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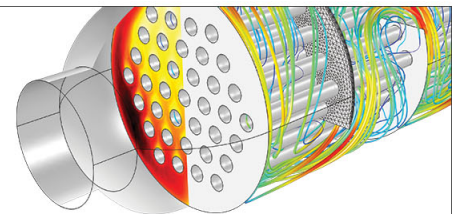
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Fe-substituted $0.92\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.08\text{PbTiO}_3$ single crystals: A “hard” piezocrystal

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The dielectric and electrically induced strain characteristics of Fe-substituted $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-\text{PbTiO}_3$ single crystals have been investigated. These investigations have shown that Fe substitution results in: (i) a lowering of the field level required to obtain large strains, (ii) an increased squareness in the $\epsilon-E$ response indicative of “hard” piezoelectric properties, and (iii) enhanced linearity in the region where saturation is approached at high field levels. Interestingly, the hard characteristics occur along with an enhanced stability of an intermediate ferroelectric orthorhombic state. © 2002 American Institute of Physics. [DOI: 10.1063/1.1507831]

Piezoelectric single crystals of $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-\text{PbTiO}_3$ (PZN-PT) and $\text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3-\text{PbTiO}_3$ (PMN-PT) have recently been investigated due to their anomalously high piezoelectric and electromechanical coupling coefficients ($d_{33}\sim 2500$ pC/N, $k_{33}\sim 95\%$), high electrically induced strains ($\epsilon\sim 1.7\%$) and low hysteresis.¹⁻⁴ Figure 1 shows the $\epsilon-E$ response of a $\langle 001 \rangle$ oriented PZN-PT crystal (data taken from Ref. 3). In this figure, three stages are identified. Stages A and B have a large ϵ at low and moderate fields, while in stage C saturation is approached. The highest value of $\delta\epsilon/\delta E$ was found in stage B. Park and Shrout^{3,4} attributed this high electromechanical performance to an induced ferroelectric rhombohedral (FE_r) to tetragonal (FE_t) phase transformation, by polarization rotation from $\langle 111 \rangle$ to $\langle 001 \rangle$.

Recent investigations have shown the presence of ferroelectric monoclinic (FE_m) and orthorhombic (FE_o) states in-between the FE_r and FE_t phases.⁵⁻⁷ First principles calculations have indicated that the transformation under electric field between FE_r and FE_t phases proceeds by rotation of the polarization between $\langle 111 \rangle$ and $\langle 001 \rangle$, via the $\langle 110 \rangle$.^{8,9} In this case, the polarization is constrained to the $\langle hhk \rangle$ plane, which serves to bridge the $\langle 111 \rangle$ FE_r and $\langle 001 \rangle$ FE_t polarizations. Phenomenological approaches have indicated that the FE_m state is only found to be stable in the presence of a fourth order self-alloying term.¹⁰ On the other hand, synchrotron x-ray diffraction studies by Noheda *et al.*^{11,12} and neutron diffraction studies of Ohwada *et al.*¹³ on PZN-8%PT show that under electric field the crystal goes through an irreversible $R-M_A-M_C$ transformation sequence. In this case, the polarization initially moves on the R-T path but then changes irreversibly to the O-T path with the ground state of M_C symmetry. Further, in the M_C state the polarization vector rotates under electric field within ac plane and forms identical angles with the $[001]$ direction and this im-

parts pseudotetragonal symmetry to this phase as observed by optical measurements.¹⁴ Viehland has shown the presence of an intermediate metastable FE_o state with monoclinic texture.⁵ The FE_o state has been shown to be dependent upon various external variables.¹⁵

Priya *et al.* have shown that the intermediate metastable state can be stabilized at room temperature by poling at high electric fields for long times.⁷ Subsequent, $P-E$ measurements have consistently revealed sharp induced phase transitions, indicative of a first order transition. It is an interesting possibility that intermediate metastable states^{5,15} might be responsible for the high value of $\delta\epsilon/\delta E$ in the stage B of Fig. 1. Accordingly, alterations in the macroscopic properties might be obtained by varying the stability of the intermediate state. For example, by shifting the stability of stage B to lower fields, higher strains might be achieved at lower drive fields. In PZN-PT, this would have to occur by the stabilization of the FE_o state with respect to the FE_r phase.

In ferroelectric ceramics, one means to vary domain stability is by substituents.¹⁶⁻¹⁸ In particular, small concentra-

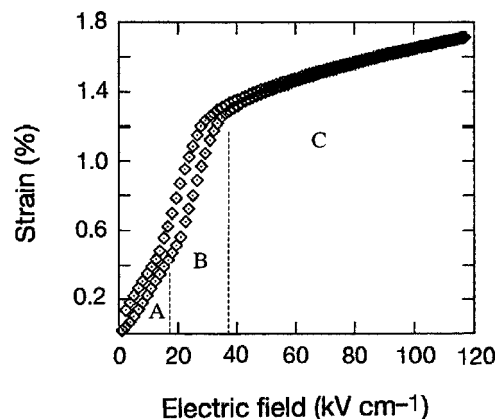


FIG. 1. Unipolar $\epsilon-E$ response for $\langle 001 \rangle$ -oriented PZN-PT crystals. These data were taken from Ref. 3. The letters A, B, and C denote stages of the transformation. Stages A and B have a large strain (ϵ) at low and moderate fields, while in stage C saturation is approached. The highest value of $\delta\epsilon/\delta E$ is found in stage B.

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tions of lower valent substituents have previously been shown to dramatically influence both ferroelectric domain and phase stability.¹⁷ For example, small additions (~ 1 at. %) of K^{1+} onto the A site or Fe^{3+} on the B site of $PbZrO_3$ can stabilize a FE_o phase from an antiferroelectric one. The effect of lower valent substituent in complex perovskites of type $Pb(B_I B_{II})O_3 - PbTiO_3$ is strongly dependent on B-site positional ordering.^{19,20} Due to the presence of small amplitude charge fluctuations and nano-scale ordering in systems having a B_I/B_{II} of 1:2, the effects of small concentrations of aliovalent substituent may be dramatically different than those in systems having a B_I/B_{II} of 1:1.²¹ Hence it has been found that Fe^{3+} is effective in inducing hard characteristics in PZN-PT^{21,22} ceramics but is ineffective in PMN-PT²¹ ceramics.

In this letter, we report the investigation of Fe-modified 0.92PZN-0.08PT single crystals. Small concentrations of Fe substituents have been found to enhance the stability of the FE_o phase, resulting in a lowering of the field level required to obtain large electrically induced strains.

Single crystals of Fe modified PZN-PT were grown using a self-flux method. To confirm the presence of a pure perovskite phase, x-ray diffraction analysis was performed. Individual crystals were oriented along the $\langle 001 \rangle$ direction using a Laue back reflection camera. Rectangular-shaped specimens were prepared for dielectric and piezoelectric property measurements. Crystals were poled at room temperature. The polarization and strain field curves were obtained using a modified Sawyer-Tower circuit in conjunction with a linear variable differential transducer. Permittivity as a function of temperature at various frequencies (0.1, 1, and 10 kHz) were acquired on the poled samples from 0 to 220 °C, using a HP 4284A LCR meter equipped with a Delta Design 2300 temperature chamber.

Figure 2(a) shows the unipolar $\epsilon - E$ response for an unmodified PZN-PT single crystal. At an applied field of 22.5 kV/cm, an electrically induced strain of $\sim 0.35\%$ can be seen which has low hysteretic losses. On removal of the electric field, the specimen recovered its original state. Up to this field level, neither stages B nor C were observed for this specimen, as previously reported and shown in Fig. 1. The data in Fig. 2(a) do not demonstrate any evidence of either electrically induced FE_r or FE_o transformations.

Figures 2(b) and 2(c) show the unipolar $\epsilon - E$ response for PZN-PT crystals substituted with 0.3 and 0.5 at. % Fe, respectively. The data in these figures show clear evidence of electrically induced phase transformations, demonstrating all three stages A, B, and C. With increasing Fe content, the field level at which the induced transformation occurred decreased. In fact, in Fig. 2(c), the stability range of stage A is rather limited. Another important change with increasing Fe content is that the $\epsilon - E$ response becomes increasingly square. This demonstrates that the properties of PZN-PT are "hardened" by Fe substitution. The introduction of hard characteristics is due to polarization pinning by extended defect structures.^{17,23} The data in Fig. 2 show several important changes in the properties of PZN-PT which are: (i) a lowering of the field level required to obtain large strains, (ii) an increased squareness in the $\epsilon - E$ response indicative of hard piezoelectric properties, and (iii) enhanced linearity in the

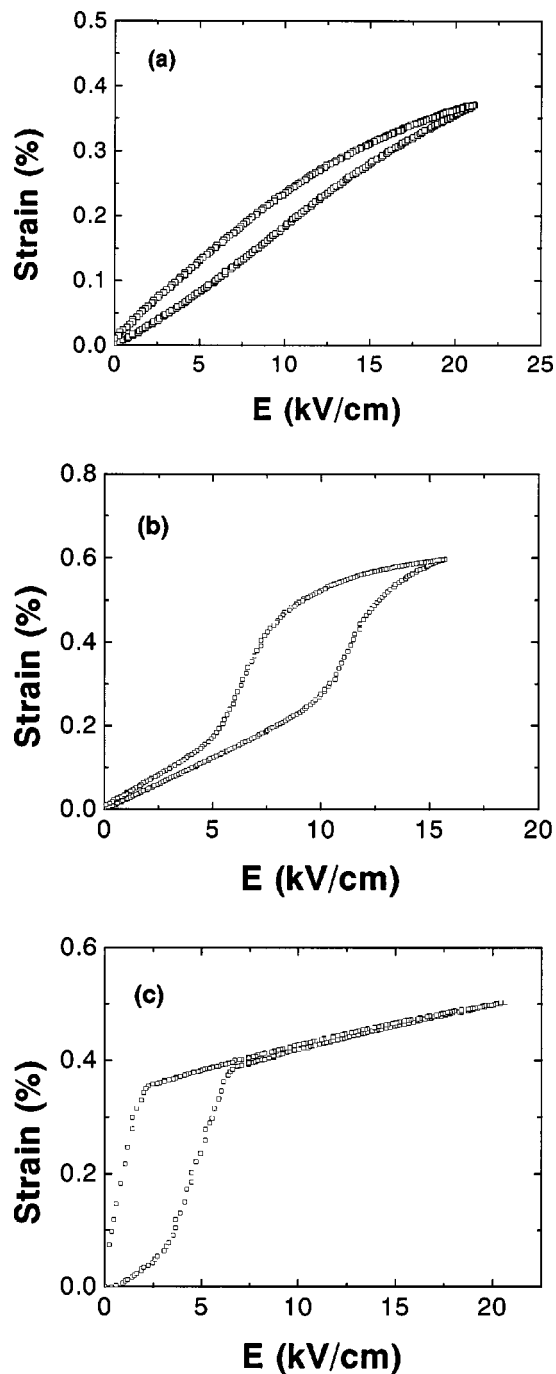


FIG. 2. Unipolar $\epsilon - E$ response for various $\langle 001 \rangle$ -oriented PZN-PT crystals. (a) Pure PZN-PT, (b) 0.3 at. % substituted PZN-PT, and (c) 0.5 at. % substituted PZN-PT.

region where saturation is approached at high field levels. These changes can be explained on the basis of the stabilization of the intermediate FE_o state.

Dielectric measurements shown in Figs. 3(a)-3(c) provide further evidence of the enhanced stability of the FE_o state with increasing Fe content. For unmodified PZN-PT, three transitions can be seen in Fig. 3(a), consistent with previous reports of a transformation sequence of FE_r to FE_o to FE_t for this composition.¹⁵ In Fig. 3(a), a $FE_r - FE_o$ transition can be seen near 98 °C followed by a narrow temperature range of stability for the FE_o phase, a $FE_o - FE_t$ transition then occurs at ~ 110 °C, and finally the FE_t to paraelectric transition occurs near 170 °C. Substitution with

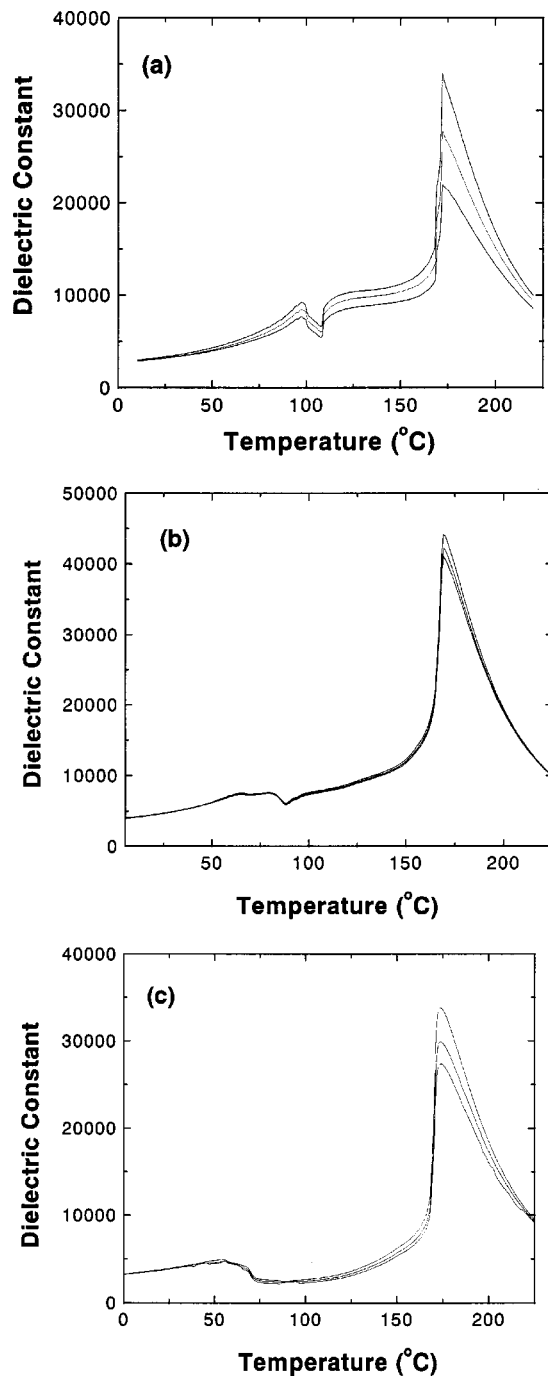


FIG. 3. Dielectric constant as a function of temperature for various (001)-oriented PZN-PT crystals. (a) Pure PZN-PT, (b) 0.3 at. % substituted PZN-PT, and (c) 0.5 at. % substituted PZN-PT.

Fe resulted in changes in the dielectric response. Figure 3(b) shows that 0.3 at. % Fe resulted in a shift of the $FE_r - FE_o$ and $FE_o - FE_t$ transformations to ~ 64 and 79 °C, respectively. In addition, the transformation between $FE_r - FE_o$ can be seen to be more diffuse than for the unmodified specimen, as can be seen by comparisons of Figs. 3(a) and 3(b). Increment of the Fe content to 0.5 at. % resulted in the presence of only a diffuse peak, between the FE_r and the FE_o temperature range. This peak was shifted down to ~ 55 °C. The results of Fig. 3 demonstrate that the stability of the FE_o state and FE_t phase are shifted towards room temperature by Fe

substitution. The closer the transformation temperature to 25 °C, the lower the field strengths which need to be applied to induce them at room temperature, consistent with the results in Fig. 2.

In Fig. 1 the strain levels achieved at the stages A, B, and C are 0.55%, 1.2%, and 1.8%, respectively, each stage occurs at certain threshold field levels and the magnitude of strain is in proportion to applied field level. The transformation from stage B to stage C occurs at field levels of more than 40 kV/cm and at the onset of Stage C, corresponding to the polarization state along (001), the strain levels reach 68% of the full strain (1.75%) of the tetragonal phase.^{3,9,11} The results in Figs. 2(b) and 2(c) show that the transformation from stage B to C occurs at much smaller field of 20 kV/cm and this transformation produces strains of the order of $\sim 0.5\%$ in agreement with the results of Fig. 1. Larger strains of the order $\sim 1\%$ can be achieved by driving the crystal deep into the tetragonal state by applying higher electric fields.

In summary, the electrically induced strain and dielectric properties of Fe-substituted PZN-PT crystals have been investigated. Modification with Fe has been shown to: (i) enhance the stability of the FE_o state, (ii) reduce the electric field required for high electrical strains, and (iii) impart square or hard characteristics to the $\epsilon - E$ response. These changes are believed to be caused by built-in dipolar fields that pin the polarization.

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