High-Resolution Calorimetric Study of $Pb(Mg_{1/3}Nb_{2/3})O_3$ Single Crystal

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Motivated by the long-standing unresolved enigma of the relaxor ferroelectric ground state, we performed a high-resolution heat capacity and polarization study of the field-induced phase transition in the relaxor ferroelectric single crystal $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) oriented along the [110] direction. We show that the discontinuous evolution of polarization as a function of the electric field or temperature is a consequence of a true first order transition from a glassy to ferroelectric state, which is accompanied by an excess heat capacity anomaly and released latent heat. We also find that in a zero field there is no ferroelectric phase transition in bulk PMN at any temperature, indicating that the nonergodic dipolar glass phase persists down to the lowest temperatures.

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Relaxor ferroelectric materials, which are characterized by their unique dielectric, electromechanical, and electro-optical properties as a result of site and charge disorder, still attract considerable attention due to several unresolved questions [1–3]. In particular, the physical nature of the low temperature relaxor state remains the subject of some controversy [4–15].

Extensive experimental studies have supported the widely accepted notion that the elementary dipolar entities in relaxors are polar nanoregions (PNRs) [1] which appear below the so-called Burns temperature [16]. There exist, however, two distinct scenarios regarding the evolution of the low-temperature relaxor ground state. (a) The first of these is the so-called random field (RF) scenario [7,17,18]. Here, on cooling the PNRs undergo a gradual transition into a disordered paraelectric state, which is broken up into polarized nanodomains under the influence of quenched local random fields [7,17]. A standard theoretical model for the RF scenario is the random field Ising model [19], for which it has been shown rigorously [20] that long-range order exists in zero applied field ($E = 0$) for spatial dimensionality $d > 2$. This seems to be supported by experiments of Fu *et al.* [18], who found that nanodomains in PMN [110] may order ferroelectrically in zero field below $T_C \sim 225$ K, a conclusion reached on the basis of first-quadrant dielectric D-E loops with fields up to $E \sim 10$ kV/cm and TEM on thin samples. A tentative phase diagram for the RF scenario is displayed in Fig. 1(a). The conversion line, not reported by Ref. [18], is a schematic boundary between the nanodomain paraelectric phase and a field-induced microdomain ferroelectric phase. It should be noted that on crossing the conversion line, including the point at $E = 0$, a specific heat anomaly should occur together with a change of enthalpy and a latent heat if the transition is of first order. (b) The second concept goes one step further by assuming that in a disordered environment the cooperative interactions between the PNRs must also contain a random component or so-called *random bonds*. If the average random interaction is stronger than the cooperative one, a special kind of dipolar glass (DG) state appears, the main features of which can be well described by the spherical random-bond random-field model of relaxor ferroelectrics [21,22]. In the DG scenario, the relaxor state can, however, be transformed into a long-range ferroelectrically ordered state by applying a sufficiently strong electric field $E \geq E_C$, where E_C is the critical electric field [6,8,23–29]. The ferroelectric ordered state can be established by crossing the corresponding transition line [see Fig. 1(b)] either in the temperature direction at constant field (horizontal arrows) or in the field direction at constant temperature (vertical arrow). At the freezing temperature $T_f(E)$ (dotted line), the system undergoes a transition from an ergodic to a nonergodic dipolar glass state below T_f, where the PNR orientations are frozen. This transition is accompanied by a broadening of the relaxation spectrum, a divergence of the longest relaxation time, and an increase of the dielectric nonlinearity [10]. The solid lines in Fig. 1(b) represent true phase boundaries between the spherical dipolar glass state and the long-range ferroelectric state. The line of weakly first-order transitions terminates at a critical point (T_{CP},E_{CP}) similar to that observed in the PMN-$PbTiO_3$ (PMN-PT) system [13,26–28]. On crossing the line, rather sharp anomalies are expected to occur in the bulk polarization, which plays the role of an effective order parameter, as well as in the heat capacity. However, it should be stressed that no such anomalies are expected anywhere at $E = 0$.

In order to decide whether the relaxor ground state in PMN can be better described by the RF or by the DG scenario, we performed high resolution calorimetric and polarization measurements as a function of the electric field

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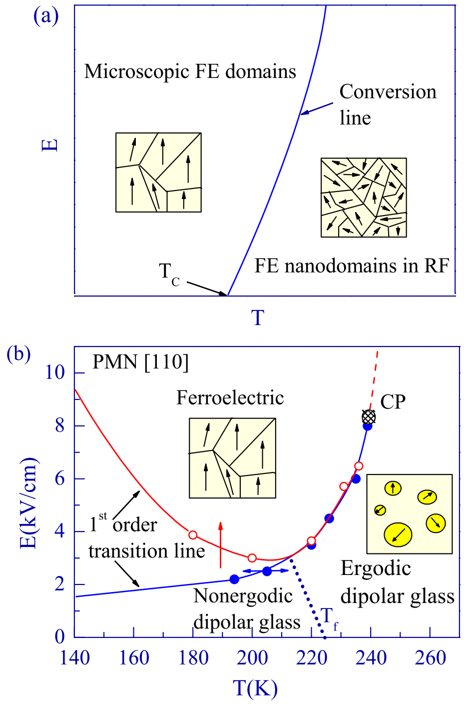

FIG. 1 (color online). Two established types of E-T phase diagram for PMN [110]. (a) Random field (RF) scenario: theory [19,20] predicts the existence of microscopic ferroelectric (FE) ordering at $T = T_C$ in zero field. Experiments by Fu *et al.* [18]: $T_C \sim 225$ K. Solid line: schematic conversion line where nanodomains subject to random fields RFs undergo a FE phase transition in a bias field E. (b) Dipolar glass model with randomly interacting PNRs. Solid lines with horizontal arrows: first order phase transition line between nonergodic relaxor and ferroelectric phase as observed in isofield experiments. Solid circles: data obtained from polarization and heat capacity anomalies [cf. Figs. 2(a) and 2(b)]. Solid line with vertical arrow: same but for isothermal experiments. Open circles: data from polarization and calorimetric measurements [cf. Figs. 2(c) and 3(a)]. CP and dashed line denote the critical point and the Widom line [35], respectively.

and temperature near the relaxor-to-ferroelectric transition. Two platelet-shaped samples of the PMN single crystal were cut perpendicular to the [110] direction and polished. The geometry of platelets was $4.05 \times 2.7 \times 0.414$ mm^3 and $3.85 \times 1.80 \times 0.266$ mm^3. Gold electrodes were sputtered onto the samples by an evaporation technique, and a heater and thermistor were attached on the opposite sides of the platelet together with gold contact wires. High-resolution calorimetric measurements were performed in the ac and relaxation mode (for details see Ref. [30]) in such a way that the E-T phase diagram was scanned either in the temperature direction at several constant dc bias electric fields or in the field direction at several constant temperatures. In the former case the temperature was changed in the ac mode at the cooling or heating rate of 2 K/h while the dc bias field was kept constant at the predefined value (typically between 0–15 kV/cm).

Within the ac mode, it is possible to measure quantitatively only continuous variations of the enthalpy (δH) [30]. In the relaxation mode, however, it is possible to detect quantitatively the total enthalpy changes (ΔH) including the latent heat (L) [30]. We modified the operation of the calorimeter in such a way that it was possible to perform isothermal heat capacity or enthalpy measurements while the bias electric field was linearly ramped between 0 and 10 kV/cm. In this case the E-T phase diagram was scanned in the field direction at given fixed temperatures. In addition, the relaxation mode was modified to operate in such a way that the sample electrocaloric temperature changes could be traced with an accuracy of 0.1 mK when linearly ramping the electric field between ±15 kV/cm in the time period of 1000 seconds. Such operation of the calorimeter allows precise determination of the enthalpy changes when crossing the line in the E-T phase diagram.

Similarly to enthalpy measurements, the polarization playing the role of the order parameter was also measured in both temperature and field directions in the E-T phase diagram, i.e., as a function of the temperature at various constant electric fields and as a function of electric field at various constant temperatures. In the polarization hysteresis-loop measurements, the electric field was slowly cycled linearly with the frequency of 0.001 Hz between ±10 kV/cm. In all polarization experiments, the corresponding charge was measured by a Keithley 617 programmable electrometer. Details of the polarization measurement procedure can be found in Refs. [13,31].

Prior to each measurement, the sample was annealed at ~380 K to recover a history independent state [10,11]. In the case of polarization temperature scanning runs, the rates were ~60 K/h. The evolution of the polarization when crossing the ferroelectric transition line is shown in Fig. 2(a) for both isofield and isothermal experiments. Hysteresis loops obtained at different temperatures show typical relaxor response [6,23,24,32]. A slim hysteresis is observed at temperatures above 240 K, which becomes broader at temperatures below the freezing temperature $T_f = 224$ K (see upper panels) as a consequence of the freezing process and divergence of the longest relaxation time [13]. Besides the hysteresis-loop broadening, a discontinuous increase of the polarization can be observed [23,24,32] when crossing the long-range ferroelectric transition line either in the temperature direction (bottom left panel) or the field direction (bottom right panel). From the temperature dependence of the polarization the value $E_C(T = 100\text{ K}) \sim 1.5$ kV/cm can be deduced. This rapid first-order-like increase of polarization is related to the onset of long-range ferroelectric order at $E = E_C$. A discontinuous change of the polarization can be observed only for $E_C \leq E < E_{CP}$. Here $E_{CP} \cong 8$ kV/cm for the PMN [110] crystal. Such behavior is similar to that observed in PMN-PT and PMN [111] and [001] crystals, and

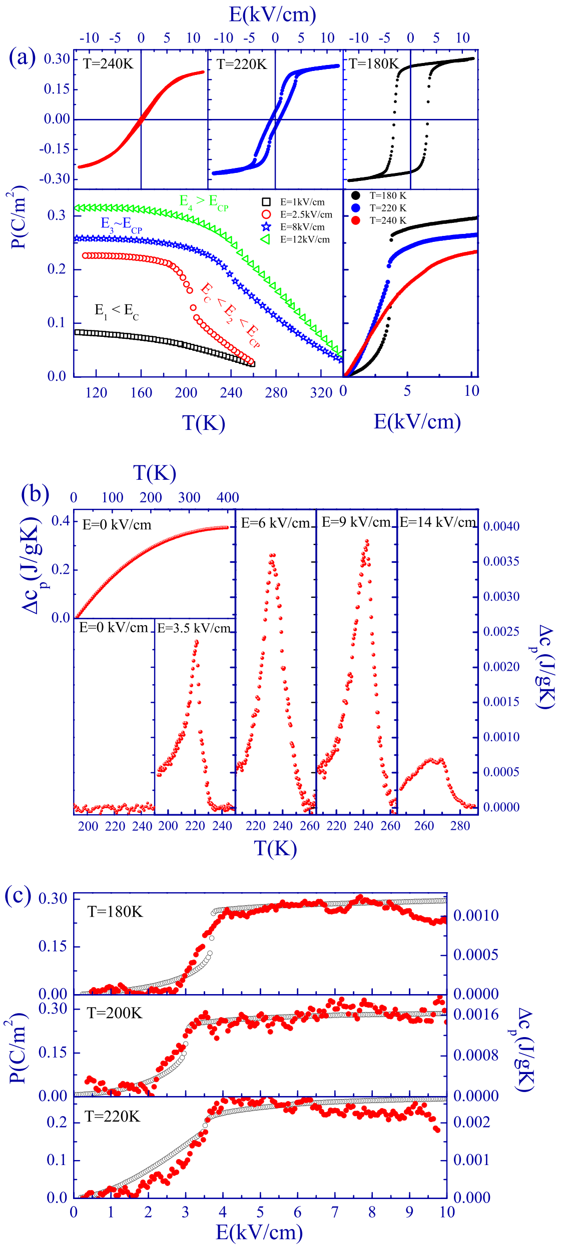

FIG. 2 (color online). Electric field and temperature evolution of the polarization and excess specific heat obtained in the single crystal PMN along the [110] axis. (a) Hysteresis loops obtained at different temperatures (see upper panels). Temperature evolution of the polarization is shown in the bottom left panel. Discontinuous change of the polarization in isothermal experiments is presented for several temperatures in the bottom right panel. (b) Temperature dependence of the excess specific heat data obtained in the ac mode at various constant bias electric fields. (c) Discontinuous steps in the polarization (open circles) and specific heat (solid circles) are observed when isothermally crossing the ferroelectric conversion line.

indicates the existence of a liquid-vapor type critical point [13,26–28] which appears at E_{CP}. Although the discontinuity observed in the polarization temperature profile may suggest a behavior typical for a first order phase transition as expected for the glass-to-ferroelectric phase transition, one should also consider a possibility that such a sharp increase of polarization could be the result of rather rapid domain switching around a very sharply defined coercive field. In this case, discontinuous steps would not represent the actual ferroelectric phase transition but merely the collective switching of already established randomly frozen ferroelectric domains according to the RF picture [7,17,18]. Despite the very indicative critical behavior of the polarization, which favors a glassy scenario, it is obvious that the polarization studies alone cannot provide a definitive answer about the ground state of relaxors.

In order to detect the enthalpy changes the ac and relaxation measurements of the heat capacity (C_p) were conducted. The temperature and the electric field dependence of the excess heat capacity (ΔC_p) obtained from the ac measurements in the PMN [110] single crystal are displayed in Figs. 2(b) and 2(c), respectively. The temperature evolution of C_p at various bias electric fields clearly shows an excess heat capacity only if $E \geq E_C$ [see Fig. 2(b)]. At a much higher electric field, $E = 14$ kV/cm, the C_p anomaly is suppressed indicating supercritical behavior. The obtained behavior of the excess heat capacity is similar to that observed at the cubic to tetragonal (C-T) phase transition in PMN-PT [26]. The isofield excess heat capacity anomalies therefore represent direct evidence of a long-range ferroelectric state formation when crossing the long-range ferroelectric transition line [solid lines in Fig. 1(b)]. Additional proof that the excess heat capacity is truly connected with the established ferroelectric order is provided by the isothermal heat capacity measurements in which C_p is measured as a function of the electric field at constant temperature [see Fig. 2(c)]. The overlapping discontinuous steps in the polarization and excess ac heat capacity presented in Fig. 2(c) indicate that the observed sharp steps in the polarization are indeed the consequence of a first order ferroelectric transition. Thus one may expect that latent heat will be observed when crossing the ferroelectric transition line, which in the case of isothermal experiments, presented in Fig. 2(c), will result in a sharp sudden heating of the sample and vice versa if the field is reduced. From measurements of such a sharp electrocaloric increase (decrease) of the sample temperature it is possible to estimate the released (absorbed) latent heat.

In order to prove the existence of the latent heat, a modified relaxation calorimetry, which is sensitive to released latent heat at the phase transition, was utilized. The variation of the sample temperature with increasing electric field is presented in Fig. 3(a). At $E = E_C$, an extremely sharp increase of the sample temperature ΔT_s exceeding 0.2 K at lower temperatures is clearly visible. The released latent heat is subsequently dissipated into the surrounding bath resulting in an exponential decay of the sample temperature back to the initial bath temperature [see Fig. 3(a)].

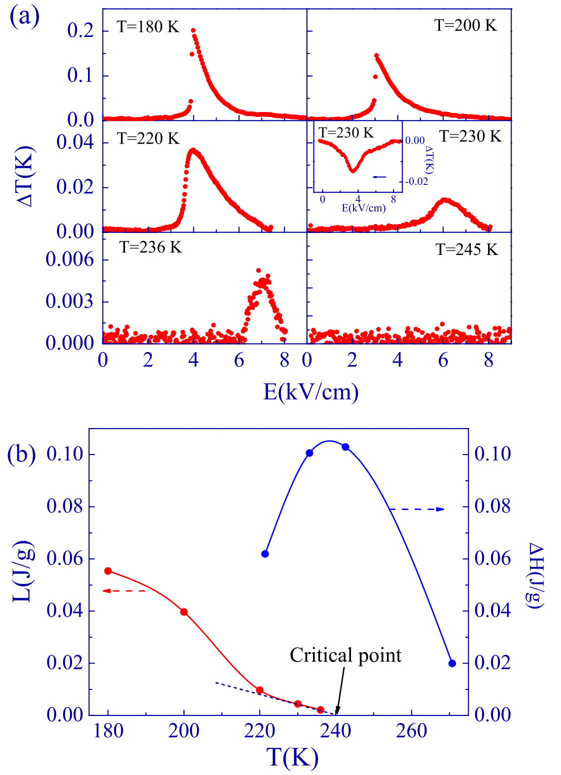

FIG. 3 (color online). (a) Change of the sample temperature for the PMN [110] single crystal as a consequence of the released latent heat at the field induced ferroelectric transition measured at several constant bath temperatures. The inset at 230 K shows the change of sample temperature under electric field reversal. (b) Released latent heat and total enthalpy change at the ferroelectric conversion as determined by high resolution calorimetry.

The inverse cooling effect was clearly observed in the field reversed cycle [see the inset in Fig. 3(a)]; however, some hysteresis exists in the position of the inverse cooling effect, in agreement with polarization hysteresis loops. The origin of this hysteresis is partially related to the first order transition and partially to the glassy dynamics as discussed in Ref. [13]. With increasing bath temperature the magnitude of ΔT_s gradually decreases with increasing E_C, indicating that the latent heat decreases and finally vanishes at the critical point [26,27,33]. In a first approximation $\Delta T(t)$ can be fitted by the simple exponential decay ansatz $\Delta T(t) = \Delta T_s \exp(-t/\tau)$. Here, $\tau = RC_p$ [30] is the external thermal time scale, which is separately determined from the relaxation calorimetric experiment. From such experiments, ΔT_s and thus the latent heat $L = c_p \Delta T(0)$ can be determined within a few percent accuracy.

The temperature dependence of the estimated released latent heat and the total enthalpy change at the ferroelectric transition for PMN [110] is shown in Fig. 3(b). The presence of latent heat at the ferroelectric transition demonstrates the existence of a first order transition line separating the glassy from the ferroelectric state. The latent heat vanishes at $T_{CP} \cong 240$ K and $E_{CP} \cong 8$ kV/cm, which corresponds to an isolated critical point. For fields above E_{CP} the broadened evolution of the polarization and C_p indicates the supercritical regime. The value of the total enthalpy change at the glassy to ferroelectric transition reaches a maximum in the vicinity of the critical point. It should be stressed that our results also exclude any ferroelectric ordering which would take place in zero field below 400 K, because no specific heat or enthalpy anomalies as well as no latent heat were observed in the zero-field experiments between 4 and 400 K [see the lower left panel on Fig. 2(b)].

In summary, the nature of the ferroelectric transition line in the PMN single crystal oriented in the [110] direction has been investigated by high-resolution heat capacity and polarization measurements. Discontinuous steps in the temperature and electric field evolution of the polarization and the heat capacity, the presence of latent heat, as well as the temperature evolution and the magnitude of the latent heat and enthalpy confirm the existence of a real phase transition line $E_C(T)$ between the zero-field ground state and the ferroelectric long-range order state stabilized by the applied electric field. The line of first order ferroelectric transitions terminates at a critical point of the liquid-vapor type, above which the system becomes supercritical. These findings strongly support the physical picture of a dipolar glass for the canonical relaxor ferroelectric PMN, in agreement with recent thermal conductivity data [34].

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