High-temperature macroscopic piezoelectricity in Nb-doped PbZr$_{1-x}$Ti$_x$O$_3$ ceramics driven by the existence of polar regions

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The dielectric, elastic, and piezoelectric properties of a niobium-doped PbZr$_{1-x}$Ti$_x$O$_3$ ceramic with a composition located near the morphotropic phase boundary have been studied from 25 to 400 °C. A strong softening of the elastic coefficients was observed far below the temperature corresponding to the dielectric permittivity maximum, $T_{\varepsilon max} = 366$ °C. The steep decrease of the stiffness coefficient c_{44} from 400 to 350 °C is probably a stepwise anomaly which is expected at an improper ferroelastic transition. In addition, it was found that all macroscopic piezoelectric activity had disappeared well above $T_{\varepsilon max}$. This is explained by the combined effects of compositional fluctuations in the Zr/Ti sublattice and the presence of polar nanoregions. The elastic properties have an anomaly at the temperature at which the lattice becomes predominantly centrosymmetric. The piezoelectric activity vanishes when the polar nanoregions reach a critical size below which they can no longer interact coherently through the nonpolar matrix to induce a macroscopic piezoelectric response.

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INTRODUCTION

PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) ceramics are one of the most commonly used materials in piezoelectric device applications.[1] PZT compounds located near the morphotropic phase boundary (MPB) are of special interest because they exhibit very high values of the piezoelectric and dielectric parameters, making them attractive candidates for applications in microelectronics. However, most PZT properties, including the elastic and piezoelectric coefficients, have only been determined at ambient temperatures. Because of the practical importance of PZT-based materials, it is not surprising that recent studies have reexamined the structural properties and mechanisms that drive the phase transitions in these compounds. This renewed interest in PZT and other piezoelectric materials in the range of the MPB has been particularly motivated by the discovery of a monoclinic phase, or other low-symmetry phases, near the MPB.[2] As a result, the phase diagram of PZT published by Jaffe *et al.*[1] had to be modified to take into account the results of structural investigations using neutron and synchrotron x-ray diffraction methods (e.g., Ref. 2). The specific rotation (in plane) of the polarization allowed by the monoclinic symmetry and the disorder of the Pb position[3] in the perovskite structure were considered to be the main factors responsible for the exceptionally strong piezoelectric properties.[2,4,5] Glazer *et al.* recognized in Ref. 4, however, that the role of fluctuations in the Zr and Ti ion distributions has not been adequately discussed in the literature. In order to clarify the possible effect of these fluctuations on the dielectric and piezoelectric properties, we have undertaken an investigation of a PZT ceramic with the nominal composition Pb(Zr$_{0.52}$Ti$_{0.48}$)$_{0.98}$Nb$_{0.02}$O$_3$. The addition of a small amount of niobium was needed to limit exaggerated grain growth during sintering,[6] to improve the ceramic density, and to obtain a smaller and more homogeneous grain size.[7] It was determined that the presence of Nb only weakly influences the structural properties, causing a small decrease in the tetragonal-to-cubic transition temperature.[6] The results described below concern the temperature evolution of the elastic and piezoelectric properties of this PZT ceramic over the temperature range 25–400 °C.

EXPERIMENT

Ceramics with nominal formula Pb(Zr$_{0.52}$Ti$_{0.48}$)$_{0.98}$Nb$_{0.02}$O$_3$ were prepared by hydrothermal synthesis.[8] That this composition lies close to the MPB region was confirmed by x-ray diffraction patterns, which showed the coexistence of rhombohedral and tetragonal phase at room temperature.[8] For the dielectric and electromechanical measurements, samples with dimensions $4 \times 1 \times 1$ mm^3 were cut from a pellet.[9] Gold electrodes were evaporated onto the ceramic faces, and thin gold wires were glued at the center of the electrodes for electrical contact. For the piezoelectric measurements, the samples were poled under an external dc electric field of 2 kV cm^{-1} applied at 350 °C and then slowly field cooled to room temperature.

All of the electromechanical coefficients for the poled ceramic—i.e., the elastic s_{11}, s_{33}, s_{55}, piezoelectric d_{31}, d_{33}, d_{15}, and coupling factors k_{31}, k_{33}, k_{15}—were determined by the piezoelectric resonance method. The forced harmonic oscillator model was applied to calculate these coefficients.[10] The piezoelectric resonances were determined by measuring the complex admittance as a function of frequency by means of a Hewlett-Packard 4192A impedance analyzer. The temperature dependence of the real part of the dielectric permittivity ε' was determined by recording the capacitance of the sample from 25 to 400 °C at a heating/cooling rate of 2 K min^{-1}, at several frequencies.

RESULTS AND DISCUSSION

Figure 1 shows the evolution of the permittivity ε' with temperature of the Nb-doped PZT material at 1 kHz, 10 kHz,
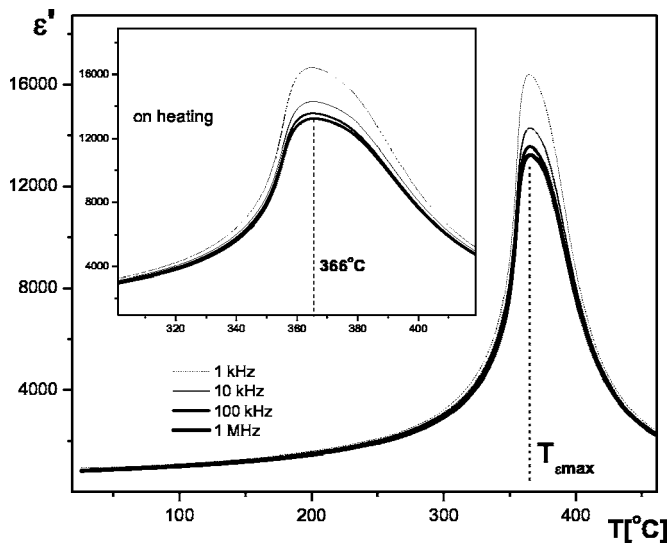
FIG. 1. Temperature dependence of the real part of the dielectric permittivity ε' on cooling at four frequencies for the Nb-doped PZT ceramic. The inset shows the asymmetric behavior of $\varepsilon'(T)$ near $T_{\varepsilon max}$.

FIG. 2. Temperature dependence of the real part of the elastic compliances s_{11}^E, s_{33}^E, s_{55}^E and s_{11}^D, s_{33}^D, s_{55}^D of the Nb-doped PZT ceramic.

100 kHz, and 1 MHz. The maximum value of ε' is around 14 000–16 000 and occurs at the temperature $T_{\varepsilon max}$ $\sim$ 366 °C. A dielectric dispersion is clearly seen near this temperature, but the positions of these maxima do not strongly depend on frequency, as they do in typical relaxors. A small thermal hysteresis of about 3° over one heating/cooling cycle was detected in the dielectric permittivity data. The permittivity $\varepsilon'(T)$ exhibits, however, a diffuse and asymmetric character that is clearly shown in the inset to Fig. 1. The rounding of the dielectric peak, which for a first-order transition should be sharp, is apparently due to a compositional inhomogeneity that was revealed by energy dispersive spectroscopy (EDS) microanalysis, and will be discussed later in the text.

A peak was reported earlier from a differential scanning calorimetry (DSC) investigation that coincides in temperature with that of the main anomaly in $\varepsilon'(T)$ at $\sim$366 °C.[8] It is worth noting that almost the same behavior of $\varepsilon'(T)$ is observed in poled ceramics. This result clearly suggests that the dielectric permittivity anisotropy in these ceramics is small, as is also observed in PZT ceramics (e.g., Ref. 1) and strontium-doped PZT ceramics with very similar compositions.[11] This probably means that poling only causes 180° domain walls to move, which does not influence the second-rank dielectric permittivity tensor.

The temperature dependences of the real parts of the elastic compliances are presented in Fig. 2. The relation s_{jj}^D $= s_{jj}^E(1-k_{ij}^2)$ (Ref. 1) with $i = 1,3$ and $j = 1,3,5$ allows all of the elastic coefficients s_{jj}^E and s_{jj}^D, respectively, at constant electric field E and electrical displacement D to be calculated. The difference between them is proportional to the product of the piezoelectric and dielectric properties $s_{jj}^E - s_{jj}^D$ $= d_{mj}d_{nj}\beta_{mn}$ where $\beta = 1/\varepsilon$.[12] According to the data presented in Fig. 2, all six elements s_{ij} of the elastic matrix start changing above 300 °C. The difference $s_{jj}^E - s_{jj}^D$ decreases upon heating towards 350 °C, but stays nonzero. At this point one
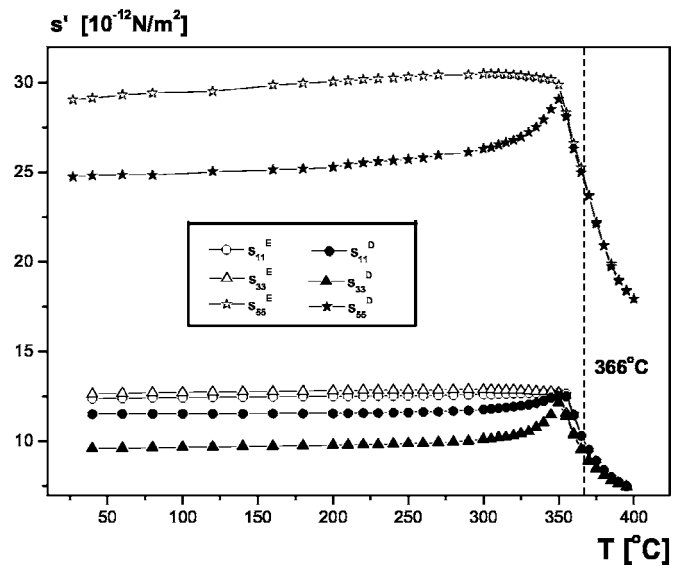
should recall that if the sample undergoes a transition to the cubic $Pm3m$ phase, as is expected for our PZT material, then there will be no difference between the respective elastic coefficients; i.e., the conditions $s_{11}^E = s_{11}^D = s_{33}^E = s_{33}^D$ and s_{44}^E $= s_{44}^D$ would be fulfilled.[12] On the other hand, the cubic $Pm3m$ symmetry rules out any macroscopic piezoelectric activity. In our case, the nonzero difference between the respective elastic coefficients was detected up to 400 °C—i.e., to much higher temperatures than those associated with the anomaly in the elastic properties or with the maximum value of the dielectric permittivity. In our opinion, these results are convincing proof of the existence above 350 °C of a structural phase that is related to the presence of polar nanoregions. The abrupt reduction in the difference between the elastic coefficients near 350 °C is a sign that above this temperature the dominant phase is cubic and one in which the polar nanoregions are randomly spread out. The dynamics of these regions in an external electric field, which depends on size and correlation length, is what determines the characteristic temperature $T_{\varepsilon max}$ corresponding to the maximum of ε'. The nonvanishing macroscopic piezoelectric activity means that the polar nanoregions are sufficiently large to enable interactions through the cubic matrix. Since a DSC peak[8] was reported close to the temperature at which the piezoelectricity disappears, one can speculate that it accompanies a quick contraction of the polar nanoregions followed by a gradual disappearance. In fact, polar nanoregions several hundred angstroms in size were reported to be present in PZT above 400 °C by Tan *et al.*,[13] but they were unable to correlate this observation with a nonzero average macroscopic piezoelectric response.

Figure 3 shows the temperature evolution of the square root of the real part of the elastic constant c_{44}. In the presence of tetragonal symmetry the relation $c_{44} = c_{55} = 1/s_{55}$ (Ref. 12) is satisfied. Thus knowing the $s_{44}^E(T)$ and $s_{44}^D(T)$ dependences, those for $c_{44}^E(T)$ and $c_{44}^D(T)$ can easily be deter-
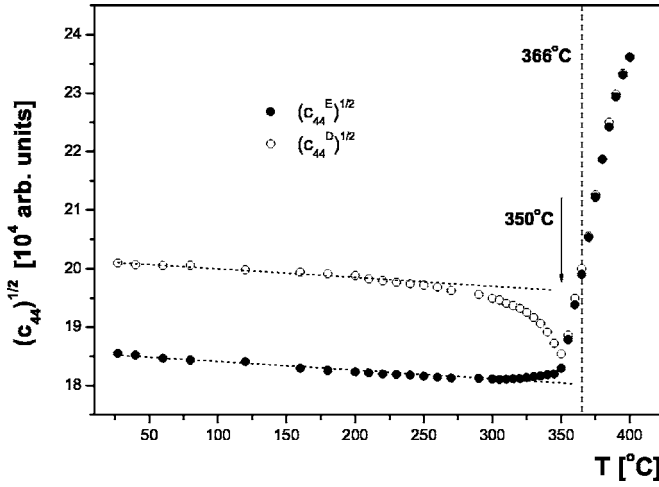
FIG. 3. The square roots $\sqrt{c_{44}^E}$ and $\sqrt{c_{44}^D}$ of the real part of the stiffness coefficient versus temperature.

mined. It is also known that for tetragonal symmetry the slopes of the transverse acoustic phonon branches Λ_5(TA) and Δ_1(TA) are respectively proportional to $\sqrt{c_{44}^E}$ and $\sqrt{c_{44}^D}$ as the phonon wave vector tends towards zero.[14] The notations Λ and Δ represent high-symmetry directions in the Brillouin zone for a simple tetragonal lattice. Especially interesting are the $\sqrt{c_{44}^D}(T)$ data, which show how the Δ_1(TA) phonon couples with the Δ_1(TO) phonon.[14] Above ~ 250 °C the $\sqrt{c_{44}^D}(T)$ dependence becomes nonlinear, indicating a distinct temperature evolution of the coupling between the soft optic and acoustic phonons that is proportional to the order parameter (P_s).[15] The difference $(\sqrt{c_{44}^D} - \sqrt{c_{44}^E})$ shows that this coupling starts from almost zero at 350 °C and then saturates below 200 °C where most likely the order parameter (P_s) also saturates.

Much weaker is the coupling between the Λ_5(TA) and Λ_5(LO) phonons described by the $\sqrt{c_{44}^E}(T)$ dependence. The data indicate a slight deviation of $\sqrt{c_{44}^E}(T)$ from a linear dependence only above ~ 325 °C. At 350 °C the rate of convergence of $\sqrt{c_{44}^D}$ and $\sqrt{c_{44}^E}$ is highest and points to a major transformation developing in the sample in the vicinity of this temperature. Above 350 °C a further decrease in the difference $(\sqrt{c_{44}^D} - \sqrt{c_{44}^E})$ was observed, which eventually vanished when the piezoelectric response disappeared. In fact, one would have expected that the elastic properties would have an anomaly at $T_{\varepsilon max}$. In our opinion it does not happen here mainly because of the dominant role of the compositional fluctuations on the B sublattice, which will be discussed in the next paragraph.

From our point of view the steep decrease in c_{44} from 400 to 350 °C is interesting. It is very probably a stepwise anomaly, smeared by the compositional fluctuations, which is expected at an improper ferroelastic transition due to a coupling term between the order parameter and deformation appearing in the paraelectric free-energy expansion.[15] To confirm this, it is necessary to know the behavior of the elastic properties in PZT compounds at many more (and higher) temperatures than those at which the piezoelectric
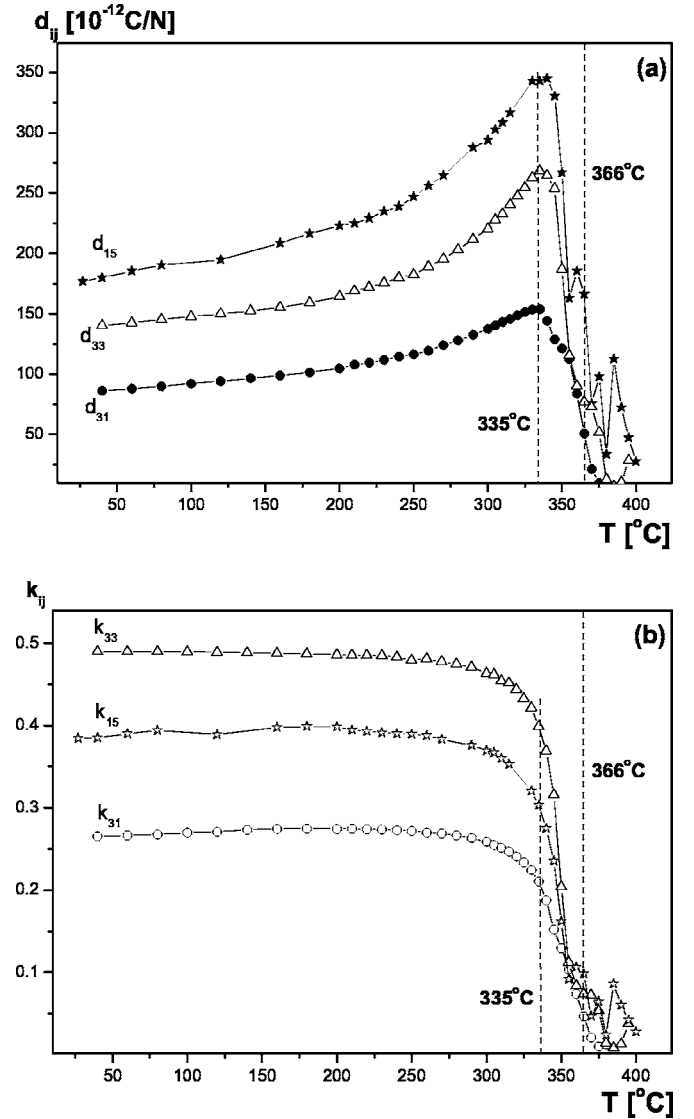

FIG. 4. (a) Temperature dependence of the piezoelectric moduli d_{31}, d_{33}, d_{15} and the (b) electromechanical coupling factors k_{31}, k_{33}, k_{15}.

experiments have been done. However, such data, to the best of our knowledge, are not available.

We cannot exclude an additional shift of the point at which the elastic properties takes the minimal values due to a dispersion effect. Because of the low frequency of the piezoelectric resonance, the evaluated elastic properties are essentially static and no further dispersion in elastic behavior is expected below this frequency. However, the shift observed may be explained by a domain-wall dispersion possible in this temperature and frequency range.

To complete the electromechanical characterization of our sample, the piezoelectric moduli and the coupling coefficients have been determined (as shown in Fig. 4). The piezoelectric moduli vary strongly with temperature and achieve maximum values at 335 °C [Fig. 4(a)]—i.e., below the temperature associated with the strong elastic lattice softening. The electromechanical coupling factors in the range 0.3–0.5 are constant up to about 300 °C [Fig. 3(b)]. The highest

value of any of the piezoelectric moduli was $d_{15}=350 \times 10^{-12}$ m/V, but the most efficient transformation of electric energy into mechanical energy takes place in the d_{33} configuration. It is interesting that the piezoelectric coefficient d_{15} is the largest as predicted by Bellaiche *et al.*[16] for PZT compositions in which the existence of the monoclinic phase has been established.[2,5] To obtain the piezoelectric activity the sample must be poled and the affect of the poling field could lead to the appearance of this phase. However, the role of this phase on the value of the piezoelectric moduli seems to be important at much lower temperatures than are considered in this paper. Because of the large elastic anisotropy (s_{55} is over twice as large as s_{33}), it was determined that $k_{15} < k_{33}$. Taking the relation $d_{ij}^2 = k_{ij}^2 s_{jj} \varepsilon_{ii}$, with the assumption that the anisotropy of the dielectric permittivity is negligible as was found experimentally, the piezoelectric modulus d_{15} is greater than d_{33}.

The question remains as to why there is such a large difference in the temperatures of the anomalies observed in this ceramic. One of the most interesting and unexpected results of this study is that different temperatures were found for the maximum permittivity ($T_{\varepsilon max}$), while the anomaly of the elastic properties occurred always at the same point, in samples cut from the same ceramic block. The origin of such behavior could be due to a local fluctuation of the sample composition. The large range in temperature (365–400 °C) of the DSC anomalies supports the idea of such fluctuations. To verify this hypothesis an EDS microanalysis was also performed. We checked that the average composition of our sample, by measuring the ratio of the integrated intensities of the x-ray radiation lines coming from the Zr and Ti ions, was equal to Zr/Ti=56/44. We found that this ratio was quite different from grain to grain; the Ti concentration varied from 41 to 49%. However, for an individual grain, the EDS analysis was able to confirm that there is no Ti/Zr fluctuation within an experimental error equal to ±1%. Since changes in the Ti content near the MPB cause changes in T_c of the order of a few degrees per 1% Ti (see the phase diagram proposed by Noheda *et al.*[17–19]), the compositional fluctuations inside the grains and disorder in the Zr/Ti sublattice[20,21] can undoubtedly lead to the existence of clusters at high temperatures with symmetries different from cubic.

The fact that the anomaly in the elastic properties appears at 350 °C independent of the value of $T_{\varepsilon max}$ supports the idea that, within the range of the Ti/Zr fluctuations present in the sample, a majority of grains transforms into the cubic phase at the same temperature.

The results obtained indicate that the role of the Ti/Zr compositional fluctuations on the macroscopic properties of PZT-based ceramics should be considered more carefully. The compositional fluctuations found in the present PZT ceramic sample (prepared by hydrothermal synthesis) have also been observed by us using EDS on pure and other PZT-based ceramics having similar chemical compositions and grown by conventional and other methods such as hot-pressing. In view of our results, compositional inhomogeneities seem to be quite important. Thus the question arises of how general this is in the processing of PZT ceramics. In our opinion this issue has not been discussed in sufficient detail in other papers dealing with these materials.

A comment is also needed on the role of niobium that was intentionally introduced into the PZT ceramic sample we studied. The substitution of Nb^{5+} for Zr^{4+} or Ti^{4+} is the most likely cause[22,23] of the increase in lead vacancies. It is well known that defects such as Pb and O vacancies are also created during the growth of pure PZT because of PbO sublimation. This means that the introduction of Nb_2O_5 can provide an electrical balance between Pb^{2+} and O^{2-} point defects and, as a result, leads to low electric conductivity and efficient poling of this ceramic. We can thus exclude any significant influence of the niobium on both the creation of polar nanoregions and especially on the compositional fluctuations. In fact, an EDS analysis performed on both doped and undoped PZT ceramics showed comparable fluctuations in the Zr/Ti sublattice.

The conclusion of the present investigation is that the influence of the compositional fluctuations on the lattice dynamics and other properties in this complex PZT ceramic system can be understood by means of a detailed investigation of the temperature evolution of the piezoelectric, elastic, and dielectric properties.

CONCLUSIONS

The dielectric, elastic, and piezoelectric properties of niobium-doped PZT ceramics with compositions close to the MPB have been studied over a wide temperature range. A strong softening of the elastic properties takes place at $\sim$350 °C, far below the temperature corresponding to the dielectric permittivity maximum ($\sim$366 °C), while the macroscopic piezoelectric activity disappears far above this maximum. This behavior can be explained by a combined effect of the compositional fluctuations in the Zr/Ti sublattice and of the interactions of the polar nanoregions. The proposed interpretations are that (a) the elastic properties have an anomaly at the temperature corresponding to the structural phase transition where the lattice becomes predominantly centrosymmetric and (b) the piezoelectric activity vanishes when the polar nanoregions reach a critical size below which they can no longer coherently interact through the nonpolar matrix to induce long-range order and, thus, a macroscopic piezoelectric response.

ACKNOWLEDGMENTS

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