Temperature characteristics and development of field-induced phase transition in relaxor ferroelectric $Pb(Mg_{1/3}Nb_{2/3})_{0.87}Ti_{0.13}O_3$ ceramics

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Ferroelectric phase inducing threshold electric field E_{th} and its temperature dependence were determined in relaxor ferroelectric $0.87Pb(Mg_{1/3}Nb_{2/3})O_3-0.13PbTiO_3$ (PMN–13PT) ceramics by measuring dielectric response on a dc field pulse. Evolution of the induced ferroelectricity was observed by means of polarization measurements. An inducing threshold field was found to have a minimum of $E_{th,min}=1.55$ kV/cm at $T=-5$ °C. In contrast to pure PMN, which shows a minimum threshold field near the depolarization temperature, the temperature of the minimum threshold field differs by an amount of $\Delta T=23$ °C from the depolarization temperature $T_{dp}=18$ °C in PMN-13PT. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2993345]

In prototype relaxor ferroelectrics $Pb(Mg_{1/3}Nb_{2/3}O)_3$ (PMN), a ferroelectric long-range order can be made stable by adding pure ferroelectric $PbTiO_3$ (PT) to form a solid solution of $Pb(Mg_{1/3}Nb_{2/3})_{1-x}Ti_xO_3$ (PMN–xPT)[1] and by applying a dc electric field.[2,3] The structure of PMN exhibits average cubic symmetry down to very low temperatures.[4,5] On the other hand, a nanometer scale of 1:1 ordering of Mg^{2+} and Nb^{5+} cations leads to formation of polar nanoregions.[6] An increase in PT content gradually increases the degree of polar nanoregion evolution, thus favoring the development of a long-range polar order due to a reduced tendency of 1:1 ordering.[1] Eventually this leads to long-range dipolar correlation of the polar regions and onset of a ferroelectric rhombohedral phase. According to recent studies, however, ferroelectric distortion in low-temperature PMN–xPT ($x\leq 0.2$) appears to be limited to a short range in the bulk of a crystal with average cubic symmetry, and the polar regions of rhombohedral symmetry are present in a near-surface outer crystal.[7–9] This structural complexity makes it difficult to draw exact boundaries between adjacent phases, and it is believed to be a reason for the discovered contradiction in the PMN–PT structure.[9] Furthermore, the low-temperature ferroelectric structure develops into a tetragonal phase through intermediate monoclinic phases in the vicinity of the morphotropic phase boundary.[10,11] Thus, modification of PMN with PT enhances coupling of the polar nanoregions to the applied dc field and consequently decreases the threshold for field inducement.

The electric field-induced ferroelectric transition and its temperature dependence on relaxor ferroelectrics are influenced by the type of transition enforcement.[12–14] Mostly heating and cooling with a constant electric field have been used to determine E-T relations of both PMN[14,15] and PMN–PT.[10,16] Nevertheless, another approach with constant temperature and a variable electric field requires a different kind of study in which field-inducing behavior can be viewed separately at individual temperatures.

In this letter we study a field-induced ferroelectric transition in PMN–13PT ceramics. In particular, we examine the temperature dependence of the threshold field by measuring the dielectric response to a prepoling electric field at constant temperatures. Additionally, observations on the onset of the ferroelectric phase are made through polarization characteristics at a constant temperature.

Details of lead magnesium niobate–lead titanate ceramics preparation can be found elsewhere.[17] Dielectric measurements were performed with *LCR* meter (Agilent 4284A) in a computer controlled temperature chamber (ESPEC SU-261). A high-voltage poling pulse was provided by a function generator (Agilent 33120A) in combination with a voltage amplifier. The duration of the voltage pulse was 6.2 s. The same system with multimeter (Agilent 34411A) was used for polarization measurements at $f=0.1$ Hz. Prior to each measurement, the sample was heated to 128 °C in order to cancel out the effects of electric and thermal history.

Figure 1 shows the real part ε' of complex permittivity as a function of temperature for the studied composition at 21 Hz and 1 MHz. The specimen was prepoled at −48 °C before zero-field heating and measurement. General relaxor-type frequency dispersion can be seen as a large variation in ε' below the maximum permittivity temperature T_m, which

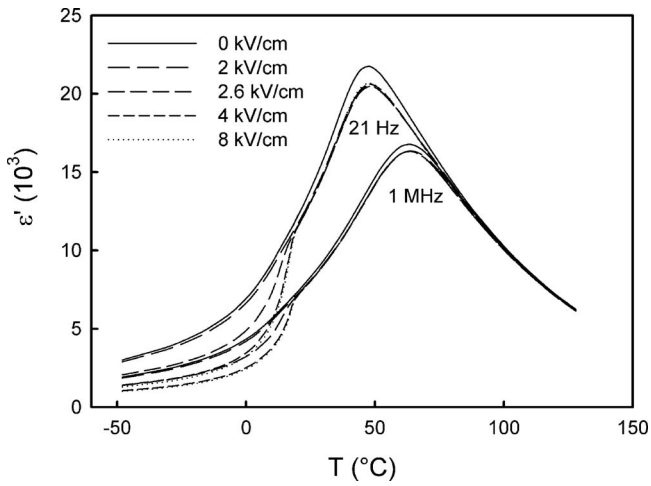

FIG. 1. Temperature dependence of the real part of the complex permittivity ε' for PMN–13PT ceramics after poling at −48 °C and subsequent zero-field heating.

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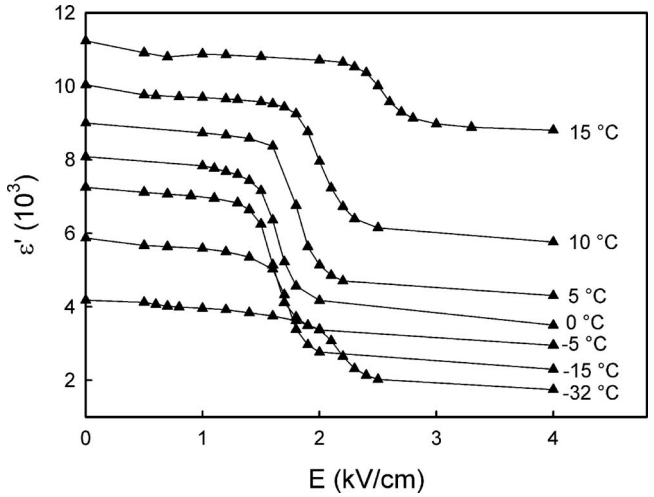

FIG. 2. Real part of complex permittivity ε' at 21 Hz as a function of the applied dc bias field at a number of different temperatures.

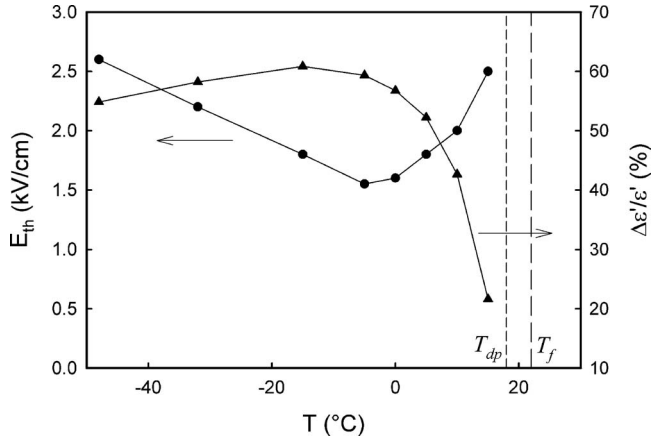

FIG. 3. Temperature characteristics of the inducing threshold field and relative reduction in the real part of permittivity ε'. Relative reduction in permittivity is calculated with fields of 0 and 4 kV/cm.

itself is also strongly dependent on frequency. Analysis of the zero-field frequency dispersion of T_m with the Vogel–Fulcher relationship gives a freezing temperature T_f=22 °C. Increasing the prepoling field results in a slight decrease in the real part of permittivity in the proximity of T_m. Further increasing the field to E=2.6 kV/cm induces an anomalous drop in ε' at low temperatures. This phenomenon can be attributed to a field-induced transition from relaxor to ferroelectric phase or a mixed state phase.[16] During the zero-field heating, the lowered permittivity increases to the value of the unpoled sample at T=18 °C, where a spontaneous phase transition to a high-temperature cubic structure occurs. This temperature equals the depolarization temperature T_{dp} derived from remanent polarization measurements[17] and it is located close to the freezing temperature as expected. Within the measurement range, the discovered transition temperature is independent of frequency and prepoling field strength.

Although it is known that a high enough PT content causes a spontaneous ferroelectric phase transition in PMN–PT relaxors, the exact amount is unclear, mainly due to the aforementioned structural complexity and differences in material preparation. In some studies,[18,19] indications of this spontaneous relaxor-to-ferroelectric transition have been found for PT inclusions as low as 10 mol %. However, dielectric measurements performed with zero-field heating and cooling did not reveal any additional distinctive transitions, and a clear discrepancy between T_m and T_{dp} is evident. Still, some partial transitions and rhombohedral distortions seem to be present, at least in the crystal skin layer,[8] and therefore they might influence the dielectric and field-inducement properties.

A more specific study on field inducement of the ferroelectric phase was carried out below T_{dp}. Dielectric measurements were employed at a constant temperature with an increasing prepoling field. The measured real part of the complex permittivity at f=21 Hz and as a function of the prepoling field at various temperatures is presented in Fig. 2. It can be clearly seen that ε' decreases rapidly above a certain electric field strength, like in Fig. 1. Above and below this threshold electric field E_{th}, ε' shows an almost constant value. When approaching the depolarization temperature, the height of the transition step decreases and is markedly lowered near T_{dp}.

Threshold field strengths and relative changes in permittivity at each measuring temperature, derived from Fig. 2 data, are shown in Fig. 3. Just below T_{dp}, the required electric field shows an exponential dependence on temperature, as found in a single crystal of the same composition by means of a field-cooling run.[16] However, E_{th}=1.55 kV/cm at T=−5 °C was discovered to be the minimum point, since the decline turned into an increase at lower temperatures. Similar U-shaped behavior has been observed previously for PLZT[12] and PMN.[13,14] Especially the results for pure PMN seem to coincide with an E-T phase diagram constructed on the basis of constant-field heating-cooling experiments.[20] The temperature of the minimum threshold field $E_{th,min}$ in the aforementioned articles is located near the freezing and depolarization temperatures, contrary to findings in the present work. While temperature T_{dp} converges toward T_m with increasing PT content and ferroelectric nature, the difference between the temperatures of $E_{th,min}$ and T_m seems to be invariant possibly due to similar dependence on PT concentration. At the same time, the relative reduction in ε' due to field inducement shows gentle growth at lower temperatures up to the temperature of $E_{th,min}$, while a rapid decrease is found above this temperature. This behavior is in line with the dependence shown in Fig. 1(a).

A clear development of the polar phase can be seen in Fig. 4, where remanent polarization P_r at T=0 °C is plotted. The inset of the figure shows that P_r in the ascending stage of the polarizing field cycle is larger below the threshold field and smaller above it when compared with the descending cycle. Increasing the electric field above E_{th} leads to damped growth in P_r when the slope of the polarization curve decreases due to a field-induced permittivity drop. A further increase in the applied field promotes the development of the polar phase and the remanent polarization saturates above 4 kV/cm. In the descending stage of the maximum polarization field, hysteresis and nonlinearity smear out like in typical ferroelectrics, and P_r decays to zero.

On the other hand, Fig. 5 shows the evolvement of P-E hysteresis loops at four different peak fields in the ascending (black curve) and descending (gray curve) stages of the polarizing field cycle with a maximum field of ±8 kV/cm. In Figs. 5(a) and 5(b), the maximum measuring field is lower than E_{th}=1.6 kV/cm, and the slope of the polarization curve is larger in the ascending stage. Apparently, polar ordering

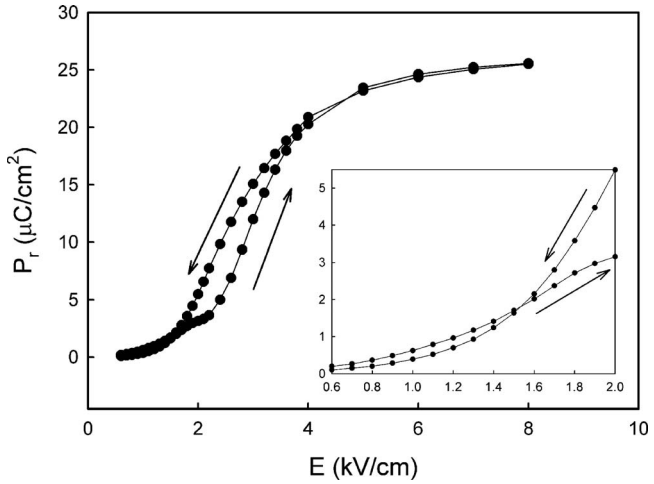

FIG. 4. Remanent polarization P_r of PMN–13PT presented as a function of electric field during a two-way polarizing field cycle (E_{max} =0 kV/cm↔8 kV/cm) at 0 °C temperature. The inset shows a detailed view of the remanent polarization behavior around the threshold field. Arrows indicate the direction of the electric field cycle.

takes place during the peak field cycle and the slope of the gray curve decreases, corresponding to damped growth as shown in Fig. 4. Above E_{th} [Figs. 5(c) and 5(d)], the hysteresis loops become wider with a higher P_r and coercive field E_C. Finally, with a 4 kV/cm polarizing field, the hysteresis curve of the ascending stage equals that of the descending stage, and the shape of the curve is similar to the ferroelectric one.

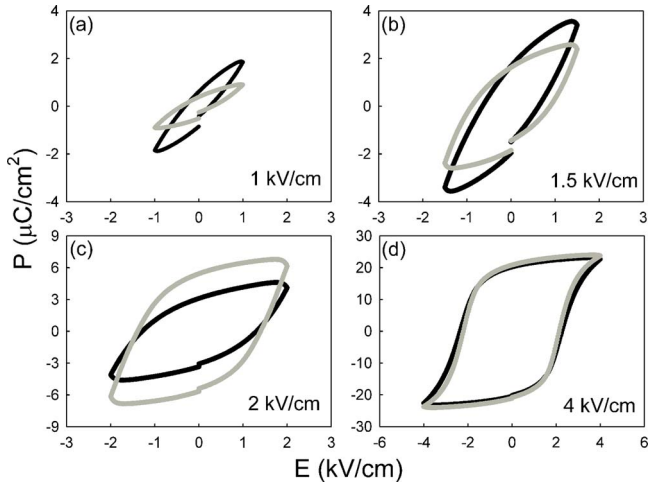

FIG. 5. (Color online) Hysteresis loops with a maximum polarizing electric field of (a) 1 kV/cm, (b) 1.5 kV/cm, (c) 2 kV/cm, and (d) 4 kV/cm during a two-way polarizing field cycle (E_{max}=0 kV/cm↔8 kV/cm) at 0 °C temperature. The black curve is measured on the ascending and the gray curve on the descending stage of the electric field cycle.

In this work, the minimum value of the inducing threshold electric field $E_{th,min}$ for PMN–13PT relaxor ceramics was found at T=−5 °C, which differs remarkably, ΔT=23 °C, from the depolarization temperature T_{dp}=18 °C. This observed behavior brings an additional aspect to the consideration of E-field-induced phase transition in PMN–xPT in comparison to PMN, which holds the minimum inducing threshold field strength value $E_{th,min}$ near the depolarization temperature T_{dp}. The observed $E_{th,min}$=1.55 kV/cm is in the same range as that observed for single crystal PMN, $E_{th,min}$ =1.75–2.5 kV/cm.[13,19–21] Further investigations with different compositions and phase transition enthalpy studies would provide a deeper understanding of this phenomenon.

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