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Piezoelectric properties of ⟨001⟩ textured $Pb(Mg_{1/3}Nb_{2/3})O_3-PbTiO_3$ ceramics

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The piezoelectric properties of $(1-x)$ $Pb(Mg_{1/3}Nb_{2/3})O_3-xPbTiO_3$ $(x=0.3-0.35)$, ceramics with a high degree of ⟨001⟩ fiber texture were investigated for possible actuator applications. Piezoelectric coefficients (d_{33}) in excess of 1200 pC/N associated with strain levels up to >0.3% were observed in samples prepared by a reactive templated grain growth process. No excess PbO was used in the starting composition. A high degree of fiber texture was achieved using ⟨001⟩ oriented $BaTiO_3$ template particles in a fine-grained precursor for the PMN–32PT matrix. High densities together with texture resulted in a significant increase in strain levels and d_{33} values compared to their polycrystalline counterparts. Peak dielectric constants on the order of 22 000 with losses of ~2% and well-saturated hysteresis loops with a $P_r \sim 27$ $\mu C/cm^2$ were recorded on the textured samples. These domain engineered, textured ceramics have tremendous potential for high-performance actuators. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1367291]

Recent studies[1–3] have shown that ⟨001⟩ oriented single crystals of PMN–PT $\{Pb(Mg_{1/3}Nb_{2/3})O_3-PbTiO_3\}$ and PZN–PT $\{Pb(Zn_{1/3}Nb_{2/3})O_3-PbTiO_3\}$ on the rhombohedral side of the morphotropic phase boundary compositions of both PMN–PT and PZN–PT exhibit extraordinarily large electromechanical coupling coefficients (>90%) and piezoelectric coefficients ($d_{33}>2000$ pC/N) coupled with ultrahigh strains. This is true despite the fact that crystallographically, ⟨111⟩ is the polar direction. However, considerable domain reorientation under bias is known to take place for this orientation and materials tend to depole upon removal of the electric field. In contrast, the ⟨001⟩ direction is found to have a stable domain configuration, and excellent piezoelectric properties have been observed.[4]

The superior properties of single crystals are not observed in ceramics because they are averaged out and clamped in polycrystalline samples in which each grain has a different crystallographic orientation. This study aims to determine whether the anisotropic properties of PMN–PT single crystals can be obtained by texturing the material. Heterogenous seeded growth has been used to grow crystals in a polycrystalline matrix.[5–7] We have shown that by aligning small crystals in a matrix we can obtain textured ferroelectric ceramics by templating growth on the aligned crystals.[5,8,9] In this letter, we describe the dielectric and piezoelectric properties of textured PMN–PT produced by templated grain growth (TGG).

A precursor of PMN–32PT was prepared by mixing $(PbCO_3)_2Pb(OH)_2$ (Aldrich), $MgNb_2O_6$ (H. C. Starck), and fumed TiO_2 (Degussa). The powder mixture was used directly for texturing PMN–PT in order to have a reactive matrix for sintering. {001} $BaTiO_3$ template crystals grown by the Remeika process,[10] with a mean thickness of <75 μm were selected, crushed and sieved to 75–150 μm in order to be used for texturing PMN–PT. The template crystals had an average thickness of ~50 μm and a diameter of ~100 μm. A slurry with 5 vol % $BaTiO_3$ templates was tape cast using a blade height of 400 μm at a shear rate of 200 s^{-1}. The tapes were dried, cut, and laminated into samples about 500 μm thick. These were hot pressed in argon at 900 °C for 30 min at 40 MPa. Hot-pressed samples were annealed at 1150 °C in an oxygen atmosphere for 10 h. Figure 1 shows the x-ray diffraction pattern of the surface of the textured sample, which corresponds to the ⟨001⟩ of the templates. The degree of ⟨001⟩ orientation was estimated from the peak intensities using the Lotgering method[11] and was found to be 0.82.

For electrical measurements, samples were cut, polished, and sputtered with gold electrodes on the larger faces. Typical samples had dimensions of $4\times3\times0.25$ mm^3. For resonance measurements, sample dimensions were in accordance with the IEEE standards for resonance measurements.[12] The piezoelectric properties were also measured using direct ob-

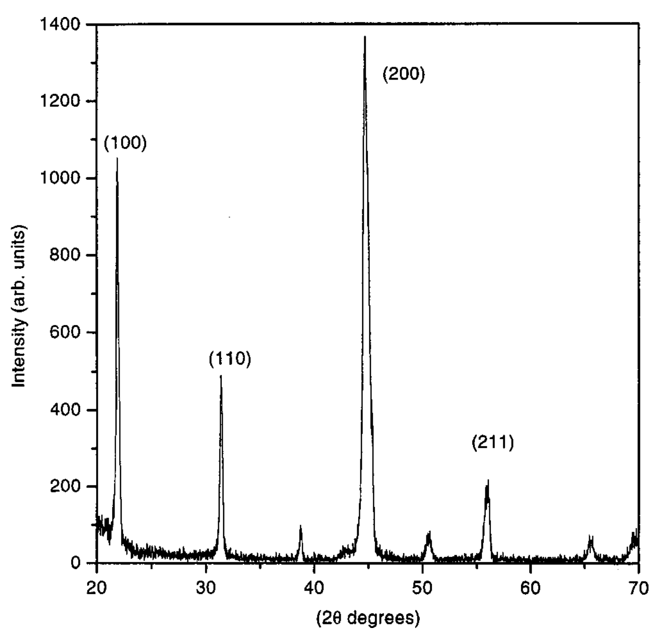

FIG. 1. X-ray diffractogram of ⟨001⟩ textured PMN–32PT.

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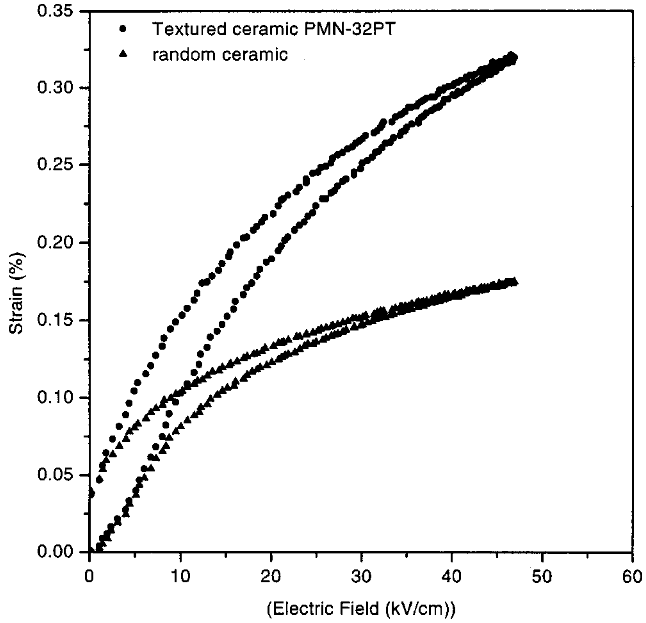

FIG. 2. Strain vs unipolar electric-field curves comparing textured and randomly oriented ceramic PMN–32PT.

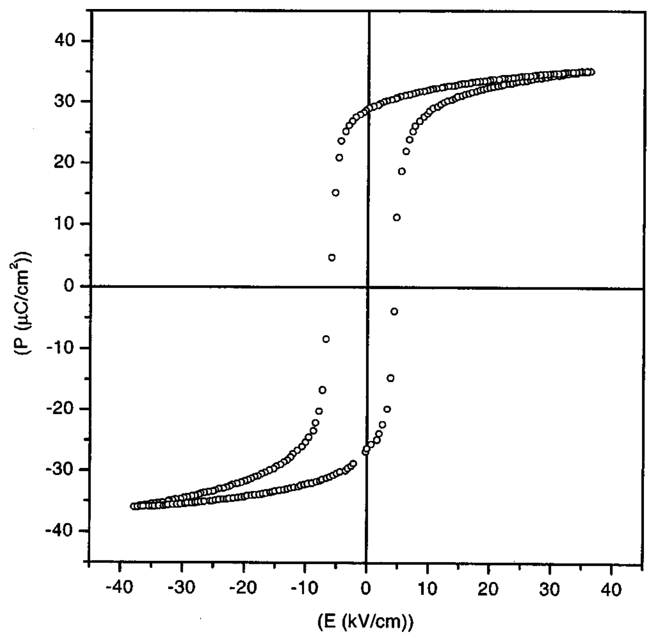

FIG. 3. Polarization (P) vs electric-field (E) curve for ⟨001⟩ textured PMN–32PT.

servation of strain-field curves and a Berlincourt d_{33} meter.[13] The strain-field measurements were performed using a modified Sawyer–Tower circuit in conjunction with a linear variable differential transducer, driven by a lock-in amplifier (Stanford Research Systems, model SR830). The applied signal was in the form of a unipolar wave with a frequency of 0.1 Hz. High fields could be generated with a Trek 609C-6 high-voltage amplifier. Samples were immersed in Galden HT-200, an insulating liquid, to prevent arcing during the measurement process. Prior to making strain measurements, samples were poled along ⟨001⟩ after determining the optimal poling conditions. Typical poling conditions involved the application of an electric field of 40 kV/cm across the sample at room temperature for 15 min. The observed values of the piezoelectric coefficient were compared with measurement results using the IEEE resonance technique.

Figure 2 shows the strain–electric-field hysteresis curve for the textured sample together with one for a randomly oriented polycrystalline ceramic. It can be seen that the ⟨001⟩ textured ceramic shows high strain with a maximum strain of ~0.32% at a field of ~45 kV/cm. This is much larger than the 0.15% strain observed in the case of polycrystalline PMN–PT of the same composition. The piezoelectric coefficient (d_{33}) determined from the slopes of the strain curves in the low-field region (<10 kV/cm) was between 1200 and 1400 pC/N for the textured PMN–PT. This value is almost twice that of the polycrystalline ceramic.

Based on the concepts of crystallographic orientation, it has been shown that both crystals and textured ceramics poled along ⟨001⟩ show superior piezoelectric properties. Thus, texturing of PMN–PT offers an alternative to single-crystal growth.

The samples showed some hysteresis, which is probably a consequence of domain reorientation. Attempts are underway to understand the origin of this hysteresis in textured PMN–PT. The piezoelectric coefficients obtained from strain measurements were confirmed by making IEEE resonance measurements on the textured materials. The values obtained from both measurements were in good agreement.

Polarization versus electric-field hysteresis loops for the textured samples were traced using a triangular pulse. Figure 3 shows a well-saturated loop with a remanent polarization (P_r) of 27.7 μC/cm^2 and a coercive field (E_c) of 4.8 kV/cm. These values are comparable to those of single crystals grown by polycrystalline conversion.[7]

Permittivity data as a function of temperature at various frequencies were acquired while cooling samples from 400 °C, using an HP 4192A impedance analyzer (see Fig. 4). The dielectric constant at room temperature was 2900 and a value of ~22 000 was observed at the transition temperature (170 °C). The dielectric data were fitted to the Curie–Weiss law and the Curie constant was estimated as 7.1×10^5 °C. The transition temperature agrees well with the values re-

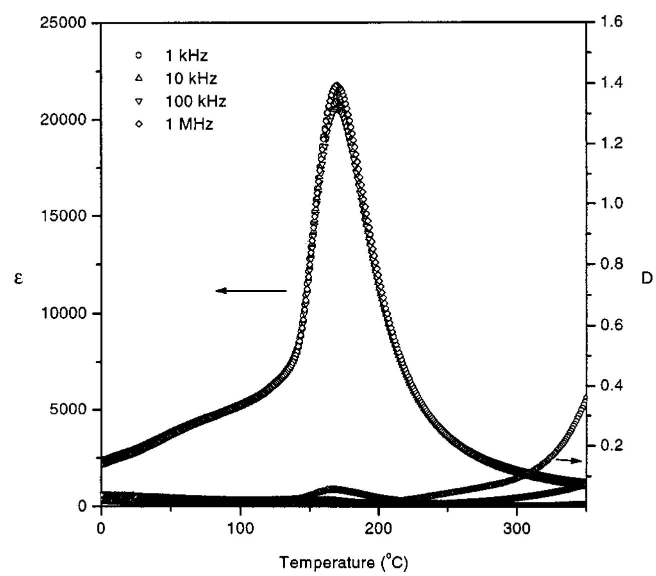

FIG. 4. Dielectric constant and loss vs temperature for textured PMN–32PT.

ported for the composition under study, and suggests that there is little Ba or Ti diffusion from the $BaTiO_3$ templates into the PMN–PT. The rhombohedral→tetragonal transition occurs at ~65 °C, as evidenced by the slope change in the dielectric curve. This is in agreement with previously reported data for this composition.[14] The values of permittivity are relatively higher than the ones reported for single crystals grown from polycrystalline precursors.[7] The loss data indicate that the dissipation is fairly low (2%) in the sample up to 100 °C. At T_{max}, the loss is ~5% and thereafter, the loss increases steadily.

In conclusion, significantly higher levels of strain have been achieved in textured ceramics of PMN–PT, than in their randomly oriented counterparts. This work also shows that the concept of domain engineering can be applied to textured ceramics, thereby offering tremendous potential for high-performance actuators.

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