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Fabrication and electrical properties of grain-oriented $0.7Pb(Mg_{1/3}Nb_{2/3})O_3-0.3PbTiO_3$ ceramics

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⟨112⟩ grain-oriented $0.7Pb(Mg_{1/3}Nb_{2/3})O_3-0.3PbTiO_3$ (PMN–0.3PT) piezoelectric ceramics with a degree of orientation of 0.35 have been produced from melt by a directional solidification method. The dielectric, ferroelectric, and piezoelectric properties were investigated, e.g., $\varepsilon_{rt}\sim 4800$, tan $\delta<0.6\%$, $d_{33}\sim 1500-1600$ pC/N, $k_t\sim 51\%$, and $k_{33}\sim 82\%$, some of these values are comparable to those of PMN–PT single crystals. The strain–electric-field curve with a maximum strain of 0.23% at a field of 22 kV/cm and well-saturated hysteresis loops with a $P_r\sim 35$ μC/cm^2 were recorded. The results demonstrate that the directional solidification method is a promising technique to fabricate high performance grain-oriented PMN–PT ceramics. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1643537]

Single crystals of $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3-xPbTiO_3$ (PZN–xPT) and $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3-xPbTiO_3$ (PMN–xPT) have been studied widely for applications in medical ultrasonic probes, high performance ultrasonic transducers, actuators, sonar detector equipments, and generators because of their anomalous dielectric and piezoelectric properties.[1–3] PMN–PT single crystals with compositions near the morphotropic phase boundary (MPB) have been reported to possess ultrahigh electrical performances: $\varepsilon_{33}\sim 6000$, $k_{33}\sim 94\%$, $d_{33}>2000$ pC/N, and large electric-field-induced strain values ($\sim 1.7\%$) for poled ⟨001⟩-oriented samples.[3,4] Compared with the single crystals, PMN–PT ceramics have lower piezoelectric responses ($k_p\sim 62\%$, $k_t\sim 46\%$, and $d_{33}\sim 720$ pC/N)[5] because the grains are randomly oriented in polycrystalline ceramics. Recently, Sabolsky *et al.*[6] fabricated ⟨001⟩ textured PMN–0.32PT ceramics by templated grain growth (TGG) technique, which showed better dielectric and piezoelectric properties than random grain-oriented ceramics. On the other hand, it has been widely accepted that ⟨001⟩ is the best direction to achieve high piezoelectric performance. Recently, ⟨011⟩ oriented single crystals with compositions near the MPB was also reported to have excellent piezoelectric properties.[7] In this letter, we produced ⟨112⟩ grain-oriented PMN–0.3PT ceramics by a directional solidification method and its dielectric, ferroelectric, and piezoelectric properties were described. It was found that the ⟨112⟩ grain-oriented ceramics also exhibited significantly high electrical performances.

The starting PMN–0.3PT materials were prepared using high-purity powders of PbO, MgO, Nb_2O_5, and TiO_2 by the columbite precursor method.[8] They were compressed and loaded into a platinum crucible. The temperature was then raised to 1380 °C. After soaking for 2 h, the crucible was pulled down at a rate of 0.8 mm/h to make the solutions solidified. Then, heat treatment was carried out. Figure 1 shows the x-ray diffraction pattern of the ceramic sample, where the measured surface was perpendicular to the solidification direction. It can be seen that the dominant grain orientation was ⟨112⟩, indicating that the ⟨112⟩-oriented grains were grown preferentially along the solidifying direction. The degree of ⟨112⟩ orientation was estimated to be 0.35 from the peak intensities using the Lotgering method.[9]

The samples were cut from an as-grown PMN–0.3PT boule, then polished and silver electroded for electrical measurements. Two kinds of samples were prepared, with dimensions of $\phi 12$ mm$\times$0.55 mm and $2\times2\times5$ mm^3, respectively. Dielectric constant and loss as functions of

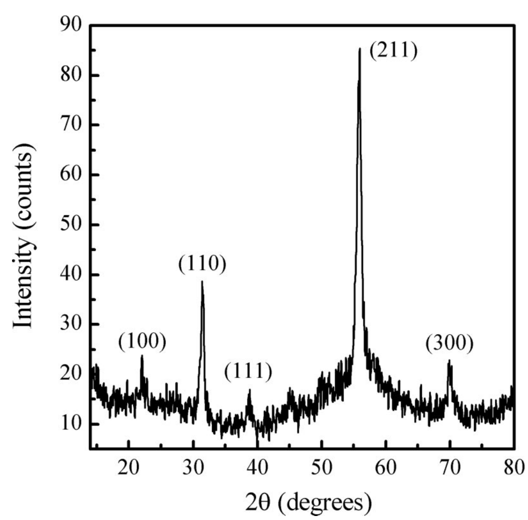

FIG. 1. XRD pattern of the grain-oriented PMN–0.3PT ceramics, where the measured surface was perpendicular to the solidifying direction.

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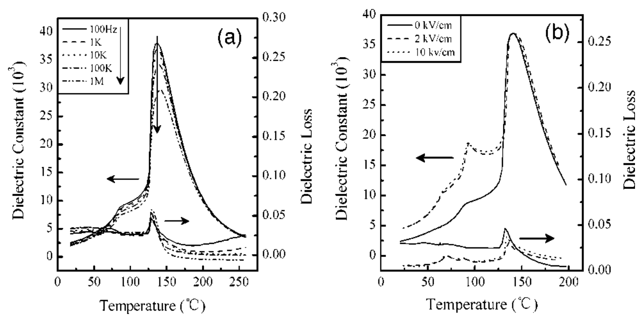

FIG. 2. Temperature dependence of dielectric constant and loss tangent (measured upon heating) of the ⟨112⟩ grain-oriented PMN–0.3PT ceramics (a) for an unpoled sample at various frequencies, and (b) for a sample poled under dc fields of 0 kV/cm, 2 kV/cm, and 10 kV/cm at 1 kHz.

temperature at various frequencies were measured with a HP 4192A impedance analyzer. The strain–electric-field measurements were performed using a DGS-6B inductance microshift meter. The piezoelectric coefficient d_{33} was measured using a quasistatic meter of Berlincourt type. The electromechanical coupling coefficients k_t, and k_{33} were calculated from resonance and antiresonance frequencies (f_s and f_p) according to IEEE standards.

Figure 2(a) shows plots of the dielectric constant and loss tangent as functions of temperature for an unpoled sample. Two peaks were observed at ~88 °C (T_{m1}) and ~138 °C ($T_{\max}$), which correspond to the phase transition from the ferroelectric rhombohedral (FE_r) phase to ferroelectric tetragonal (FE_t) phase and from the FE_t phase to paraelectric cubic phase, respectively. Figure 2(b) shows the comparison of the dielectric constants and loss tangents versus temperature at 1 kHz for a sample poled under different electric fields of 0 kV/cm (unpoled), 2 kV/cm and 10 kV/cm, respectively. Different from the unpoled sample, two small dielectric peaks at ~66 °C (T_{m1}) and ~93 °C (T_{m2}) were observed for the poled one. Similar behaviors were reported in PMN–0.3PT single crystals poled along ⟨011⟩,[10] in which an orthorhombic phase was induced by an electric field. In our case, the poling direction was mainly carried out along the ⟨112⟩ direction, which is different from ⟨001⟩ and ⟨011⟩ directions, so it is more likely that the third phase is a monoclinic phase (FE_m). Accordingly, the first small peak should coincide with a phase transition from FE_r to FE_m, while the second small peak with a transition from FE_m to FE_t. Recently, the studies showed that just the existence of FE_m or FE_o is responsible for the strong piezoelectricity of the above materials.[11–15] The values of T_{m1}, T_{m2}, $T_{\max}$, ε_{rt}, and tan δ of the ⟨112⟩ grain-oriented ceramics poled under different electric fields are listed in Table I. The grain-oriented ceramics possess high dielectric constant $\varepsilon_{rt}\sim 4800$ and low dielectric loss tan $\delta < 0.6\%$.

Polarizations versus electric field hysteresis loops were measured at 1 Hz using a triangular pulse. Figure 3 shows a well-saturated and symmetrical loop with a high value of remanent polarization (P_r) of 35 μC/cm^2 and a low coercive field (E_c) of 3.4 kV/cm. These values are comparable to those of single crystals (e.g., $P_r \sim 31\,\mu$C/cm^2 and $E_c \sim 3.5$ kV/cm for the ⟨001⟩-oriented PMN–0.33PT and $P_r \sim 33\,\mu$C/cm^2 and $E_c \sim 3.6$ kV/cm for ⟨001⟩-oriented PMN–0.35PT).[16] The high P_r may be related to the fact that the ⟨112⟩ direction is closer to the orientation of the spontaneous polarization than ⟨001⟩ direction.

The strain versus electric-field curve was shown in Fig. 4. It can be seen that the grain-oriented ceramics show a strain of ~0.23% at a filed of ~22 kV/cm, which is obviously higher than the values of PZT–5H ceramics (~0.15% strain at 25 kV/cm).[17] And the strain versus electric-field curve showed good linear in the low-field region (<5 kV/cm). The piezoelectric coefficient (d_{33}) determined from the slopes of the strain curve in the low-field region (<5 kV/cm) was larger than 1600 pC/N.

Table II shows the piezoelectric and electromechanical coupling coefficients measured by the resonance technique for the ⟨112⟩ grain-oriented PMN–0.3PT ceramics. As a

TABLE I. Dielectric properties of unpoled and poled ⟨112⟩ grain-oriented PMN–0.3PT ceramics at 1 kHz.

Samples	T_{m1}	T_{m2}	$T_{\max}$ (°C)	ε_{rt}	tan δ_{rt}
Unpoled	88.3	⋯	137.9	2500	0.031
Poled (2 kV/cm)	66.2	92.9	138.5	4700	0.006
Poled (10 kV/cm)	66.4	92.3	139.7	4800	0.005

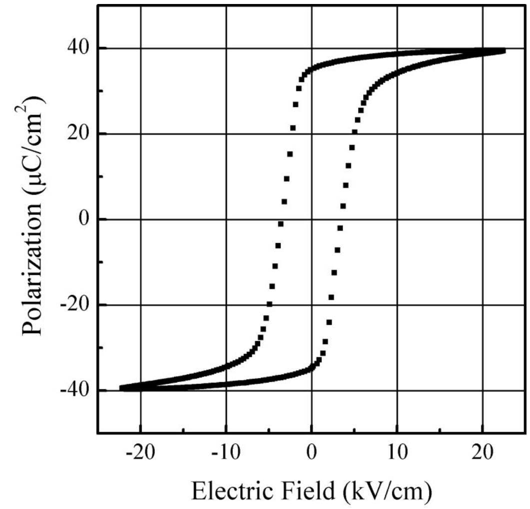

FIG. 3. Polarization vs electric-field hysteresis loop for ⟨112⟩ grain-oriented PMN–0.3PT ceramics.

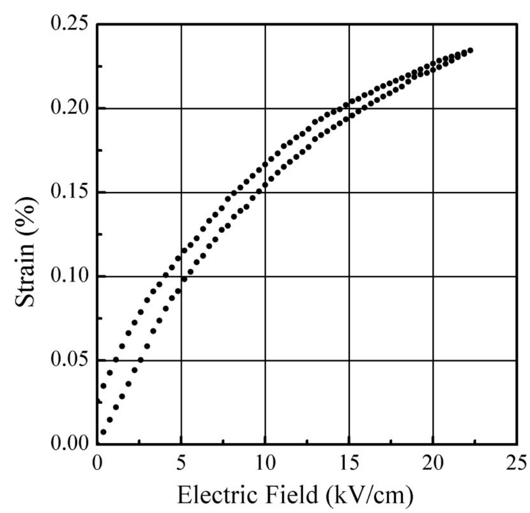

FIG. 4. Strain vs electric-field curve for the ⟨112⟩ grain-oriented PMN–0.3PT ceramics.

TABLE II. Piezoelectric properties of the ⟨112⟩ grain-oriented PMN–0.3PT ceramics in comparison with the ⟨001⟩ textured ceramics, random-oriented ceramics, and single crystals from other works.

Materials	d_{33} (pC/N)	k_t	k_{33}	N_t (Hz m)
⟨112⟩ grain-oriented PMN–0.3PT ceramics	~1500–1600	0.51	0.82	2084
⟨001⟩ textured PMN–0.32PT ceramics[a]	~1200–1400	⋯	0.755	⋯
Random-oriented PMN–0.3PT ceramics[b]	450	0.41	⋯	⋯
⟨001⟩-oriented PMN–0.3PT single crystals[c]	1200	⋯	0.90	⋯
⟨011⟩-oriented PMN–0.3PT single crystals[c]	1000	⋯	0.88	⋯

[a]See Ref. 6
[b]See Ref. 5.
[c]See Ref. 7.

comparison, the properties of random oriented ceramics, single crystals, and ⟨001⟩ textured ceramics produced by TGG are also listed. For the ⟨112⟩ grain-oriented ceramics, the piezoelectric coefficient d_{33} was measured to be ~1500–1600 pC/N when the samples were poled by applying an electric field as low as 2 kV/cm, though the E_c was 3.4 kV/cm, and d_{33} remained relatively unchanged when the electric field increased to 10 kV/cm. The ceramics also exhibited large electromechanical coupling coefficients k_t ~51% and k_{33}~82%. The piezoelectric properties of the ⟨112⟩ grain-oriented ceramics are obviously superior to random oriented ceramics and comparable to those of single crystals. The piezoelectric coefficient d_{33} of the ⟨112⟩ grain-oriented ceramics is three times greater than random oriented ceramics.

In summary, ⟨112⟩ grain-oriented PMN–0.3PT ceramics were prepared from melt by a directional solidification method, and which present excellent electrical properties, e.g., $\varepsilon_{\mathrm{rt}}\sim 4800$, $\tan\delta < 0.6\%$, $\varepsilon_{\max}\sim 37000$, $d_{33}\sim 1500$–1600 pC/N, $k_t\sim 51\%$, $k_{33}\sim 82\%$, $E_c\sim 3.4$ kV/cm, $P_r\sim 35\ \mu\mathrm{C/cm}^2$, and the strain levels up to $>0.23\%$ at 22 kV/cm. The results show that the enhanced electrical performance of the oriented piezoelectrics is not constrained to the ⟨001⟩ and ⟨011⟩ orientation, the ⟨112⟩ orientation is also an important direction in domain engineering and fabrication of both ceramics and single crystals of relaxors. And, further study is needed to understand the underlying physics. On the other hand, the directional solidification method is a promising fabrication technology for high performance grain-oriented PMN–PT ceramics.

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