Basic study of relaxors: Materials for high technological devices

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Abstract. Ferroelectric relaxors belong to a subgroup of ferroelectric materials. Relaxors are characterised by unique dielectric, polarization, electromechanical and electro-optical properties. These extraordinary properties make them suitable for high technological electronic devices such as sensors, actuators, electro or elasto-optic and photorefractive elements. Understanding the origin of these properties and physical background is a key for useful applications. In this paper we show the investigation of the nature of the relaxor ground state which is one of the unresolved enigmas of relaxors. We will interpret the high-resolution calorimetric measurements of the electric field induced ferroelectric phase transition of the ferroelectric relaxor $Pb(Mg_{1/3}Nb_{2/3})O_3$ single crystal oriented in the [110] direction.

Keywords: critical point, relaxor ferroelectric, latent heat.

1 Introduction

Relaxor ferroelectric materials or relaxors offer a wide range of useful properties which make them attractive for various high technological applications. These include ferroelectric hysteresis (used in non-volatile memories), high permittivity (used in capacitors), high piezoelectric effects (used in sensors, actuators and resonant wave devices such as radio-frequency filters), high pyroelectric coefficients (used in infra-red detectors), strong electro-optic effects (used in optical switches) and anomalous temperature coefficients of the resistivity (used in electric-motor overload protection circuits). The largest and most important relaxor ferroelectric family is a perovskite structured group. It was shown that the origin of relaxor properties is due to the charge and site disorder of the perovskite structure caused by the substitution of cations with a different valence [1]. To improve or to make them suitable for useful applications we have to understand the physical background of these complex perovskite compounds.

Ferroelectric relaxor $Pb(Mg_{1/3}Nb_{2/3})O_3$ (abbreviated as PMN) is known for more than five decades and is still in the focus of the research as a prototypical example of relaxors. In contrast to ordinary ferroelectrics, relaxors like PMN show some unusual responses like: (i) a broad frequency dispersion in a complex dielectric response exhibiting maximum at T_m, (ii) the logarithmic decay of the polarization which persists even above T_m, (iii) absence of the spontaneous polarization in zero external electric field, (iv) a slim hysteresis loop at T_m and (v) slowing dynamics [1-4]. One of the key features of relaxors is the absence of a long range ordered ferroelectric phase in zero electric field at any temperature [3, 5]. It is believed that the origin of all these properties lies in an intrinsic inhomogeneity. The chemical disorder in relaxors is a basis for the formation of dipolar entities at very high temperatures. On cooling the system bellow the so-called Burns temperature [6] these dipolar entities form polar nanoregions which are randomly oriented and form in the ergodic relaxor state in a way similar to that of dipolar glasses [1, 3, 7]. By cooling the system below freezing temperature the relaxor state undergoes the transition into the non-ergodic dipolar glass state with randomly frozen polar nanoregions. This glassy state can be converted into a ferroelectric phase by application of the electric field higher than the critical electric field, $E \geq E_C$. Besides this widely accepted physical picture of the relaxor ground state, there are other possible models, such as for instance a random field (RF) mechanism [8]. The RF mechanism proposes that the relaxor state is a ferroelectric state broken up under the constraint of quenched random electric fields. It proposes also that these random fields destroy the long range ferroelectric order which can be established by applying a high enough electric field at which nanodomains align along the field. In order to understand relaxor properties the question of the relaxor ground state is one of the important issues which has to be resolved.

In the past it was shown that the polarization measurements do not provide a clear answer because the results can be interpreted in favour of both suggested models. Here, we report the results of high-resolution calorimetric measurements of the

PMN single crystal oriented in the [110] direction. The calorimetric measurements should provide the information about the presence of the latent heat at the ferroelectric transition line. The presence of the latent heat will prove that the ground state of relaxors is a state which is thermodynamically different from the ferroelectric state, i.e., the dipolar glass state is by applying E_c transformed into the long range ferroelectric state. In the case of the RF mechanism, the ferroelectric state is proposed to be established already at some higher temperature and so no significant change of the enthalpy as well as the latent heat should be observed between the low and high electric field states, because the local ferroelectric symmetry is preserved.

2 Experiments and discussion

High-resolution calorimetric measurements were performed in the ac and relaxation mode (see details in Ref. [9]) in such a way that either electric field or temperature was constant. In the former case the temperature was changed in the ac mode with 2 K/h at the constant field to measure continuous variation of enthalpy. Relaxation mode, however, is sensible also to the latent heat and so the total enthalpy change can be measured. We modify the calorimeter in such a way that it was possible to perform isothermal relaxation measurements in which the electric field was linearly ramped between ±10 kV/cm.

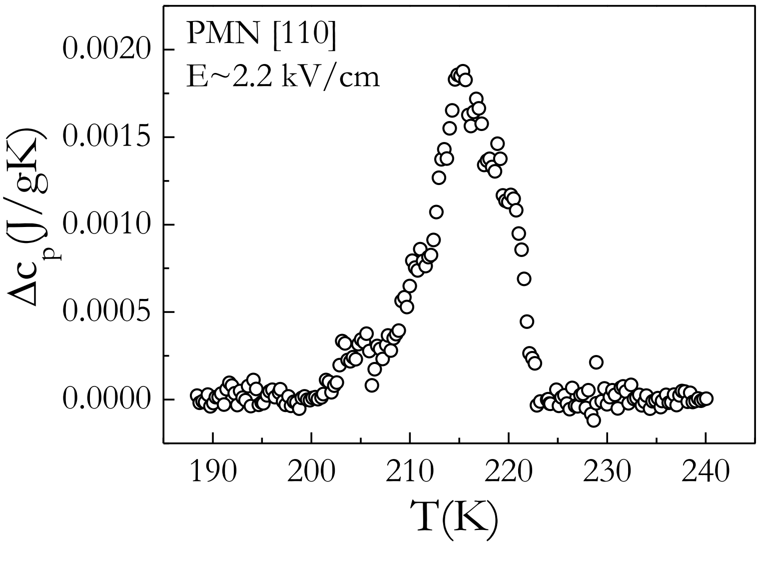

Figure 1: The temperature dependence of the excess heat capacity data obtained in the ac mode at the isofield condition.

In order to detect enthalpy changes at the ferroelectric transition the ac and relaxation measurements of the heat capacity were conducted. The temperature dependence of the excess heat capacity obtained from the ac measurement in PMN [110] single crystal is displayed in Figure 1. The excess of the heat capacity can be observed only if $E \geq E_C$. By increasing the electric field above 8 kV/cm, the excess heat capacity got suppressed and smeared out. Similar behaviour of the excess heat capacity was observed at the cubic to tetragonal (C-T) phase transition in PMN-PT system where the first order transition line separates paraelectric cubic and ferroelectric tetragonal phases and terminates in the critical point [10, 11].

To get a clear answer about the transition between the relaxor and ferroelectric state in PMN we utilized modified relaxation measurements. In the isothermal experiment we monitor the sample temperature when linearly ramped electric field was applied. At $E = E_C$, a sharp increase of the sample temperature was clearly visible (see Fig. 2). The increase of the sample temperature is directly related to the released latent heat at the electric field induced ferroelectric transition.

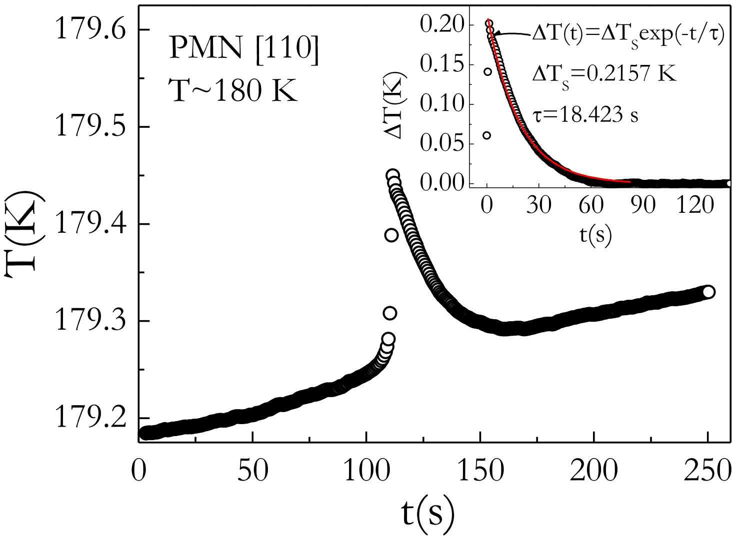

Figure 2: The change of the sample temperature for the PMN [110] single crystal as a consequence of the released latent heat at the field induced ferroelectric transition, at 180 K. The inset shows a fit to the simple exponential decay ansatz which reveals the amplitude of the sample temperature change and thus the latent heat.

To determinate the released latent heat in the first approximation we fit the dissipated latent heat into the surrounding by the simple exponential decay ansatz as shown in the inset of Fig. 2. The obtained amplitude of the sample temperature change, ΔT_S=0.2157 K, can be used to calculate corresponding latent heat. With further measurements it was shown that the amplitude of the sample temperature change decreases with increasing temperature and electric field. The presence and diminishing of the latent heat prove the existence of the first order transition line between the relaxor and ferroelectric phases which terminates at the critical point.

3 Conclusion

High-resolution heat capacity measurements were employed to investigate the nature of the electric field induced ferroelectric transition of the ferroelectric relaxor PMN single crystal oriented in [110]. The ac measurements display an excess of the heat capacity at $E \geq E_C$. At a much higher electric field the heat capacity anomaly is suppressed indicating the supercritical behaviour. The detected latent heat confirms the existence of a real phase transition line between the zero-field ground state and ferroelectric long range order. The calorimetric measurements reveal a similar behaviour as observed at the C-T phase transition in the PMN-PT system. The presence of the latent heat supports the idea of the dipolar glass like ground state of relaxors rather than the RF frozen ferroelectric state broken up into nanodomains.

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For wider interest

Relaxor ferroelectric materials represent a subgroup of ferroelectrics. $Pb(Mg_{1/3}Nb_{2/3})O_3$ is one of the most famous and widely studied relaxor. Relaxor materials are known for their unusual properties which are useful for various applications in high technological devices. Relaxors exhibit high permittivity (used in capacitors), ferroelectric hysteresis (used in non-volatile memories), high piezoelectric effects (used in sensors, actuators and resonant wave devices such as the radio-frequency filters, scanning probe microscopy, ink jet printer, adaptive optics, micromotors, vibration sensors/attenuators, Hubble telescope correction), high pyroelectric coefficients (used in infra-red detectors), strong electro-optic effects (used in optical switches, segmented displays, modulators, image storage, holographic data storage) and anomalous temperature coefficients of the resistivity (used in electric-motor overload protection circuits). Our work is dedicated to understanding the ordering process in this material which is of a fundamental importance for the further application progress as well as engineering new materials with enhanced properties.

In this work we represent the study of the glass-ferroelectric phase transition that addresses also the long standing question about the ground state of relaxors in zero electric field. The isofield and isothermal measurements of the heat capacity reveal an excess of the heat capacity as well as released latent heat at the field induced ferroelectric transition. The detected latent heat confirms the existence of the real ferroelectric phase transition and support the physical picture of the dipolar glass like ground state of relaxors.