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Heat Capacity of PMN near an Electric-Field-Induced Phase Transition

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The heat capacity of a single crystal of $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) in an electric filed with $E = 3$ kV/cm applied along the [111] direction has been measured using adiabatic calorimetry over the temperature range 170–250 K. Anomalies in C_p have been found, which correspond to a field-induced phase transition from a relaxor to a ferroelectric state at 225 K under field cooling conditions or at 235–240 K on the subsequent field heating. The field-induced ferroelectric phase persists in a metastable state at low temperatures and is destroyed on zero-field heating at 210 K. The small entropy change $\Delta S \approx 0.028$R in the field-induced phase transition suggests an insignificant change in the volume fraction of existing polar nanoregions.

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Relaxor ferroelectrics have attracted considerable interest over many years because of their special dielectric and piezoelectric properties and the possibility of using them in various technological devices.

As a result of studies performed using dielectric, structural, spectroscopic, and other techniques, it was found that the main peculiarities of relaxors are related to the compositional and structural heterogeneity of these materials and the occurrence of interacting polar nanoregions in a nonpolar matrix. The possible mechanisms of the appearance of this heterogeneity and mechanisms responsible for the formation of polar nanoregions have been intensively discussed in the literature. It is likely that these mechanisms are different in different groups of relaxor ferroelectrics.

The studies of the structure and physical properties of relaxors revealed the following three critical temperature points: T_d, T_m, and T_c. Polar domains appear on cooling below the Burns temperature T_d. The interaction of these domains can result in an inhibition of dynamic fluctuations, a permittivity maximum at T_m, and the formation of an isotropic relaxor state with the random orientation of polar nanoregions. As the temperature is further decreased, a polar phase with macroscopic polarization is formed in relaxors below $T_c \le T_m$.

$Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) is often considered a model relaxor ferroelectric. At high temperatures, it consists of nanoregions rich in Nb and regions with a 1 : 1 ratio between Nb and Mg. On cooling below the Burns temperature $T_d \approx 650$ K, polar distortions occurred in the Nb-rich regions and a paraelectric cubic phase of PMN transformed to the relaxor phase, which remained macroscopically cubic but was locally disordered. A frequency-dependent diffuse maximum of permittivity was observed in a crystal at $T_m \approx 260$ K; it was of relaxation nature rather than related to structural changes.

A polar long-range order in PMN did not appear down to 0 K. However, on cooling in electric fields with strengths higher than a critical value of $E_C \approx 1.7$ kV/cm, a ferroelectric phase with $R3m$ symmetry was formed in PMN. Arndt et al. [1] observed a field-induced phase transition in the x-ray studies of PMN. More recently, the structure, dielectric properties, polarization, and pyrocurrent in an electric field were studied and several versions of the E–T phase diagram were proposed [2–6]. The positions of phase boundaries and the properties of PMN in different regions of the diagram essentially depended on not only the field strength but also on the field application conditions [5].

Further acquisition of information on processes occurring in relaxors under various conditions of temperature and field changes would facilitate a more adequate understanding of the nature of relaxation phenomena in ferroelectrics. The aim of this study was to observe an anomalous heat capacity behavior and to determine the thermodynamic parameters of PMN in a field-induced phase transition to a ferroelectric state.

A parallel-sided sample 1 mm in thickness, which was cut from a single crystal of PMN perpendicularly to the [111] direction, was prepared for the studies. The surfaces with an area of ~1×1 cm^2 were covered with copper electrodes, which were deposited by vacuum sputtering. Thin wires were glued to the electrodes with

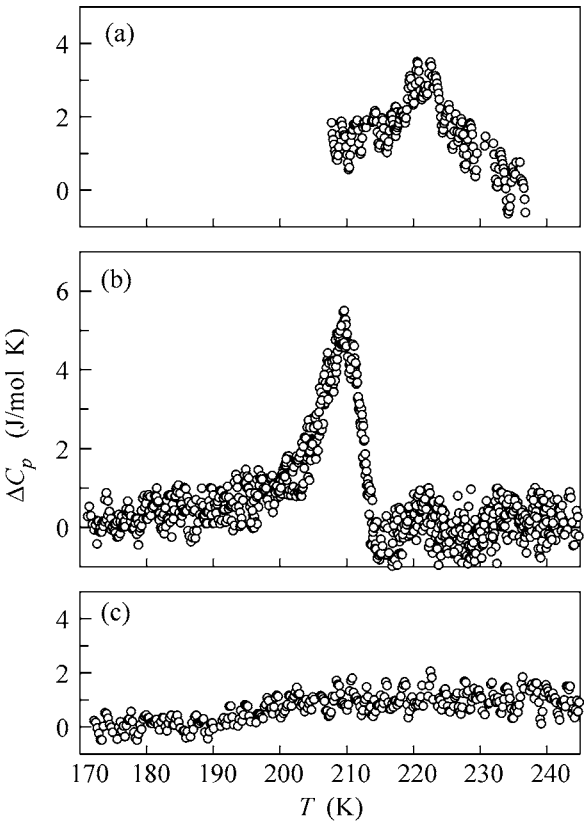

Fig. 1. Temperature dependence of anomalous heat capacity in the (a) field cooling process, (b) zero-field heating process after field cooling process, and (c) field heating process after field cooling process.

a silver paste, and a high voltage was applied from a stabilized power supply unit.

Heat capacity measurements were performed on an adiabatic calorimeter using both a standard discrete heating method with the temperature step ΔT = 1.0–2.5 K and a continuous heating method at the heating rates $dT/dt \approx$ (0.07–0.15) K/min. The measurement error depended on the method used and varied over the range 0.1–0.3%.

Because it is well known that the properties of relaxors strongly depend on the thermal history, the sample of PMN was annealed at 300 K before each series of measurements. After annealing, the sample was cooled to 100–150 K under conditions of either zero-field cooling (ZFC) or field cooling (FC) at E = 3.0 kV/cm. The heat capacity measurements on heating were performed both under conditions of zero-field heating after field cooling (ZFHaFC) and in a constant field (FHaFC) at E = 2.5–3.0 kV/cm.

Previously [7, 8], the heat capacity of PMN in a zero field was studied over a wide temperature range. Therefore, in this work, we restricted the measurements to only a narrow temperature range of 170–250 K. According to Ye and coauthors [5, 6], a field-induced phase transition occurred in this temperature range. As

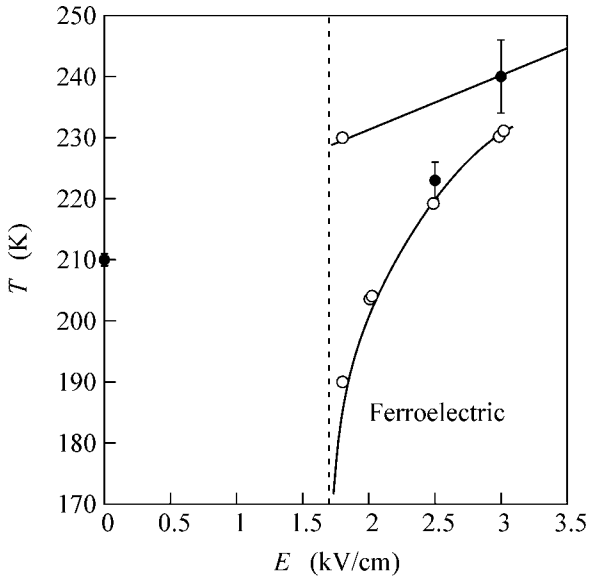

Fig. 2. Experimental phase diagram of PMN based on dielectric [5], (○) x-ray [6], and (●) calorimetric data.

expected, heat capacity anomalies were not detected in zero-field measurements over the specified temperature range. Field cooling at 2.5 kV/cm resulted in the appearance of a C_p anomaly at T_{FC} = 223 K. This result is consistent with the detection of a sharp increase in polarization under these conditions [5], and it provides support for the formation of a new ferroelectric phase below T_{FC}. An anomalous heat-capacity component, which was determined as the difference between heat capacities measured at $E = 0$ and $E \neq 0$ was 3 J mol^{-1} K^{-1} (Fig. 1a).

A field-induced phase, being formed on cooling below T_{FC}, occurred at low temperatures and persisted in a frozen metastable state with the field off. On zero-field heating, a transition to a stable nonpolar state and the corresponding heat capacity anomaly were observed at T_{ZFHaFC} = 210 K (Fig. 1b). In this case, the anomalous heat-capacity component ΔC_p was as high as ~6 J mol^{-1} K^{-1} or ~5% of the lattice heat-capacity component. A sharp decrease in polarization [5] and a narrow peak of ΔC_p are indicative of a first-order phase transition.

The polar state induced on cooling degraded under conditions of field heating at E = 3 kV/cm at $T_{FHaFC} \approx$ 230–240 K. The heat-capacity anomaly ΔC_p was diffused over a wide temperature range, and it reached a value of ~1 J mol^{-1} K^{-1} (Fig. 1c). The character of the heat-capacity anomaly and the polarization behavior [5] allowed us to conclude that, in this case, the transition was a second-order phase transition.

Figure 2 shows the found phase-transition temperatures and the data of dielectric [5] and structure [6] studies.

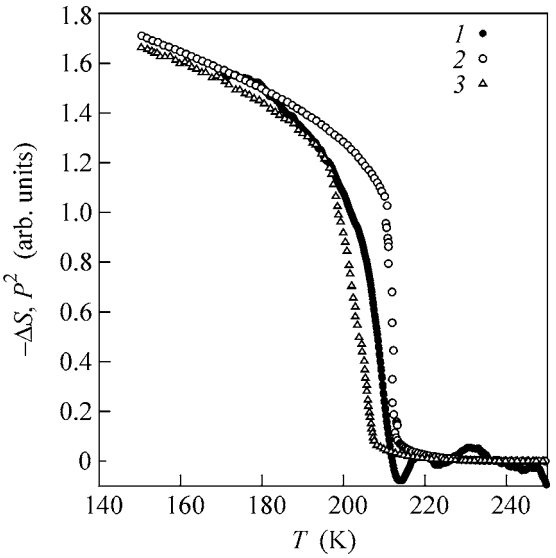

Fig. 3. Comparison between (*1*) the temperature dependence of entropy change and (*2*, *3*) that of polarization (*2* and *3* refer to data published by Sommer et al. [3] and Ye and Schmid [5], respectively).

Under all of the field application and removal conditions, the entropy change due to the anomalous behavior of the heat capacity was as low as $\Delta S \approx 0.028R$. In the zero-field measurement of the heat capacity of the PMN [7] over the wide temperature range 100–750 K, an anomalous behavior of $C_p(T)$ was found at the Burns temperature $T_d \approx 650$ K, at which polar distortions occurred in niobium-rich regions, and at the permittivity maximum temperature $T_m \approx 280$–300 K. The considerable entropy change $\Delta S \approx 1R$ due to the anomalous behavior of ΔC_p at T_d and T_m suggests that order–disorder processes play an important role in the formation of polar nanoregions. Taking into account the results of structure studies and the fact that polarization (and the displacement of lead ions in the intraoctahedral cavities of the perovskite lattice) can have eight equiprobable directions such as [111], the entropy change $\Delta = R\ln 8$ would be expected on the complete ordering of the entire crystal. The experimental entropy is only 35–40% of the above value, and it is consistent with the volume fraction of the polar nanoregions, which was determined from an analysis of structure data [9].

The very low entropy change in the field-induced phase transition to a ferroelectric phase is indicative of an insignificant change of the volume fraction of polar nanoregions.

We compared the temperature dependence of the entropy change ΔS, which was determined in this work from an anomalous heat capacity component, and the temperature dependence of polarization P, which was calculated previously [3, 5] based on pyrocurrent measurements under ZFHaFC conditions. As can be seen in Fig. 3, where both entropy and polarization are given in arbitrary units, $\Delta S \sim P^2$.

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