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Acoustic emission and dielectric studies of phase transitions within the morphotropic phase boundary of xPb(Zr1/2Ti1/2)O3-(1−x)Pb(Ni1/3Nb2/3)O3 relaxor ferroelectrics

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Abstract
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Keywords
Relaxor ferroelectrics, Acoustic emission, Phase transitions, Dielectrics, Permittivity, Ferroelectric phase transitions, Lead, Ozone, Phase diagrams, Elasticity

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We have carried out a combined acoustic emission (AE) and dielectric permittivity study of the xPb($Zr_{1/2}Ti_{1/2}$)O_3-$(1-x)$Pb($Ni_{1/3}Nb_{2/3}$)O_3 relaxor ferroelectric ceramics with compositions $x=0.7-0.9$ corresponding to its morphotropic phase boundary. Temperatures of all phase transitions occurring on heating are identified accurately by AE, and a direct transition between the low-temperature (rhombohedral) and high-temperature (pseudocubic) relaxor phases is found. The AE peak intensity is generally proportional to the temperature derivative of the dielectric permittivity, in agreement with a model proposed for a thermally cycled small elastic dipole. © *2009 American Institute of Physics*. [doi:10.1063/1.3275730]

Lead-containing complex perovskites with the composition Pb($B'_{1/3}B''_{2/3}$)O_3, such as the prototypic Pb($Mg_{1/3}Nb_{2/3}$)O_3 (PMN) and Pb($Zn_{1/3}Nb_{2/3}$)O_3 (PZN) compounds, are known as relaxor ferroelectrics, or relaxors, exhibiting frequency-dispersive dielectric maxima at characteristic temperatures, T_m.[1] However, unlike normal ferroelectrics, no long range order structural phase transitions occur at T_m. In solid solutions of relaxors with normal ferroelectrics, e.g., $PbTiO_3$ (PT), substitution of Ti^{4+} ions for the complex $(B'_{1/3}B''_{2/3})^{4+}$ ions enhances the formation of ergodic polar nanodomains which (on cooling) develop into a macroscopic polar phase through local ferroelectric phase transitions.[2] The resulting long-range ferroelectric phase changes symmetry upon increasing the PT-content at compositions corresponding to the morphotropic phase boundary (MPB).[3,4] The broadly studied xPT-$(1-x)$PMN and xPT-$(1-x)$PZN solid solutions with compositions near the MPB exhibit very high piezoelectric coefficients, large electrically induced strains and high electromechanical coupling factors.[4–8]

Recently, solid solutions between a classical ferroelectric Pb($ZrTi$)O_3 (PZT) and a relaxor ferroelectric Pb($Ni_{1/3}Nb_{2/3}$)O_3 (PNN), namely xPZT-$(1-x)$PNN, have attracted special attention due to their richness in phase transitions within a narrow temperature range, from room temperature to 300 °C.[9] In particular, the compounds with $x=0.4-0.9$ gradually transform from pseudocubic to rhombohedral to tetragonal symmetry upon increase in the PZT concentration, as confirmed by the x-ray diffraction and Raman spectral measurements. The MPB of this binary system is located at around $x=0.8$, where the dielectric permittivity versus temperature (ε-T) measurements reveal a shoulder at $T=195$ °C indicating a rhombohedral to tetragonal phase transition (and a maximum permittivity of 36 000 at $T_m=277$ °C and 10 kHz).

Although the dielectric permittivity measurements are widely used for studying phase transitions and phase diagrams in relaxors,[10–13] they do not allow to determine precisely the onsets of phase transformations in the complex phase fields of relaxor/ferroelectric systems, which are smeared out in the ε-T curves. Also, the dielectric data alone do not provide a full insight into the kinetics of such transformations. This void can be filled by employing an additional characterization method, namely the acoustic emission (AE) measurements. The material's acoustic activity is, for example, sensitive to the nature of the crystallographic lattice mismatch at the interphase boundaries. Therefore, pronounced AE responses are registered through the phase transitions in normal ferroelectrics[14] as well as in relaxors.[15–17] In particular, the AE method has been applied to refining the phase diagram of xPT-$(1-x)$Pb($Fe_{2/3}W_{1/3}$)O_3 relaxor ferroelectric solid solution in the case where dielectric response is particularly insensitive to the phase transitions.[17]

The purpose of the present work is to study the abundance of phase transitions in the xPZT-$(1-x)$PNN relaxor ferroelectric solid solutions with $x=0.7-09$ (comprising the MPB compositions) using the combined dielectric and AE measurements. The phase diagram of the material is thus revisited, and the intensities of AE responses during the various phase transitions is discussed in terms of thermally induced mechanical stresses associated in part with the temperature behavior of the dielectric permittivity.

The xPZT-(1−x)PNN material was synthesized using the columbite precursor method.[9] Sintered ceramic samples in the form of disks, 11 mm in diameter and 1 mm in thickness, were prepared and studied using the dielectric method.[9] Sputtered gold and air-dried silver paint were applied to the samples as electrodes. The relative dielectric permittivity, ε_r, and the dielectric loss, tan δ, were measured at 100 Hz in the 25–400 °C temperature range using an automated system that consisted of an LCR meter (HP-4284A, Hewlett-Packard Inc.) in connection with a Delta Design 9023 temperature chamber and a sample holder (Norwegian Electroceramics) capable of high temperature measurements. A heating rate of 3 °C/min was used during these measurements. In the AE measurements,[17] cylindrical samples, 11 mm in diameter and 10–13 mm in height, were used. Each sample was coupled with a heat conducting silicon fluid (Hunpol LS-6006, stable to above 400 °C) to the polished

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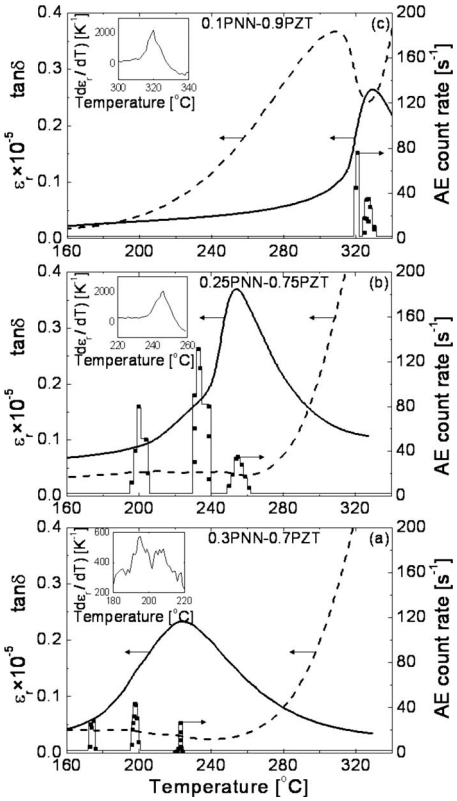

FIG. 1. Temperature dependences of AE count rate and dielectric permittivity and dielectric loss measured at 100 Hz in course of heating samples with compositions: (a) 0.7PZT-0.3PNN, (b) 0.75PZT-0.25PNN, and (c) 0.9PZT-0.1PNN. Insets: temperature derivatives of dielectric permittivities.

side of a fused silica acoustic waveguide. A PZT-19 piezoelectric sensor was attached to the rear end of the waveguide. The sensor was electrically coupled to a 500 kHz bandpass low noise (≤ 1 μV) variable (up to 40 db) preamplifier linked to a detector-amplifier (40 db). A chromel-alumel thermocouple junction was glued to the waveguide near the sample. The lower part of the acoustic waveguide and the sample attached to it were mounted in a resistance element tube furnace. Both the thermocouple and amplifier outputs were interfaced with a personal computer for a coupled readout. The waveguide attenuation did not exceed 10 db, and the discrimination level of the AE signals was approximately 20 db. AE activity (dN/dt, s^{-1}) measurements were carried out from room temperature to 400 °C at an average heating rate of ~1–3 °C/min.

The $\varepsilon_r(T)$, tan $\delta(T)$, and $dN/dt(T)$ dependences of the three samples are presented in Fig. 1. All samples exhibit prominent diffuse permittivity peaks with maxima, T_m, which according to the previously established preliminary phase diagram[9] correspond to transformations from an intermediate relaxor pseudocubic (F_{PC}) phase to paraelectric cubic (P_C) phase. The permittivity peaks are relatively broad, at least with respect to the narrow AE peaks. No peak structure can be distinguished also in the dielectric loss temperature dependencies. The strong increase in tan δ toward T_m in the $x=0.9$ sample [Fig. 1(c)] is common for ferroelectric systems near the phase transition temperature.[18] Therefore, the highest temperature AE peaks have been used to determine the maximum ε_r temperatures more accurately. Thus measured T_m values are: 223 °C for $x=0.7$, 253 °C for $x=0.75$, and 327 °C for $x=0.9$ [Figs. 1(a)–1(c), respectively]. These results imply that the Vegard's law is approximately fulfilled in terms of T_m as already stated previously.[9] Other important experimental observations are that the sample with the 0.75PZT-0.25PNN composition has the highest ε_r maximum of about 36 500, being in the midst of the MPB range. The increase in the T_m magnitude is observed starting from even lower x values,[9] which is explained by the increase in the PZT content controlling the homogeneously polarized states. Also, the widths of the peaks in the ε_r curves becomes narrower across the $x=0.7\rightarrow0.9$ compositional range. The latter can be well understood in terms of the gradual transformation from the relaxor to ferroelectric behavior with the increasing content of PZT.

Lower temperature phase transitions cannot be revealed with a reasonable degree of certainty based solely on the dielectric method. There are only barely observable slope changes in the temperature dependences of ε_r. Insets in Figs. 1(a)–1(c) show the ε_r derivatives around temperatures corresponding to the largest slope changes. Apparently, the derivatives also exhibit broad peaks, with still remaining uncertainties in the phase transition temperatures. In contrast, relatively sharp peaks of the AE activity arise at the onset of phase transitions that are associated with acoustic waves produced by collective atomic movement.[2,14] It is noteworthy that the AE signal contains no contribution from either thermally induced stress in the heated sample or residual stress caused by preliminary mechanical polishing, since (a) a highly elastic thermally conducting glue is used also as a mechanical buffer between the sample and the waveguide and (b) the samples are routinely annealed at high temperatures, 50 °C above the T_m, after mechanical polishing. This explains also the very good reproducibility of the AE results.

We refer initially to the $x=0.7$ sample [Fig. 1(a)], where the initial AE peak appears at 174 °C, and a slight increase in the $\varepsilon_r(T)$ slope can be distinguished at the same temperature as well. Since the 0.7PZT-0.3PNN material is known to exist in the rhomohedral (relaxor) phase in the ground state (room temperature), based also on the x-ray diffraction measurements,[9] the rhombohedral-to-tetragonal phase transition must take place at 174 °C. Above this temperature, the compound is introduced into the MPB range. No such transition is observed in the AE responses of either $x=0.75$ or $x=0.9$ compounds, since they are already within the MPB in the ground state (the latter is presumably at the high-PZT-content end of the MPB). A complete transformation from the relaxor ferroelectric (rhombohedral) to normal ferroelectric (tetragonal) state, or the $F_R\rightarrow F_T$ transition, occurs at around $T=198$ °C in both the $x=0.7$ and 0.75 compounds. Stronger AE peaks (with respect to the 174 °C peak in the $x=0.7$ sample), especially for the $x=0.75$ composition, appear at this temperature as shown in Figs. 1(a) and 1(b). This transition is also marked by slight changes in their $\varepsilon_r(T)$ slopes.

The most intense AE peaks are observed in the $x=0.75$ and 0.9 compositions at higher temperatures corresponding to the onset of a relatively sharp increase in the dielectric permittivity. We note again that it is difficult to pinpoint the associated phase transition temperatures using the permittivity or dielectric loss temperature dependences alone. Fortunately, the relevant AE activity peaks are well pronounced, and the transition temperatures can be defined accurately. These temperatures are different for the $x=0.75$ and 0.9 com-

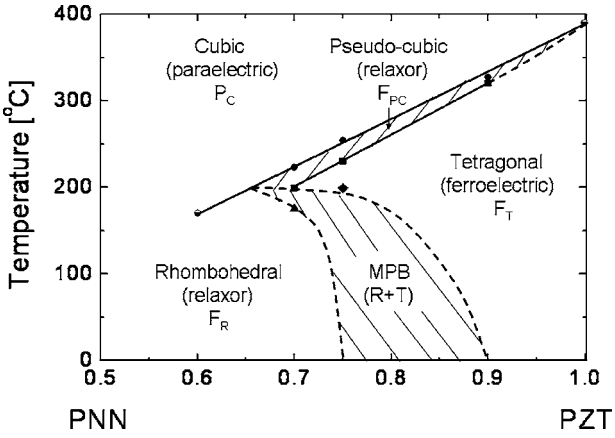

FIG. 2. Partial phase diagram of xPZT-$(1-x)$PNN solid solutions. The $x=0.6$ and 1.0 data and the ground state boarders of the MPB are adopted from previous work (see Ref. 9).

positions: 233 and 320 °C, respectively. This combined dielectric and acoustic effect has been attributed to a reverse transition from the normal ferroelectric (tetragonal) to another relaxor state exhibiting a pseudocubic structure (F_{PC}).[9] The sharp increase in the dielectric permittivity upon the $F_T \rightarrow F_{PC}$ phase transition is characteristic for the development of a pure relaxor state. It is noteworthy that no similarly prominent increase of the permittivity is observed in the case of the $x=0.7$ composition. Moreover, there is no separate AE peak featuring the $F_T \rightarrow F_{PC}$ transition. We presume, therefore, that the $F_R \rightarrow F_T$ and $F_T \rightarrow F_{PC}$ transitions occur at about the same temperature for the $x=0.7$ composition, and the two peaks are indiscriminate in the AE versus temperature curve. The lack of dramatic changes in the dielectric permittivity and tan δ within this temperature range can thus be explained by the fact that most of the sample volume transforms from one relaxor phase (F_R) to another (F_{PC}). We reiterate that the highest temperature AE peaks, at $T=223$, 253, and 327 °C for the $x=0.7$, 0.75, and 0.9 compositions, respectively, coincide with the T_m peaks of the $\varepsilon_r(T)$ characteristics. The combined dielectric and AE measurements data can now be used to construct a modified phase diagram of the PZT-PNN solid solution system. This partial phase diagram around the MPB composition range is presented in Fig. 2. Two main differences in comparison with the previously published phase diagram are found: (1) a direct $F_R \rightarrow F_{PC}$ transition occurs at $x=0.7$ and (2) the pseudocubic relaxor phase at the MPB compositions is wider than previously reported.[9] It still narrows with the increase of x due to the decreasing relaxor stability.

The intensity of an individual AE peak depends on a number of factors. The issue has been recently considered based on a theory of excitation of elastic radiation by small electrically polarized elastic dipoles subjected to thermal cycling.[19] This implies that temperature changes create thermal stresses. The dynamics of this process is described by the appropriate Landau–Khalatnikov equation, and its solution in the wave approximation is similar to that of a damped oscillator vibrating with a frequency ω. Assuming that the time derivative of the vibrating elastic dipoles is proportional to the time derivative of the stress, σ, the activity (count rate) of AE can be expressed as following:

$$dN/dt = v\omega(\Delta\sigma/\Delta T), \tag{1}$$

where $v=dT/dt$ is the velocity of heating/cooling and the stress differential can be expressed as

$$\Delta\sigma = \left[g\left(\frac{dP^2}{dT}\right) + \frac{\varepsilon_0}{2}E^2\left(\frac{d^2\varepsilon_r}{dTd\eta}\right)\right]_E \Delta T, \tag{2}$$

where g is the electrostriction tensor, P is the polarization, T is the temperature, ε_0 is the vacuum permittivity, E is the electric field, and η is the local inhomogeneous strain. It is clear from Eqs. (1) and (2) that the AE activity is maximal when the electric polarization and/or dielectric permittivity jumps or diverges. No experimental data allowing to assess the magnitude of the left term in Eq. (2) are available. The electrostrictive and properties of the material will be studied when PZT-PNN single crystals become available. At the present stage we presume that the second term in Eq. (2) is dominant. This explains why the 233 °C [Fig. 1(b)] and 320 °C [Fig. 1(c)] peaks of AE corresponding to the $F_T \rightarrow F_{PC}$ phase transitions are most intense (130 and 80 s^{-1}, respectively)—they appear at the onset of the sharpest changes in the $d\varepsilon_r/dT$ derivatives. In proof, a smaller but still significant change in the permittivity is observed above 198 °C in the $x=0.75$ sample [Fig. 1(b)], and it is also accompanied by an intense (80 s^{-1}) AE peak at $T=198$ °C. The AE activity at T_m (permittivity maxima) is relatively weak for all studied compositions. This may be understood in terms of the nature of the pseudocubic to cubic (paraelectric) phase transition releasing a small amount of elastic energy, or producing small stresses due to the closer compatibility of the lattice structures.

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