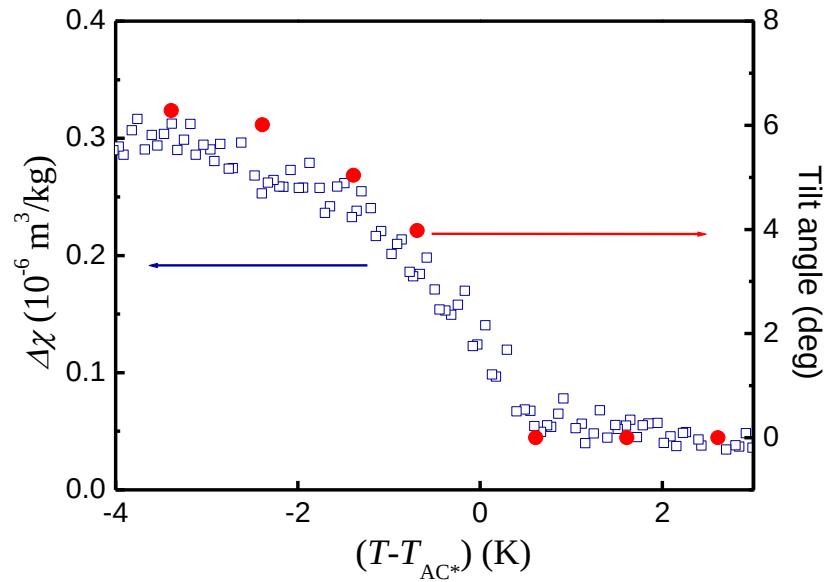


Figure 74: Excess magnetic susceptibility $\Delta\chi = \chi - \chi_{\text{background}}$ (open squares) and tilt angle $\theta(T)$ (solid circles) for SCE9 LC mixtures with magnetic NPs of diameter around 20nm with $x = 0.14$. The SmA-SmC* transition temperature $T_{AC^*} = 332$ K [223, 224].

However, to confirm the position of the phase transition and to additionally check the smearing of the transition caused by the magnetic NPs, the calorimetric measurements were made in the temperature range from 325 K to 337 K (Figure 75) [173]. The scanning rate was 0.3 K/h. The excess heat capacity data (ΔC_p) shows that the anomaly in $\Delta\chi$ appears below the SmA-SmC* phase transition temperature (see Figure 76) and the smearing of the phase transition is less than 0.5 K, even for a high concentration of NPs. These results strengthen the case that the orientation of magnetic NPs is directly coupled to the LC director field. Such coupling allows the possibility of indirect coupling between the magnetic and ferroelectric order since it is known that the director can be controlled by the electric field-induced polarization switching [225]. This makes mixtures of ferroelectric LC and magnetic NPs the best candidates for soft indirect magnetoelectrics.

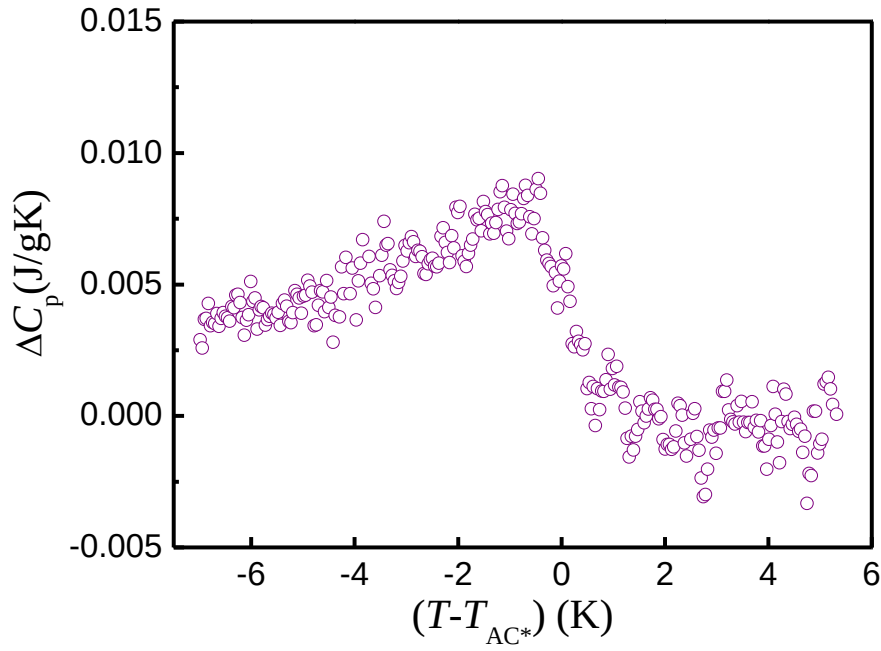


Figure 75: Excess heat capacity ΔC_p of SCE9 LC mixtures with magnetic NPs of diameter around 20nm with $\chi = 0.14$. The SmA-SmC* transition temperature $T_{AC^*}=332$ K [173].

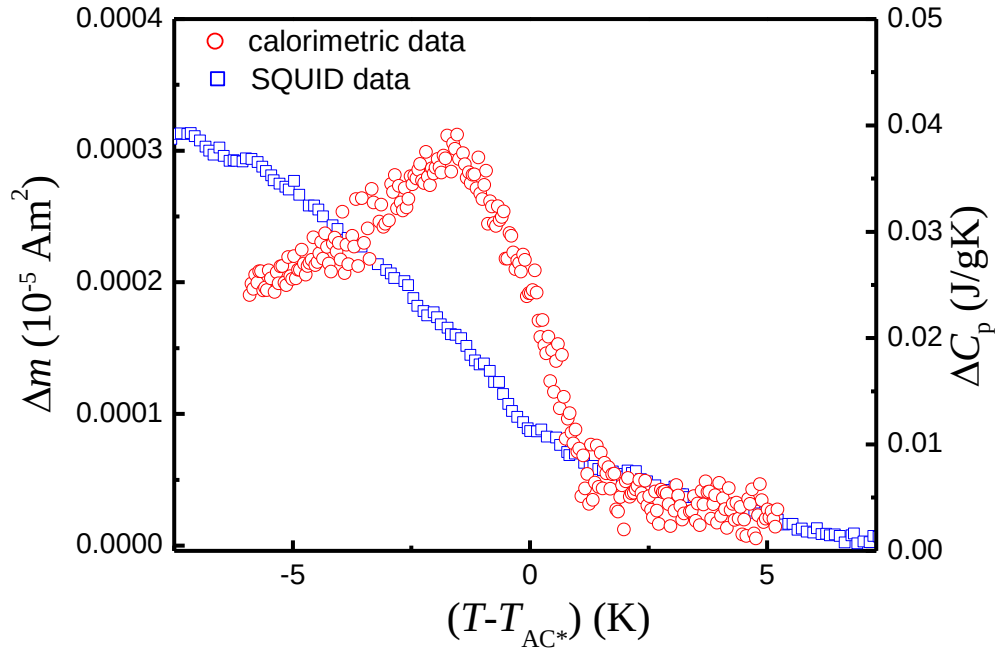


Figure 76: Excess magnetization $\Delta m = m - m_{\text{background}}$ (blue squares) and excess heat capacity ΔC_p (red circles) of SCE9 LC compound mixed with magnetic NPs of diameter around 20nm with $\chi = 0.14$. Here $m_{\text{background}}$ represents the linear temperature dependence of the magnetization in the SmA phase extrapolated to low temperatures. The SmA-SmC* transition temperature $T_{AC^*}=332$ K [172].

Similar experiments to those described above were also performed on mixtures of the Felix 015/100 ferroelectric LC and the same magnetic NPs, i.e., maghemite ($\gamma\text{-Fe}_2\text{O}_3$) ferromagnetic NPs [222]. The concentration of the prepared mixture was $x = 0.14$. Here the magnetic susceptibility measurements were made with a SQUID magnetometer in the temperature range close to the bulk Felix 015/100 LC SmA-SmC* phase transition temperature, i.e., between 330 and 350 K. The sample was first heated to 350 K in a zero magnetic field. At 350 K an external magnetic field of $\mu_0 H = 10$ mT was applied, and the temperature dependence of the sample's magnetic susceptibility was measured first down to 330 K, and then back up to 350 K with a cooling/heating rate of 0.15 K/min. At the end the sample was measured again in the same magnetic field from 350 K to 330 K with a faster cooling rate of 1 K/min (Figure 77). Again, the excess magnetic susceptibility $\Delta\chi$ shows a significant change below the SmA-SmC* phase transition temperature $T_{AC^*} = 341$ K.

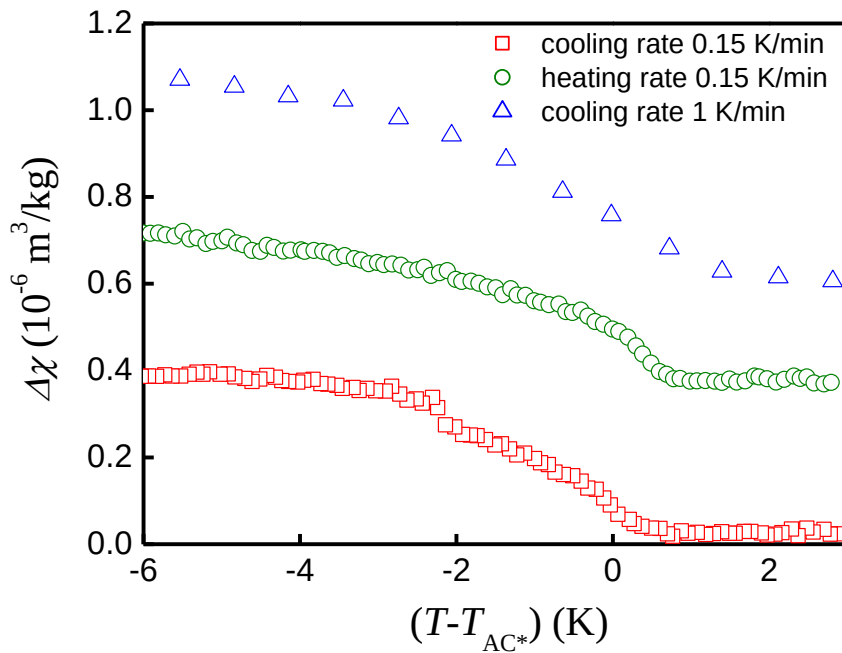


Figure 77: Excess magnetic susceptibility $\Delta\chi = \chi - \chi_{\text{background}}$ of Felix 015/100 LC compound mixed with maghemite magnetic NPs of diameter around 18 nm with $x = 0.14$. The SmA-SmC* phase transition temperature $T_{AC^*} = 341\text{K}$; The $\Delta\chi$ data obtained during the heating (open circles) and cooling runs (open triangles) were shifted by $0.4 \cdot 10^{-6} \text{ m}^3/\text{kg}$ and $0.8 \cdot 10^{-6} \text{ m}^3/\text{kg}$ for clarity. Here, $\chi_{\text{background}}$ denotes the magnetic susceptibility of the SmA phase extrapolated into the SmC* phase [222].

The above results also confirmed the coupling between the director field and the magnetization of the maghemite NPs in Felix 015/100 ferroelectric LC, thus indicating that such coupling could be found in a variety of LC compounds. This, of course, enhances greatly the chances to synthesize soft magnetoelectric materials of the second rank, i.e., composite material with indirect magnetoelectric coupling.

The next step was to verify that the magnetization in the above-described mixtures can be manipulated by the external electric field.

5.4 Magnetoelectric response in soft magnetoelectrics: magnetization control via the electric field

As shown above, the theory [222] predicts coupling between the liquid crystal electric polarization and the nanoparticle magnetization. This is a direct consequence of Eq. (96), i.e., $\alpha \neq 0$. Further, the measurements of the magnetization as a function of temperature show the anomaly in the magnetization near the SmA to SmC* phase transition, indicating the coupling between the liquid crystal director field and the magnetization of the nanoparticles. In order to confirm the existence of the magnetoelectricity in our soft composite material, it should be shown that in these materials the indirect coupling exists between the nanoparticles' magnetization and the liquid crystal polarization via the director field, i.e., $\alpha \neq 0$.

This can be verified by an experiment in which the control of the magnetization by the electric field coupled to the polarization is tested [224]. We chose this way rather than the control of the polarization via the magnetic field, since in this latter case the magnetic field also couples to the LC director field due to the magnetic anisotropy of the LC molecules, and it is a much less reliable method. In the former method, the electric field couples only to the polarization and not to the magnetic NPs, and thus the control of the magnetization via the external electric field is much clearer in the experiment.

In such an experiment the magnetization is continuously measured as a function of time and the electric polarization P is switched by the external electric field E . And then it can be shown whether the changes in the magnetization follow the changes in the applied electric field.

The electric field E is coupled to the LC electric polarization P . Via this coupling it is possible to influence the director field with the external electric field. The electric field has two impacts on the director field (Figure 78). First, the tilt angle increases due to the electroclinic effect and, second, the director rotates on the conus for a given angle related to the strength of the electric field following the rotation of the polarization vector in the smectic plane. From the experiments presented above the existence of the coupling between the director field and the magnetization is observed.

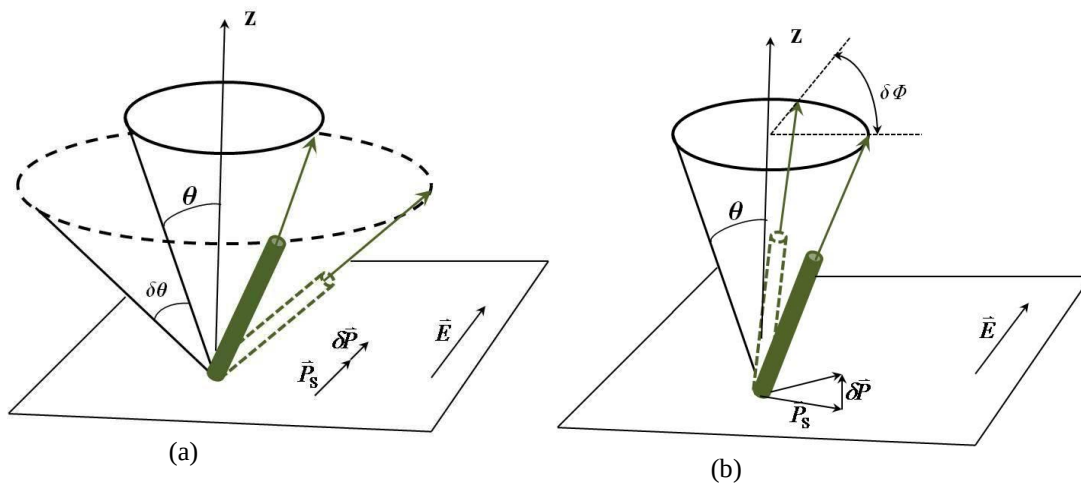


Figure 78: Schematic representation of the (a) tilt angle change and (b) director rotation on the conus.

Thus, it is expected that the changes in the director field cause the changes in the magnetization. Consequently, it is plausible to expect that the electric field induced changes in the director field due to the polarization rotations should be reflected in the changes of the magnetization. The observation of such changes caused by the electric field would then be a proof of the indirect coupling between the magnetization and the polarization via the director field and thus $\alpha \neq 0$.

This prediction was tested by the experiments on the mixtures of liquid crystals and magnetic nanoparticles presented below [224]. The two ferroelectric liquid crystals, SCE9 and Felix 015/100 and the maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles with diameter of 20 nm were used. For this experiment a sample was prepared in the same way and using the same cell as in the case of the dielectric measurements (Figure 71 (a)). Measurements of two systems, i.e., a mixture of LC SCE9&magnetic NPs and LC Felix 015/100&magnetic NPs, were made with the SQUID susceptometer and the external field was generated by a high-voltage generator, the same that was used for the electrocaloric measurements. The external field E (applied along the smectic planes) and the small magnetic field H necessary to detect the magnetization were perpendicular. The magnetization was measured near the SmA-SmC* phase transition as a function of time and during the measurements the electric field was alternately switched on and off. The typical time interval between switching the field on and off was about 10 minutes. The value of the applied voltage was between 100 and 300 V. This is equal to the electric field between 8 and 24 kV/cm, respectively, since the sample thickness was around 120 μm .

The results are presented in Figure 79 for the SCE9 mixture as well as for the Felix 015/100 mixture. It is clearly shown that when an electric field is applied the magnetization increases, and after the removal of the electric field it decreases. In this case the field also helps in ordering the whole system in a monodomain state by unwinding the LC helical structure, and thus together with the electroclinic effect enhancing the magnetization of the system. The same effect is observed for a positive and negative electric field, as expected for the symmetry of the SmC* phase. Here the change of the sign of the electric field just rotates the director on the conus (Figure 78 (b)) causing no change in the magnetization, but due to the electroclinic effect it increases the tilt by the same amount as the positive field, thus causing the same change in the magnetization.

Therefore, it is shown that the magnetization can be controlled by controlling the polarization via the electric field. This proves the existence of the indirect coupling between the NP magnetization and the LC polarization.

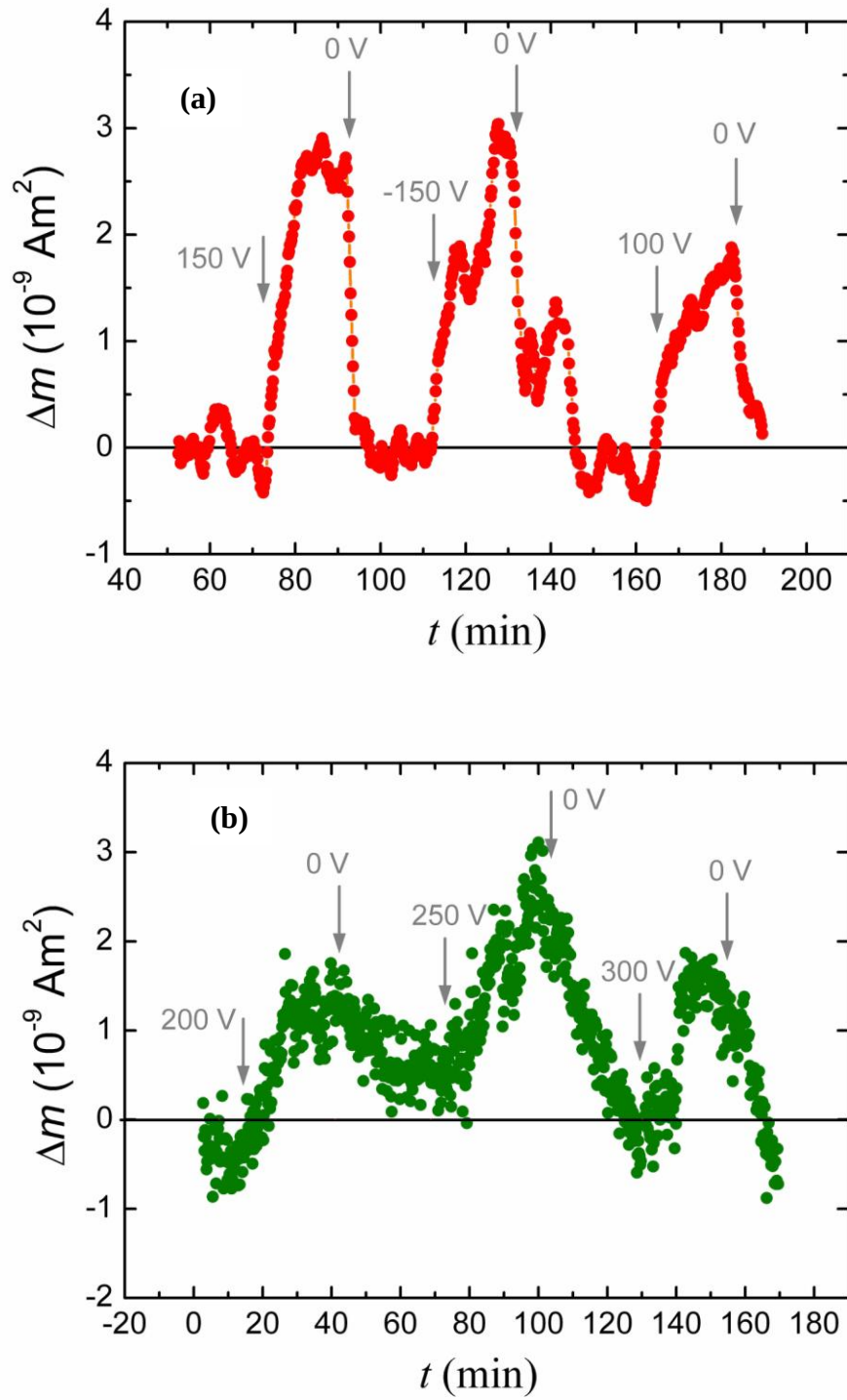


Figure 79: The excess magnetization of (a) SCE9 liquid crystal compound and (b) Felix 015/100, both mixed with maghemite nanoparticles of 20 nm during the applied/removed electric field. When an electric field is applied the magnetization increases, and the removal of the electric field results in a decrease of the magnetization [224].

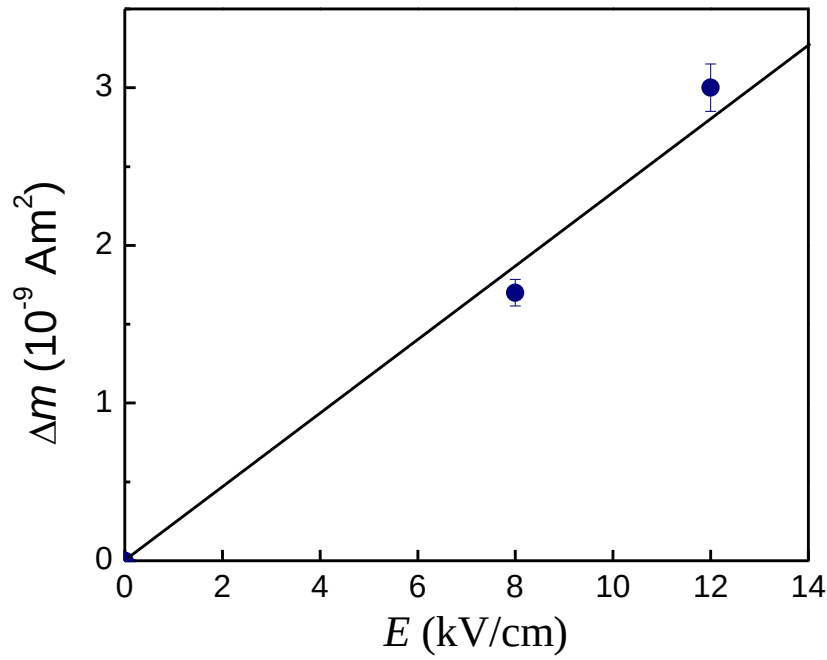


Figure 80: The excess magnetization of SCE9 liquid crystal mixed with maghemite nanoparticles of 20 nm as a function of the applied external electric field [224].

As shown in Figure 80, our results confirm the existence of the linear magnetoelectric effect, as predicted by the theory in which the magnetic moments are oriented perpendicular to the director. The magnitude of the linear magnetoelectric coupling coefficient α will be determined more precisely in future experiments.

5.5 Short summary of the results obtained in the soft magnetoelectrics

From the experimental results presented in this thesis it is shown that besides the disordering effects of the magnetic nanoparticles on the director field, there also exist the coupling between the orientation of the magnetic nanoparticles and the liquid crystal director field. And also it is shown that the electric field has an impact on the magnetization. This is a consequence of the indirect coupling between the LC polarization and NP magnetization, thus making these mixtures candidates for soft magnetoelectrics.

6 Conclusions

The main aim of this thesis was to contribute to an understanding of different energy conversion effects in various soft and solid advanced materials, specifically, in liquid crystal elastomers, electrocalorics and soft magnetoelectrics, and thus to bring them closer to their possible application in everyday life.

In particular, the three giant effects related to different conversions of energies have been studied. In the nematic liquid crystal elastomers the thermomechanical effect or the conversion of thermal to mechanical energy has been investigated. The electrocaloric effect or conversion of electrical to thermal energy has been studied in organic and inorganic materials, while the magnetoelectric effect or the electric control of the magnetization has been verified in newly synthesized mixtures of ferroelectric liquid crystals and magnetic nanoparticles.

Several experimental methods have been utilized in the above investigations. In the case of LCEs the nature of the paranematic-nematic phase transition was investigated by the high-resolution calorimetry and the electrocaloric effect was measured with so called electrocaloric thermometry. This method is based on high-resolution calorimetry with a small modification that instead of driving the sample with the heat power a special form of electric field is applied to the sample. The magnetoelectric effect in new soft magnetoelectric materials was tested by SQUID susceptometry and dielectric spectroscopy. Various supporting data were obtained by different microscopy and spectroscopy techniques, such as SEM, TEM, and SAXS.

Liquid crystal elastomers are novel materials that combine the properties of liquid crystals and elastomers and due to the very large thermomechanical effect they are very promising for many applications, such as a new generation of sensors, actuators and artificial muscles. In the vicinity of the phase transitions the LCEs spontaneously stretch or shrink due to the temperature change in the vicinity of different phase transitions. So far, the most interesting and largest effects were observed near the transition from the paranematic to the nematic phase. The nature of this transition in main-chain LCEs was not yet completely clear. In this thesis, various tools for controlling the thermomechanical response from on-off or discontinuous to a continuous one via changing the nature of the PN-N phase transition have been demonstrated.

The existence of the critical point has already been demonstrated in the side-chain LCEs. In this thesis a systematic study of the main-chain LCEs has been made in order to clarify which mechanisms in general affect the liquid crystal elastomers. It has been shown that the critical behavior in the MC-LCEs and thus the type of the thermomechanical response could be controlled, besides via the crosslinker density, also via two physical parameters such as the applied external mechanical field that is used during the second crosslinking step and the temperature at which the second crosslinking step was taken.

Electrocalorics are materials that show an interesting electrocaloric effect in which the conversion of electrical energy to heat and vice versa takes place. The ECE generates great interest due to its potentially broad range of applications in novel environmentally friendly heating and cooling devices, with practically no moving parts and better energy efficiency. Possible applications include household refrigerators, heat pumps, devices for

cooling computer chips, applications in microrobotics, sensors, actuators, etc. Although the background of the ECE is not yet fully understood, the main idea for its explanation lies in the change of entropy of the dipolar subsystem induced by the applied electric field, which is compensated by the change of the lattice entropy under adiabatic conditions. This results in an increase or decrease of the material temperature if the field is increased or decreased adiabatically, respectively.

The electrocaloric effect has been known for long time but it was not interesting and useful for commercial applications, due to its small magnitude in previously known materials. The interest in electrocalorics was renewed recently by the first predictions of a giant ECE in some inorganic and organic materials, as published in two scientific papers in *Science* by A. Mischenko, et al. in 2006 and by B. Neese, et al. in 2008. These predictions were based on indirect measurements of the electric polarization as a function of temperature and electric field.

In this thesis the direct ECE measurements of the ECE in various organic and inorganic ferroelectrics and relaxor ferroelectrics have been presented. Some of them have been the first direct measurements confirming the existence of a giant electrocaloric effect in bulk and thin film materials. It has been observed that a relatively large temperature change of around 3 K exists at a modest field of 90 kV/cm in bulk ceramic materials, while in thin films the ECE was in the range between 10 and 40 K at an electric field between 200 kV/cm and 1 MV/cm. Such large electric fields could be used in thin film materials due to the very high break-down electric fields.

It has been shown that the observed ECE magnitude is generally consistent in ferroelectrics with recent predictions based on indirect measurements. On the other hand, in relaxor ferroelectrics a significant discrepancy has been observed between the ECE results obtained in an indirect and a direct way. This indicates the breakdown of the Maxwell thermodynamic expression in relaxor materials as a consequence of the ergodicity breakdown in these materials.

The experiments also indicated that the effective ECE responsiveness has a maximum value near the critical point, demonstrating its relevance for the enhancement of the ECE in bulk and thick perovskite relaxor materials. In contrast, the maximum of the responsivity has not been achieved in thin films, even for the highest applied electric fields thus indicating that in these materials the maximum of the responsivity is shifted toward higher electric fields. It has also been shown that the ECE behavior in the vicinity of the critical point obtained from the direct measurements is in a good agreement with the theoretical predictions.

The quality of the cooling material that has been determined from the refrigerant capacity indicated that the irradiated P(VDF-TrFE) polymer films and PLZT relaxor ferroelectric thin films show an extremely large ECE and are the best candidates for application.

Magnetoelectrics are materials that exhibit simultaneously ferroelectric and ferromagnetic properties, and in such materials it would be possible to control the magnetic properties via the electrical ones, and vice versa. These materials attract considerable scientific attention because of their potential for applications as actuators, transducers, and memory devices. The development and discovery of new magnetoelectric materials is of great importance for such applications. The theory shows there is a possibility for the existence of the indirect coupling between the magnetization and polarization via the orientational director field in mixtures of ferroelectric liquid crystal and ferromagnetic nanoparticles. In this thesis the study of the magnetoelectric effect has been addressed in the first ever prepared stable soft magnetoelectric mixture of ferroelectric liquid crystal and ferromagnetic nanoparticles. Moreover, the way how to avoid the problem related to producing stable colloidal mixtures of LC and magnetic NPs

and how to successfully prepare these mixtures that are stable on a time scale exceeding several months has been presented.

To conclude, all the materials presented in this thesis, liquid crystal elastomers, electrocalorics and soft magnetoelectrics, show promise for various applications in everyday life. Here, the basic research of their most interesting material properties has been presented, which could help to advance their better understanding and to engineer new, even more improved, advanced materials.

However, there are still many open questions related to these materials and their application, and maybe some further experimental and theoretical studies will help to resolve those problems. Actually, I believe that there is still a lot of interesting research waiting to be done in order to further improve the advanced materials presented in this thesis.

*Vsak tiho zori, počasi in z leti,
a kamorkoli že greš,
vse poti je treba na novo začeti.*

(T. Pavček)

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Appendix: Personal bibliography for the period of 2007-2011

Publications related to this thesis

I. Scientific articles (first author)

1. Rožič, B.; Krause, S.; Finkelmann, H.; Cordoyiannis, C.; Kutnjak, Z. Controlling the thermomechanical response of liquid-crystalline elastomers by influencing their critical behavior. *Appl. Phys. Lett.* **96**, 111902 (2010).
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27. *B. Rožič, M. Jagodič, S. Gyergyek, M. Drofenik, S. Kralj, Z. Jagličić, Z. Kutnjak*: Mixtures of magnetic nanoparticles and the ferroelectric liquid crystal: New soft magnetoelectrics.
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