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Quasivertical line in the phase diagram of single crystals of $PbMg_{1/3}Nb_{2/3}O_3$-$xPbTiO_3$ ($x=0.00$, 0.06, 0.13, and 0.24) with a giant piezoelectric effect

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We show that the phase diagram of the (001) $PbMg_{1/3}Nb_{2/3}O_3$-$xPbTiO_3$ (PMN-xPT) ($x=0.00$, 0.06, 0.13, and 0.24) and (111) PMN-0.24PT lead-magnesium niobate mixed with lead titanate possesses a quasivertical line in the E electric field – T temperature plot, which hardly depends on the field. The existence of this line has been confirmed by independent studies of single crystals grown in different laboratories, by measuring the dielectric permittivity, compliances, and optical transmission, also in different laboratories. A thermal hysteresis inherent to first order phase transitions complicates the phase diagram. The piezoelectric coefficients of the (001) PMN-xPT ($x = 0.06$ and 0.13) have two peaks versus temperature, at finite fields. The first peak is due to the quasivertical phase boundary. The second is in the vicinity of a turning point of the $T_m(E)$ temperature of the dielectric permittivity diffuse maximum. We show that the second peak prevails at reasonable fields, and the piezoelectric coefficients have comparatively large values at this peak, even at small x.

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The $PbMg_{1/3}Nb_{2/3}O_3$-$xPbTiO_3$ ($x=0.00, 0.06, 0.13$, and 0.24) (PMN-xPT) disordered relaxor lead magnesium niobate doped with ferroelectric lead titanate (x is the concentration) attracts much attention because of a remarkable piezoelectric property that has extremely wide applications nowadays.[1–3] The understanding of the piezoelectric properties is important for both the fundamental physics and applications. A real breakthrough was achieved by showing (on the basis of first-principles computations) that the strong piezoelectricity property of this solid solution is connected with "the polarization rotation,"[4] which results in the appearance of a large strain under the field, when passing the boundary between the tetragonal and rhombohedral phases through the intermediate monoclinic phase.

Very recently a supplementary idea helped to understand the giant piezoeffect in PMN-xPT.[5] The measurements performed on single crystals at $x=0.295$ have shown that the piezoelectric coefficients were maximal not at zero field but rather at a finite field value corresponding to the saturation of the $T_0(E)$ dependence where T_0 is the temperature of the heat capacity maximum and E is the bias electric field (see Fig. 3 in Ref. 5). The behavior of the system was shown to be critical at this point as it happens at a critical end point or at a liquid-gas-like critical point (CP). The presence of the maximum of the piezoeffect versus E was explained by a critical behavior of the system near the CP.

However, earlier, it was found that, in the E-T phase diagram of an (111)-oriented PMN single crystal,[6,7] there is an intersection of the field heating after field cooling (FH) and field cooling (FC) lines. This fact was interpreted in Ref. 8 as the existence in this phase diagram of a liquid-gas-like CP, and the FC and FH lines were interpreted as the boundaries of the stability of the macroscopic relaxor and ferroelectric states (or, equally, as the boundaries of the coexistence of the relaxor and ferroelectric phases). In contrast to this, limited measurements on (001) PMN-xPT ($0.06 \leq x \leq 0.13$) single crystals[8] showed that the FC line did not intersect the FH line, in these crystals, at all. Rather, a quasivertical portion appeared on the FC line at high enough E.

In order to highlight the problem, we show in Fig. 1(a) combined data obtained for PMN-0.295PT.[5] The open circles show the $T_0(E)$ position of the heat capacity maxima obtained on FH. The filled circles mark the position of the $T_m(E)$ dielectric permittivity maxima. Though the $T_m(E)$

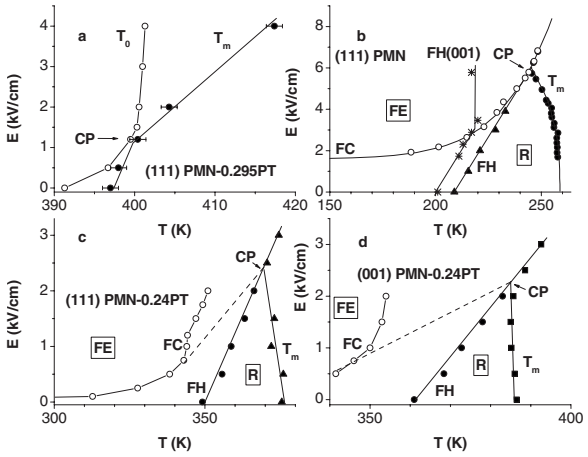

FIG. 1. *E-T* phase diagrams for PMN-*x*PT crystals constructed from the data on the dielectric permittivity (a)–(d) and heat capacity (a) studies. The lines are guides for the eye. FE: ferroelectric phase and R: relaxor phase. The panels show the data obtained for (a) (111) PMN-0.295PT (Ref. 5). Open and solid symbols correspond to T_o the maximum of heat capacity and T_m the dielectric permittivity maximum, respectively. (b) (111) PMN. The asterisks mark the FH line for (001) PMN. For this line, the actual field values were reduced $\sqrt{3}$ times in order to have the projection to a [111] direction. (c) (111) PMN-0.24PT. (d) (001) PMN-0.24PT. In all panels, the points corresponding to $E=0$ on the FH lines were obtained after FC under the field strong enough to induce the ferroelectric phase. All other points in the FH lines were obtained after cooling the samples subject to the same electric fields as were applied, then, on heating.

lines do not correspond to any phase transition boundary, their position is helpful in locating the position of the CP. Indeed, it has been shown[8] that, in PMN-*x*PT, $T_m(E)$ has a turning point close to a CP. The data presented in Fig. 1(a), show that $T_m(E)$ in PMN-0.295PT also has a turning point, which is close to the CP. At the same time, the CP is close to the vertical portion of $T_0(E)$. These data do not allow one to decide if the vertical portion of $T_0(E)$ is important to maximize the piezoelectric properties.

To clarify this situation, we did further experiments and expanded our analysis to another concentration region of the PT component compared to the one, which has been studied hitherto. The present study has the goal to establish the presence and position of the quasivertical line in the *E-T* phase diagram of PMN-*x*PT single crystals with differing orientations and compositions by using not only dielectric spectroscopy but also elastic compliances and optical transmission. We also perform a principal critical experiment on PMN-*x*PT, which helps to decide whether the piezoelectric coefficients have the maximal values at the quasivertical line. This experiment is important not only for the fundamental understanding of the superb piezoelectric properties of PMN-*x*PT but also for further advanced improvements of the effectiveness of the piezoelectric devices.

In the present study, we use two sets of single crystals of PMN-*x*PT having two different orientations, (001) and (111). The first set involves the (001) oriented single crystals of PMN-0.13PT, PMN-0.06PT, and (111) oriented PMN, which are transparent plates cut from the flux grown crystals prepared at the Physics Research Institute of the Rostov State University.[9] The second set comprises the (001) and (111) oriented PMN-0.24PT single crystals grown by a modified Bridgman method at the Shanghai Institute of Ceramics.[10] The dielectric measurements were performed in the same manner as in Refs. 8 and 10. We study the piezoelectric response under a *dc* bias by the common resonance-antiresonance technique, by using (001)-oriented bars of single crystal PMN-*x*PT with the dimensions of approximately $5\times2\times1$ mm^3 and electroded with sputtered Pt or Al. In these measurements, the samples, previously annealed at $T>T_m$, where T_m is the temperature of the dielectric permittivity peak, were cooled in a zero field to a certain fixed temperature, and a dc bias field was applied in steps of about 0.5–0.8 kV/cm up to the maximal value of 4–8 kV/cm. We measure the resonance f_R and antiresonance f_A frequencies at each field value and at a fixed temperature. After switching the field off, both the f_R and f_A were measured under zero bias at the same temperature. Then, we annealed the samples at $T>T_m$ for 15–20 min in order to erase the polarization memory effect, and we cooled the samples down to another fixed measuring temperature after this annealing. The optical transmission measurements were carried out by using a He-Ne laser ($\lambda=632.8$ nm) in the course of cooling at a rate of 1.5 to 4.5 K/min. We applied a dc bias electric field in the [100] direction, and the light propagated along [001]. After each application of the field and before the subsequent measurement cycle, we annealed the samples for 10–15 min at a temperature exceeding T_m by approximately 100 K.

The phase boundaries in the *E-T* phase diagrams shown in Figs. 1 and 2 were determined by finding the positions of the steps (for the (001) oriented crystals [Fig. 2(a)]) or additional maxima [for the (111) oriented crystals] in the dependence of the dielectric permittivity (both the real and imaginary parts), compliances, and optical transmission. We took into account a possibility of slightly diffused first order phase transitions, and we treated the experimental data (e.g., by using the derivatives) so to localize the shoulders on the permittivity-temperature curves for $E>1$ kV/cm more precisely. One should bear in mind that the position of the lines in the *E-T* phase diagrams is only tentative. It was shown recently that, e.g., the position of the FC line depends on the cooling rate, especially at low fields.[11] The dielectric permittivity and optical transmission data used for drawing the *E-T* phase diagrams have been published already elsewhere.[8,10,12] This is why we do not repeat these data here.

Figure 1(b) shows the *E-T* phase diagram of a (111)-oriented PMN single crystal. One can see that the FC line intersects (and converges with) the FH line, and T_m has an inflection point, in the same region. Actually, this part of the phase diagram looks like a textbook example of a *E-T* phase diagram in crystals possessing a first order phase transition.[13] The convergence of the FC and FH lines occurs, in this theory, in the CP. The dielectric permittivity diverges at this point, but the phase transition is first order in all other points of the FH and FC lines. Notice that the dielectric anomaly around the CP is rounded in relaxors because of the random fields, which are at the heart of their properties.[14]

In the same figure, we added the FH line for a (001)-

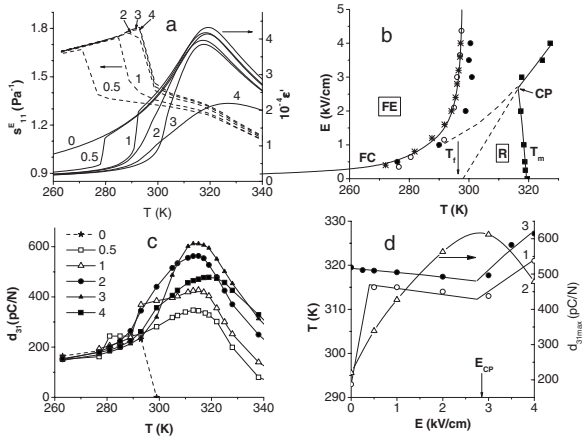

FIG. 2. (a),(c) Temperature dependences of the real part of the dielectric permittivity measured at 1 kHz in the FC mode [panel (a), solid lines], elastic compliance constant [panel (a), dashed lines], and piezoelectric constant d_{31} [panel (c)] for (100) PMN-0.13PT crystal at different E values. Numbers correspond to the E values, in kV/cm. (b) E-T phase diagram for (001) PMN-0.13PT single crystal constructed using the data of the dielectric permittivity (solid symbols), optical transmission (open symbols) and elastic compliance (asterisks). The lines are guides for the eye. FE: ferroelectric phase and R: relaxor phase. (d) Field dependences of (1) the d_{31} maximum temperature, (2) the d_{31} maximum value, and (3) the permittivity maximum temperature.

oriented PMN single crystal obtained in the Laboratoire Structures, Proprietes et Modelisation des Solides, Ecole Centrale Paris. For this line, the field values were reduced $\sqrt{3}$ times in order to have the projection to a [111] direction. While at low E's both FH lines [obtained for the (111) and (001) oriented single crystals] look very similar, a vertical portion appears for the (001)-oriented crystal at temperatures exceeding the Vogel-Fulcher temperature by approximately 20 K. These results are in line with recent data on (001)-oriented PMN (Ref. 15), where only three E values were used.

Figure 1(c) presents the E-T phase diagram obtained for an (111) oriented single crystal of PMN-0.24PT. Here $T_m(E)$ has a turning point manifesting a possibility of the presence of a CP in the vicinity of this turn.[8] However, in contrast to the phase diagram of the (111)-oriented PMN, the FC line does not intersect the FH line in the studied area of the phase diagram. Instead, a quasivertical portion appears in the FC line at a temperature, which is lower than the position of the turning point in the $T_m(E)$ dependence (and which is close to the T_f Vogel-Fulcher temperature). We have also performed measurements for an (001) oriented PMN-0.24PT single crystal, and we obtained very similar results [Fig. 1(d)].

The position and even existence of the CP is not that clear in the considered case of PMN-0.24PT and in contrast to the case of the (111)-oriented PMN single crystal. In principle, the turning point in the $T_m(E)$ line can have an origin similar to that described in the Dorogovtsev model, which considers second order phase transitions complicated by random fields and which does not assume the presence of a CP in the phase diagram.[16] However, we add to the figure dashed lines marking the phase boundaries, which are supposed to be in the phase diagram in the standard case of first order phase transitions. Notice that the corresponding anomalies are not seen in our experiment on cooling but the heating run does show the expected behavior (the FH line is shown in bold). It is possible that modest anomalies corresponding to the dashed lines are masked by much larger anomalies corresponding to the nearly vertical phase boundary, from one side, and a huge diffuse permittivity maximum, from the other side. Alternatively, the quasivertical line can finish at some finite field and then the FC line can change its behavior and can connect the highest point of the quasivertical line and CP. The study of the shape of the hysteretic loops obtained at low-frequency ac fields[9] revealed the presence of a phase boundary connecting the highest point of a quasivertical portion with a zero-field point at a higher (with respect to T_f) temperature. Checking of this assumption needs further studies using much higher fields than those employed in the present investigation. Notice that the existence of the CP as well as the first order phase transition scenario were not considered in Ref. 9. Rather an Almeida-Thouless like scenario was assumed.

Figure 2(b) shows the E-T phase diagram of PMN-0.13PT obtained on the basis of different experiments (specifically, from dielectric spectroscopy, compliances, and optical transmission). The field induced phase transition is manifested by an abrupt decrease of the optical transmission due to the light scattering on the large-scale net of domains of the appearing ferroelectric phase.[12] A small shift between the curves obtained from these experiments can be well understood as they were obtained for different samples having different geometry. All data in the present study support the existence of the quasivertical line in the E-T phase diagram for both (001)- and (111)-oriented PMN-xPT crystals [excluding the (111) samples of pure PMN], and this line is separated from the CP by some temperature interval. The dashed lines on the E-T diagram [Fig. 2(b)] show a supposed behavior of the FC and FH lines in the case of the standard theory of first order phase transitions (the FH run has not been performed for this sample). The lines, which were determined experimentally, are in bold. The $T_m(E)$ dependence has a turning point at about 3 kV/cm and 315 K, which can manifest the position of the CP. Notice that not only $T_m(E)$ has a turning point. The FC line also has a point, which can be called turning, at the intersection of the quasivertical and nearly vertical portions of the FC line. One might think that this turning point manifests the existence of a CP, on cooling. However, the compliance exhibits abrupt changes in the vicinity of the FC vertical line, at low and even at high fields [Fig. 2(a)], implying that this line has nothing to do with the CP. In contrast to this, dielectric permittivity does not show any jumps at the turning point of the $T_m(E)$ dependence that supports the idea about the existence of a CP in close vicinity of the turn of the $T_m(E)$ dependence.

In the majority of the samples studied, the position of the quasivertical portion in the FC line is close to the T_f Vogel-Fulcher temperature. Only in pure (001) PMN, we found the position of the quasivertical line slightly (about 20 K) above the Vogel-Fulcher temperature while, in the PMN-0.06PT and PMN-0.13PT, this vertical portion practically coincides with T_f. It is common to say that the properties of the PMN-

*x*PT solid solutions are different above and below this temperature. For example, at this temperature, the depolarization of the poled samples takes place on heating, in zero field. Also, the dynamics of the polar nanoregions is believed to freeze on cooling as seen from the frequency dependence of dielectric permittivity. The polarization hysteresis loops change at this boundary dramatically.[9] One can add to this list the fact that the soft mode rejenuvates on cooling, at this temperature.[17] Neutron scattering[18] also shows a strong increase of the polar size region, at $T=T_f$. Very limited data show that this temperature does not practically change under the field.[19]

The temperature interval between the quasivertical line and the possible position of CP [the turning point in the $T_m(E)$ dependence] strongly increases when x decreases.[8] This fact suggests that one should perform the measurements of dielectric and piezoelectric properties for comparatively small x. We have carried out the measurements of the dielectric permittivity, elastic compliances, piezoelectric coefficients, and optical transmission for PMN-0.13PT and PMN-0.06PT. Figure 2(b) shows the *E-T* phase diagram of PMN-0.13PT obtained by us on cooling. One can see that the quasivertical line does exist at this concentration, and it is distant from the electric CP by a substantial temperature interval. This fact provides a good chance to distinguish between the possible maxima in the piezoelectric coefficients at the vertical line and critical point under the field. We found that the temperature interval between these two anomalies is even larger for $x=0.06$ and in pure (001) PMN.

Figure 2(c) shows the temperature dependence of the d_{31} piezoelectric coefficient for PMN-0.13PT measured by us at different bias field magnitudes. At zero field, the piezoelectric coefficient has the maximum at the position of the vertical line but, at even small but finite bias fields, this maximum shifts to the position of the supposed CP and grows in magnitude. The latter increases up to the fields corresponding to the CP in the *E-T* phase diagram [Fig. 2(b)] and decreases at higher fields [Fig. 2(d)]. These data support the presence of a CP at the end point of the FH line, as well as a quasicritical behavior at this point (in fact, the random fields smear the phase transition). These data are also in line with the conclusion that the intersection of the quasivertical line with the relaxor-ferroelectric phase boundary does not correspond to a continuous phase transition.[8] Instead, we found that the dielectric permittivity and compliance experience a jump at this point [see, e.g., Fig. 2(a)] that is inherent to first order phase transitions. In contrast to this, the temperature dependence of the dielectric permittivity becomes narrower and larger (or at least the same as in low fields) being closer to the CP. When the bias field exceeds some threshold value roughly corresponding to the $T_m(E)$ turning point, the $\varepsilon(T)$ peak decreases in magnitude and diffuses. This is in line with the fact that, above CP, the relaxor phase no longer differs from the ferroelectric phase, and the diffuse maximum of the dielectric permittivity no longer corresponds to any phase transitions. Notice, that at these fields, this maximum is hardly frequency dependent, and T_m increases with the field as is inherent to ferroelectrics possessing a first order phase transition, above a CP.[8] We have obtained similar qualitative results also for $x=0.06$ (not shown here). The CP for this composition seems to be located approximately at 6 kV/cm and 290 K.

It is worth noting that a dramatic enhancement of the piezoelectric response under finite bias fields in the vicinity of T_m has been also experimentally observed earlier in PMN-*x*PT ceramics.[20] In this study, the authors obtained d_{33} values, which greatly exceeded the earlier obtained piezoelectric coefficients in piezoelectric ceramics, and they were comparable with the values obtained later on single crystals. Our data explain this fact and hint how to further improve the giant piezoelectric properties of the PMN-*x*PT ceramics and single crystals. Specifically, one can use biasing fields driving the system towards the (CP) point, at which the FH line converges (or has the shortest distance) to the $T_m(E)$ line. This crucially enhances the piezoelectric response of the PMN-*x*PT crystals and ceramics with the compositions below the morphotropic phase boundary range and substantially increases the working temperature limit of the piezoelectric devices employing the PMN-*x*PT ceramics or crystals. One can expect improving not only the piezoelectric properties at the CP but also other properties requiring large values of the dielectric permittivity together with extremely small thermal hysteresis. In particular, one can expect a dramatic enhancement of the pyroelectric and electrocaloric (if the fields are not too strong) effects.

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