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High Curie temperature piezocrystals in the $BiScO_3$-$PbTiO_3$ perovskite system

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Perovskite ferroelectric single crystals in the $(1-x)BiScO_3$-$xPbTiO_3$ (BSPT) system were grown using a flux method. The Curie temperature of rhombohedral BSPT(43/57) crystals was found to be about 404 °C, with a rhombohedral–tetragonal phase transition temperature (T_{r-t}) around 350 °C. The coercive field (E_c) was found to be 13.7 kV/cm for ⟨001⟩-oriented crystals, while the coupling factor k_{33} was determined to be ~90% at room temperature and was nearly temperature independent until 330 °C. High piezoelectric properties together with a high Curie temperature and coercive field make rhombohedral BSPT crystals promising candidates for the next generation of high-performance, high-temperature actuators and transducers. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1619207]

For piezoelectric polycrystalline materials, compositions close to a morphotropic phase boundary (MPB) between rhombohedral (R) and tetragonal (T) phases in the solid-solution $PbZrO_3$-$PbTiO_3$ (PZT) are widely utilized in transducer and actuator applications.[1,2] Since the discovery of PZTs in the 1950s, extensive research has been carried out for the search of new MBP systems. Recently, $Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PZNT) and $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMNT) systems have attracted interest in the single-crystal form[3–7] because of their ultrahigh piezoelectric and electromechanical coupling factors in the ⟨001⟩ direction, which can reach $d_{33}s > 2000$ pC/N and $k_{33} \sim 94\%$, respectively. This enhanced piezoelectric activity, however, comes with the sacrifice of the temperature stability of the properties, being limited to their relatively low Curie temperatures ($T_C \sim 140$–$170\,°C$), and further restricted by their lower phase transition temperatures ($T_{r-t} \sim 60$–$120\,°C$), the consequence of a strong curvature in their MPBs.

In most applications, especially in the automotive and aerospace industries, the need for actuation and sensing over a broad temperature range is essential.[8] Systems with enhanced piezoelectric activity and higher Curie temperature have redirected effort on single crystals in relaxor-PT systems, including $Pb(Sc_{1/2}Nb_{1/2})O_3$-$PbTiO_3$,[9] $Pb(In_{1/2}Nb_{1/2})O_3$-$PbTiO_3$,[10] and $Pb(Yb_{1/2}Nb_{1/2})O_3$-$PbTiO_3$ (PYNT).[11–13] In particular, PYNT offer the highest T_C among all the relaxor-PT systems studied to date with a $T_C \sim 350\,°C$. However, as found in PMNT and PZNT single crystals, a strongly curved MPB limits the use of the materials at the $T_{r-t} \sim 160$–$170\,°C$.[13] Recently, high-Curie-temperature ferroelectric materials based on $(1-x)BiMeO_3$-$xPbTiO_3$ solid solutions (where Me^{3+} = Sc, In, Yb, etc.) have been identified.[14] Specifically, $(1-x)BiScO_3$-$xPbTiO_3$ (BSPT) exhibits a MPB at $x = 0.64$ with a $T_C \sim 450\,°C$. Piezoelectric coefficients on the order of 500 pC/N have been demonstrated in polycrystalline ceramics comparable to soft PZTs.[15] In this work, the dielectric and piezoelectric properties of BSPT single crystals in the R phase close to the MPB were investigated.

BSPT(43/57) single crystals were grown using the high temperature solution method in which Pb_3O_4 and Bi_2O_3 were selected as a self-flux.[16] The as-grown crystals were blue-green in color and rectangular in shape, being 3–8 mm in size. The samples for measurement were oriented along the crystallographic direction ⟨001⟩ and sputtered with gold. The samples were poled at 120 °C with the application of a 20–30 kV/cm electric field for 10 mins. The room-temperature dielectric permittivity (ε_r) of ⟨001⟩-oriented BSPT(43/57) crystals was found to be ~3000, with a dielectric loss ~4% after the poling process. Dielectric permittivity and loss as a function of temperature were performed from room temperature to 500 °C using a multifrequency LCR meter (HP4284A) and are shown in Fig. 1. A dielectric maximum was observed at 404 °C, which was assumed to be the Curie temperature, corresponding well to polycrystalline ceramic data.[15] A second dielectric anomaly in Fig. 1 was observed at 349 °C, being the result of a R–T ferroelectric phase transition. It should be noted that the dielectric permit-

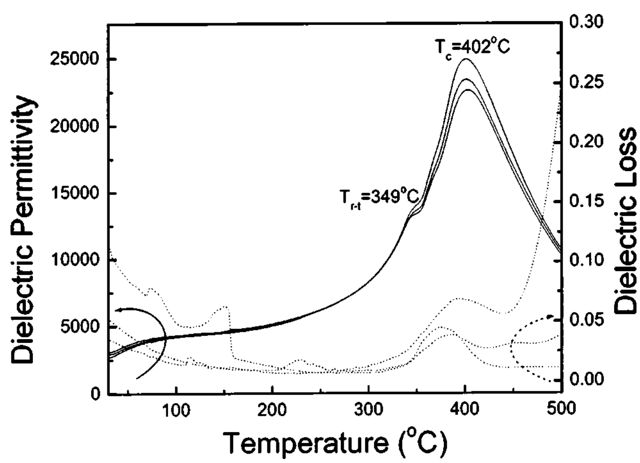

FIG. 1. Dielectric permittivity and loss as a function of temperature for ⟨001⟩-oriented BSPT(43/57) single crystals.

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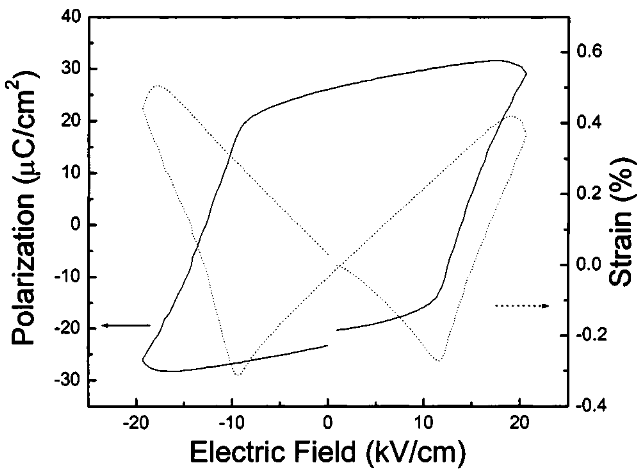

FIG. 2. Bipolar $P-E$ loops and $S-E$ loops for ⟨001⟩-oriented BSPT(43/57) single crystals.

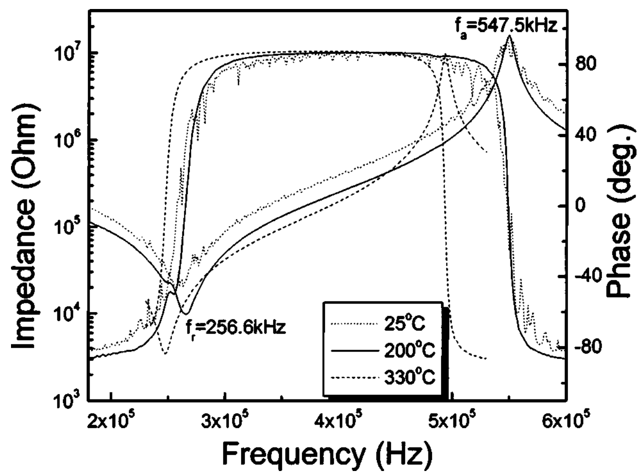

FIG. 4. Resonance and antiresonance frequency characteristics of impedance and phase for the ⟨001⟩-oriented BSPT(43/57) single crystals with different temperatures.

tivity is nearly temperature independent in the range of room temperature to 300 °C ($\partial\varepsilon/\partial T \sim 20/°C$), indicating thermal stability associated with a high T_C piezoelectrics. The dielectric loss was found to decrease to 2% in the temperature range of 150 to 350 °C and reached a peak at the Curie temperature, after which it increased rapidly owing to conductive losses.

Typical hysteresis and strain-field loops determined using a modified Sawyer–Tower circuit driven by a lock-in amplifier (Stanford Research System, Model SR830) at 1 Hz and 20 kV/cm electric fields for ⟨001⟩-oriented BSPT(43/57) crystals were measured, and are presented in Fig. 2. The coercive field (E_c) was found to be ~13.7 kV/cm with a remnant polarization of 23 μC/cm^2. The coercive field is significantly higher than that for PZNT and PMNT systems, being on the order of 2–3 kV/cm.[12] The unipolar strain behavior of ⟨001⟩-oriented BSPT(43/57) single crystals exhibited low hysteresis, with strains reaching 0.12% at 10 kV/cm, as shown in Fig. 3. The piezoelectric coefficient d_{33} calculated directly from strain-field curve was ~1200 pC/N, similar to that measured by using a Berlincourt d_{33} meter. A maximum strain value of ~1.1% was reached with an electric field of 30 kV/cm, as the crystal transformed from the R to T state with large hysteresis.

The resonance (f_r) and antiresonance (f_a) frequencies for a ⟨001⟩-oriented BSPT(43/57) rod (size: $0.6\times0.6\times3.05\ \mathrm{mm}^3$) measured using an impedance analyzer (HP4194A) were used to determine the electromechanical coupling factor. As shown in Fig. 4, the f_r and f_a were found to be 256.6 and 547.5 kHz at room temperature, respectively, and the longitudinal electromechanical coupling factor k_{33} was calculated to be 90%. The calculated piezoelectric coefficient d_{33} of 1150 pC/N was in good agreement with the values obtained from the unipolar strain measurement. As a function of temperature in the range of 25 to 320 °C, both f_r and f_a shifted a little bit with k_{33} decreasing to 89%. Above 330 °C, f_a shifted lower and the coupling factor decreased to 88.5%, decreasing further to only 83% when the temperature reached 340 °C, as shown in Fig. 5, corresponding to the value of coupling factor for BSPT tetragonal crystal.[16] The same tendencies for the piezoelectric coefficients were also observed and are shown in Fig. 5. This sudden drop above 340 °C in the coupling factors and piezoelectric coefficients were the result of the R–T phase transformation as evident in the dielectric behavior.

The various dielectric, piezoelectric, and electromechanical property characterizations of BSPT(43/57) crystals

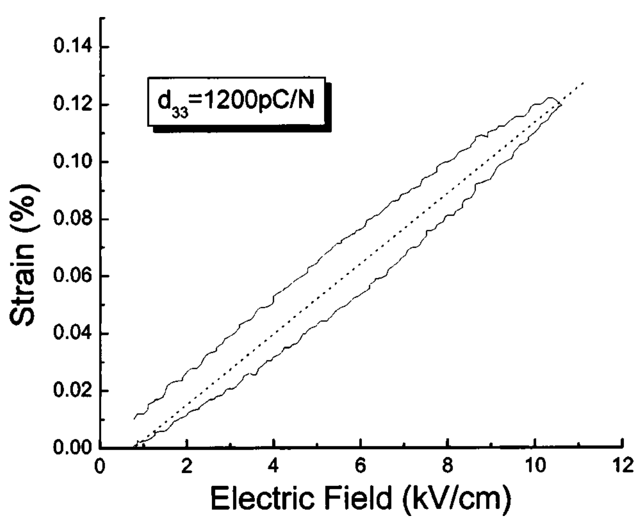

FIG. 3. Unipolar $S-E$ loop for ⟨001⟩-oriented BSPT(43/57) single crystals.

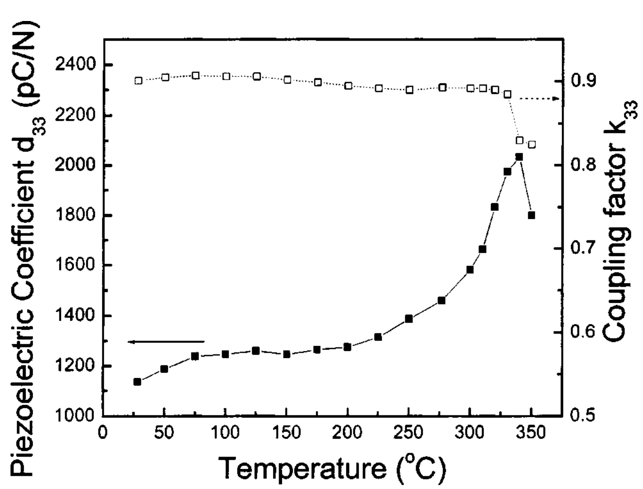

FIG. 5. Longitudinal electromechanical coupling factors k_{33} and piezoelectric coefficients d_{33} as a function of temperature.

TABLE I. Dielectric, piezoelectric, and electromechanical properties of the ⟨001⟩-oriented BSPT(43/57) single crystals compared with ⟨001⟩-oriented relaxor-PT single crystals and BSPT ceramics.

	T_C (°C)	T_{r-t} (°C)	K_{33}^T	Loss	P_r (μC/cm^2)	E_c (kV/cm)	d_{33} (pC/N)	k_{33}
BSPT57 crystal[a]	402	349	3000	4%	23	13.7	1150	90%
BSPT64 ceramic[b]	450	/	2010	5%	32	20	460	/
PYNT40 crystal[c]	270	168	2700	2%	26.5	10	1200	88%
PMNT30 crystal	138	98	5000	0.5%	26	2.3	1600	89%
PZNT4.5 crystal	155	120	5000	0.5%	27	3	1800	90%
PZNT8 crystal	170	90	6000	0.5%	30	4	2500	93%

[a]This work.
[b]See Ref. 15.
[c]See Ref. 17.

are presented in Table I. For comparison, values are also given for various relaxor-PT crystals and polycrystalline BSPT ceramics.

In summary, rhombohedral BSPT(43/57) single crystals possess a high Curie temperature>400 °C and phase transition temperature>340 °C, with coercive fields greater than 13 kV/cm. Together with high piezoelectric coefficient d_{33} $\sim$1200 pC/N, coupling k_{33}>90%, and temperature-independent properties, BSPT single crystals are attractive candidates for the next-generation high-temperature, high-performance actuators and transducers.

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