Recent Developments in High Curie Temperature Perovskite Single Crystals

Shujun Zhang, Clive A. Randall, and Thomas R. Shrout

Abstract—**The temperature behavior of various relaxor-PT piezoelectric single crystals was investigated. Owing to a strongly curved morphotropic phase boundary, the usage temperature of these perovskite single crystals is limited by $T_{R\text{-}T}$—the rhombohedral to tetragonal phase transformation temperature—which occurs at significantly lower temperatures than the Curie temperature T_c. Attempts to modify the temperature usage range of $Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PZNT) and $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMNT) rhombohedral crystals ($T_c \sim 150$–$170°C$, $T_{R\text{-}T} \sim 60$–$120°C$) using minor dopant modifications were limited, with little success. Of significant potential are crystals near the morphotropic phase boundary in the $Pb(Yb_{1/2}Nb_{1/2})O_3$-$PbTiO_3$ (PYNT) system, with a $T_c > 330°C$, even though $T_{R\text{-}T}$ was found to be only half that value at $\sim 160°C$. Single crystals in the novel $BiScO_3$–$PbTiO_3$ system offer significantly higher T_cs $> 400°C$, while exhibiting electromechanical coupling coefficients $k_{33} > 90\%$ being nearly constant till the $T_{R\text{-}T}$ temperature around 350°C, which greatly increases the temperature range for transducer applications.**

I. Introduction

RELAXOR-BASED single crystals, such as PZNT and PMNT offer significant electromechanical coupling ($k_{33} > 90\%$) in contrast to $Pb(Zr,Ti)O_3$ (PZT) polycrystalline ceramics ($k_{33} \sim 75\%$), making them promising candidates for medical ultrasound transducers [1]–[6]. However, their relatively low Curie temperature ($T_c \sim 150$–$170°C$) and their substantially lower ferroelectric (rhombohedral to tetragonal) phase transition temperatures ($T_{R\text{-}T}$) $\sim$ 60–120°C), see Fig. 1, may limit their implementation in transducers in which thermal stability is desired in terms of dielectric and piezoelectric property variation and depolarization as a result of postfabrication processes. Among all the relaxor-PT systems, $Pb(Sc_{1/2}Nb_{1/2})O_3$–$PbTiO_3$ (PSNT), $Pb(In_{1/2}Nb_{1/2})O_3$–$PbTiO_3$ (PINT), and ternary system $Pb(In_{1/2}Nb_{1/2})O_3$–$Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PIMNT) possess relative high Curie temperatures near the morphotropic phase boundary (MPB) composition [7], [8]. Henceforth, numerous researches focused on these systems in single crystals form [9]–[14] in order to achieve high performance over a wide temperature range. For these systems, T_c is on the order of 260–310°C, but $T_{R\text{-}T}$ is still in the range of only 50–120°C. Furthermore, the growth of these systems is limited to the flux growth and with only moderate success using the solution Bridgman method.

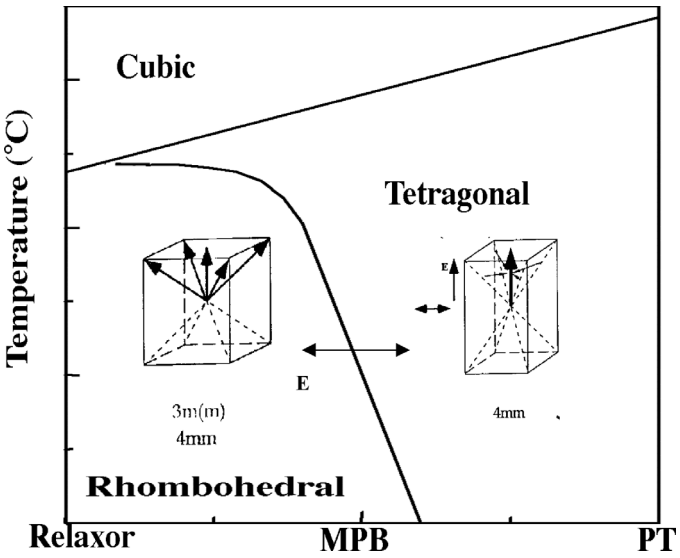

Fig. 1. A generic phase diagram for relaxor-PT systems depicting a strongly curved morphotropic phase boundary (after [2]).

In this work, three approaches were used to enhance the temperature usage of rhombohedral single crystal perovskites. First, dopant modifications (∼1 mole%) were made to PZNT and PMNT systems to examine the effect on both T_c and $T_{R\text{-}T}$. This approach was selected because of the commercial viability of these systems using Bridgman growth [5]. Second, crystal growth and characterization of compositions near the MPB in $Pb(Yb_{1/2}Nb_{1/2})O_3$–$PbTiO_3$ (PYNT) system, which possesses the highest T_c for a relaxor-PT system reported, being on the order of ∼350°C [15]–[22]. Third, the crystal growth of novel MPB compositions in the $Bi(Me)O_3$–$PbTiO_3$ ($Me = Sc^{3+}$, In^{3+}, Yb^{3+}) family [23]–[26]. Based on a perovskite tolerance factor T_c relationship, this new family of MPB systems has been shown to exhibit T_c's $> 450°C$ in polycrystalline ceramics [27]. Specifically, when $Me = Sc^{3+}$ (BSPT), a $T_c \sim 460°C$, has been reported for the MPB composition (PT content 64%) with properties comparable to soft PZT (DOD type II) [28]. Significant high level of piezoelectric activity and excellent temperature stability are thus anticipated for the single crystals in BSPT systems [25], [26].

II. Experimental

The high temperature flux method was used to grow a series of doped and novel perovskite compositions. The

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Pb_3O_4 or PbO-Bi_2O_3 was chosen as the flux with a typical flux/solvent mole ratio of 60:40 ∼ 70:30. Dopant modifications were fixed at ∼1 mole% as to not affect crystal growth with the potential of using the Bridgman technique. Further details of the flux crystal growth method used can be found in [16], [23], [24]. Typical crystal size for modified PZNT and PMNT was 10–20 mm, being on the order of 5–10 mm for PYNT and BSPT single crystals.

Crystals obtained were oriented using a real-time Laue system (Multiwire Laboratory, Ltd., Ithaca, NY) along the pseudocubic crystallographic axis [001] and [110]. Samples were polished and sputtered with gold electrodes. The dielectric properties as a function of temperature were determined using a multifrequency LCR meter (HP 4284A, Agilent Technologies, Palo Alto, CA) from room temperature to >500°C. Polarization and strain versus direct current (DC) field were determined using a modified Sawyer-Tower circuit and linear variable differential transducer (LVDT) driven by a lock-in amplifier (Model SR830, Stanford Research Systems Inc., Sunnyvale, CA). An impedance analyzer (HP 4194A, Agilent Technologies, Palo Alto, CA) was used to measure the resonance and antiresonance frequency of appropriate sample geometries, allowing calculation of the electromechanical coupling coefficients using the IEEE standard [29]. The longitudinal mode properties were measured on [001] oriented rods, and lateral mode properties were measured on [001] poled and [110] vibrating bars.

III. Results and Discussion

A. A or B Site Modified PZNT and PMNT Single Crystals

For all B-site modifications, including Fe^{3+}, Ni^{2+}, W^{6+}, Mo^{6+}, Zr^{4+}, etc., both $T_{R\text{-}T}$ and T_c were reduced on the order of 10–30°C, intrinsically enhancing the dielectric and piezoelectric properties. As reported in [6], the Fe-doped PZNT4.5 single crystals possessed higher piezoelectric and electromechanical properties than those of pure PZNT4.5 crystals, as compared in Table I, but $T_{R\text{-}T}$ shifted down to only 85°C. Fig. 2 gives the temperature dependence of the dielectric behavior for an A-site modified and undoped PMNT (30mole% PT) crystals. As shown, the temperature curve of the modified PMNT crystal was effectively shifted up a modest ∼10°C for both T_c and $T_{R\text{-}T}$, while the piezoelectric properties were still comparable to that of the pure one, as listed in Table I. Further increasing the dopant level offered no significant benefit in Curie temperature.

B. Relaxor-PT Systems with High Curie Temperature

The projected high T_c of PYNT crystals near the MPB composition is confirmed in Fig. 3 [17]. As shown, a T_c ∼ 330°C was observed, being significantly higher than any other relaxor-PT system. However, a dielectric anomaly also was observed at ∼160°C, corresponding to a $T_{R\text{-}T}$ phase transition, reflecting once again the strong curvature near the MPB composition.

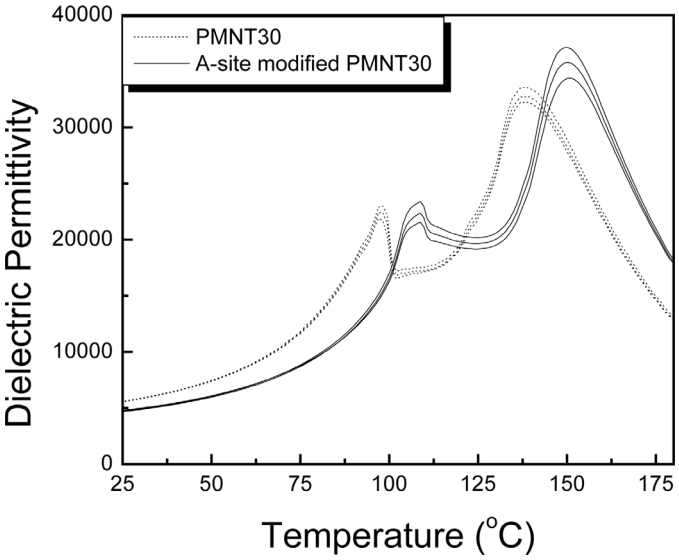


Fig. 2. Dielectric temperature dependence for A–site modified and undoped PMNT (PT content 30%) crystals.

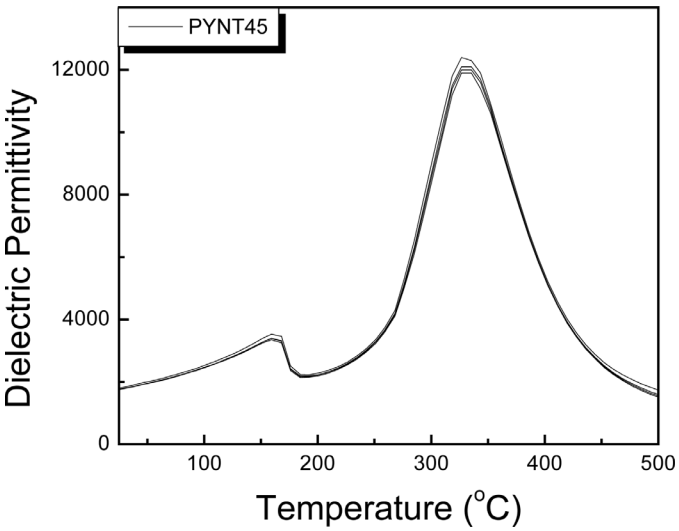
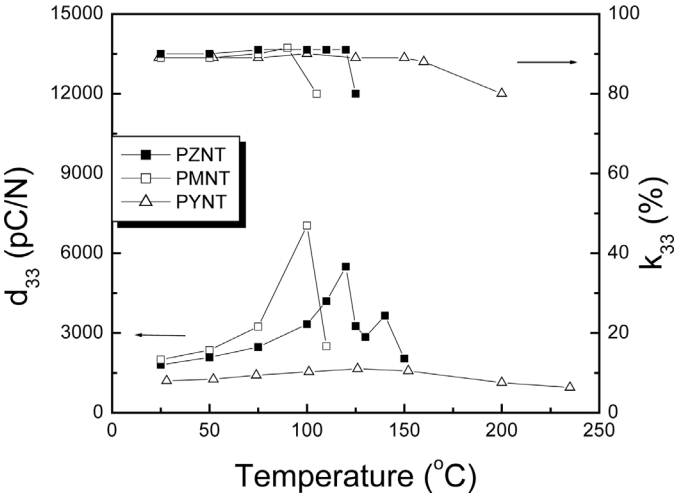


Fig. 3. Dielectric temperature dependence for a PYNT (45 mole% PT near MPB) single crystal (after [17]).

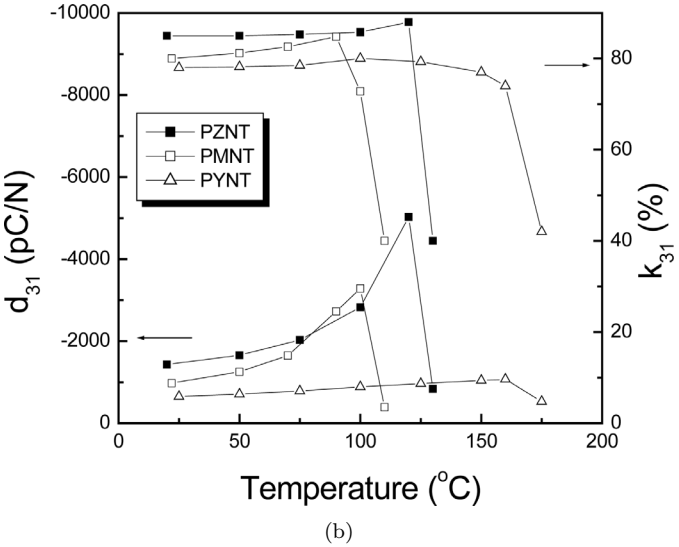
Fig. 4(a) and (b) present both the temperature dependence and temperature stability of the longitudinal and lateral piezoelectric and electromechanical coupling coefficients for various crystal systems, respectively. Though $T_{R\text{-}T}$ for PYNT is nearly half its T_c, these crystals offer a greater range of temperature usage than that for PZNT and PMNT, while maintaining high levels of piezoelectric activity. It also should be noticed in Table I that the coercive field of PYNT crystals was >10 kV/cm, which is much higher than those values of PZNT and PMNT crystals (∼2–3 kV/cm). This behavior is related to the higher Curie temperature allowing higher alternating current (AC) field driving.

TABLE I
PROPERTIES OF VARIOUS PEROVSKITE RHOMBOHEDRAL SINGLE CRYSTAL PIEZOELECTRICS.

Crystal	T_c (°C)	$T_{R\text{-}T}$ (°C)	E_c (kV/cm)	K_{33}^T	d_{33} (pC/N)	k_{33}	d_{31} (pC/N)	k_{31}
PZNT4.5	140	85	3.3	5200	2500–3500	93%	−1000	84%
B-site modified								
PMNT30	140	97	2	5100	2000	90%	−800	80%
PMNT30	150	110	2	4800	1600–2000	90%	−800	80%
A-site modified								
PZNT4.5	155	120	3.2	4400	2000–2200	90–91%	−900	83%
PYNT40	270	168	10	2700	1200	88%	−500	76%
PYNT45	325	160	12.5	2000	1200–2000	88–90%	−550	78%
BSPT57	402	349	13.7	3000	1200	90%	−560	77%
BSPT58	410	357	23.5	3200	1400	91%	−670	80%



(a)



(b)

Fig. 4. (a) Temperature dependence of longitudinal d_{33} and k_{33} for various Relaxor-PT systems, and (b) lateral d_{31} and k_{31}.

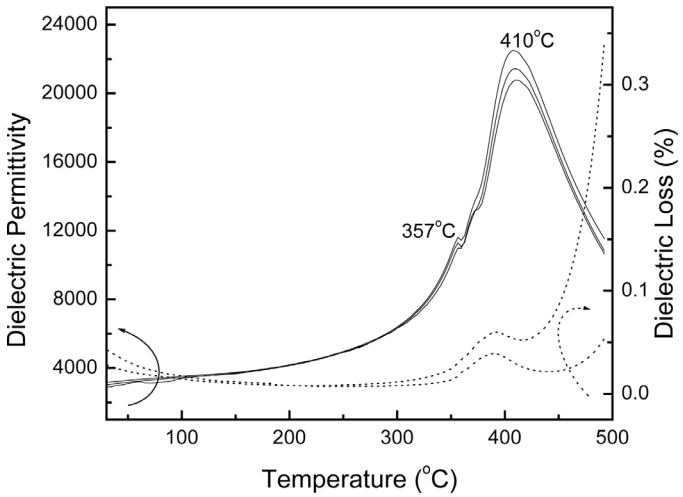
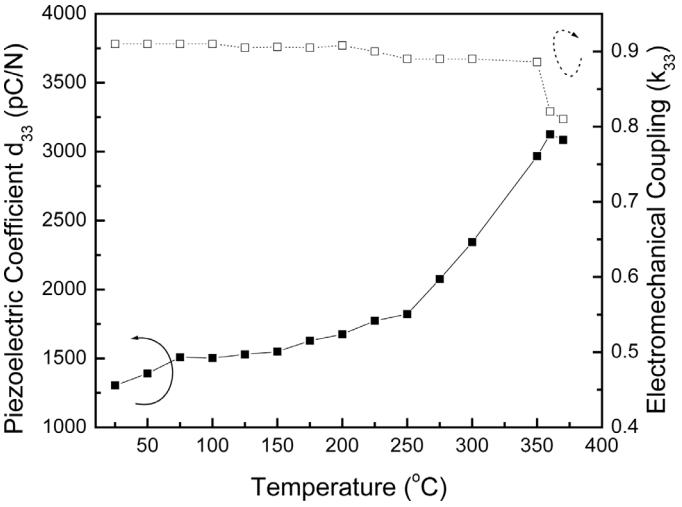


Fig. 5. Dielectric temperature dependence for a BSPT58 single crystal.

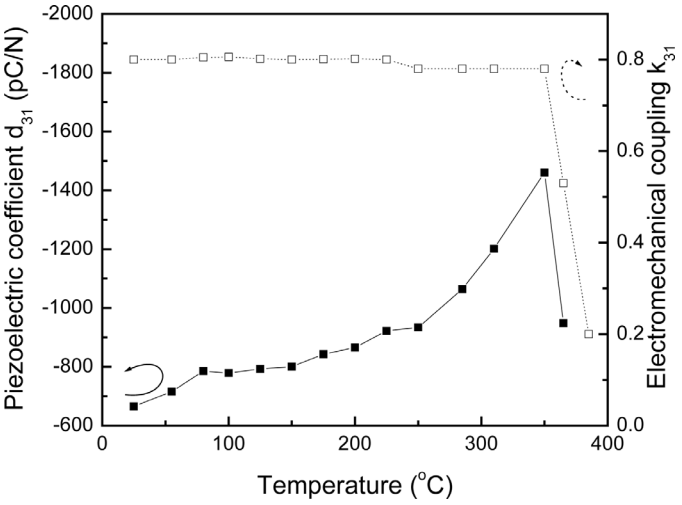
C. $Bi(Sc)O_3$–$PbTiO_3$ System

For crystals of BSPT58 with PT content at 58% near the MPB composition, the dielectric temperature behavior is given in Fig. 5. A T_c of 410°C was found being comparable to that reported in polycrystalline ceramics [28]. Though not evident for polycrystalline ceramics, a weak dielectric anomaly was observed at ∼357°C. This is again believed to be associated with a rhombohedral-tetragonal phase transformation. Compared to BSPT57 crystals [26], as listed in Table I, both the T_c and $T_{R\text{-}T}$ for BSPT58 crystals exhibit 8°C higher and the coercive field was found to be 23.5 kV/cm, also the dielectric and piezoelectric values were slightly increased, showing better properties than BSPT57 crystals.

Fig. 6(a) and (b) present the longitudinal and lateral piezoelectric coefficients and coupling factors for BSPT58 crystals as a function of temperature, respectively. As shown, the temperature stability of this system is far superior to the other perovskite crystals, maintaining a coupling coefficient $k_{33} \sim 91\%$ up to 200°C, which slightly decreases to 89% till 350°C, corresponding to the phase transition temperature $T_{R\text{-}T}$, which is decreased to 82% when



(a)



(b)

Fig. 6. (a) Temperature dependence of (a) longitudinal d_{33} and k_{33} (b) lateral d_{31} and k_{31} for BSPT58 single crystals.

the temperature is over $T_{R\text{-}T}$. Meanwhile, the piezoelectric coefficients increased from 1300 pC/N at room temperature to 3100 pC/N at 350°C. The same tendency was observed for the lateral properties for BSPT58 crystals, as shown in Fig. 6(b), with the lateral coupling factor k_{31} found to be 80% at room temperature being nearly constant till 350°C, while the lateral piezoelectric coefficient d_{31} increased from −670 pC/N at room temperature to −1500 pC/N at 350°C.

IV. Conclusions

The properties of various perovskite single crystals investigated in this work are tabulated in Table I in order of increasing transition temperature (T_c and $T_{R\text{-}T}$). Regardless of composition, domain engineered [001] rhombohedral relaxor-PT crystals offer high levels of piezoelectric activity with d_{33}'s > 1200 pC/N and electromechanical coupling factor k_{33} on the order of 90% for all systems. Attempts to expand the phase transition temperatures using minor dopant modification in PZNT and PMNT crystals were limited with B-site additions, generally reducing both T_c and $T_{R\text{-}T}$. Though the highest T_c relaxor-PT crystal system known, PYNT crystals exhibited a $T_{R\text{-}T}$ of only ∼160°C, which is still much lower than commercial PZT ceramics. The new bismuth-based perovskite MPB system-BSPT was found to possess a competitive temperature usage range to PZT ceramic (>100°C higher) while exhibiting the comparable piezoelectric properties as PZNT and PMNT single crystals. In addition, the coercive field was found to be much higher than those of PZNT, PMNT, and PYNT crystals. Fig. 7 presents the overall temperature usage range for the various relaxor-PT systems, including PZNT, PMNT, PSNT, PINT, PYNT, and BSPT systems. As shown, the strongly curved MPB ($T_{R\text{-}T}$) limits the temperature usage range of these systems far less than T_c. Of particular promise are crystals in the BSPT system, with T_cs > 400°C and $T_{R\text{-}T}$ ∼ 350°C, which offer great potential for the next generation high-temperature, high-performance transducer materials.

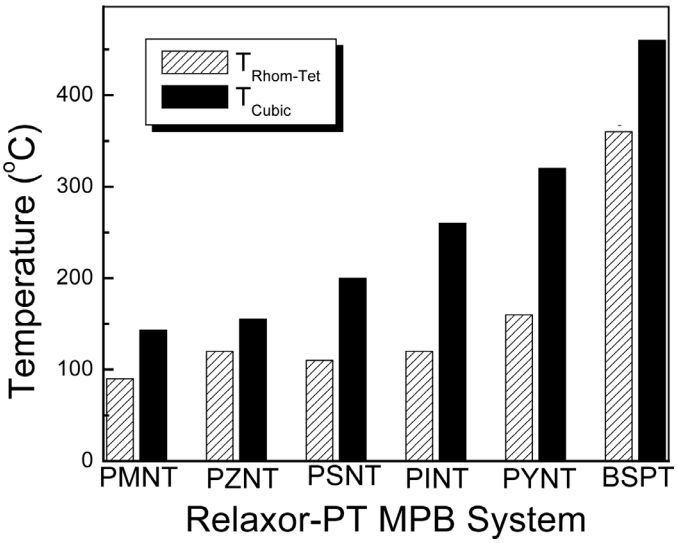


Fig. 7. Temperature usage range of various single crystal piezoelectrics.

Acknowledgments

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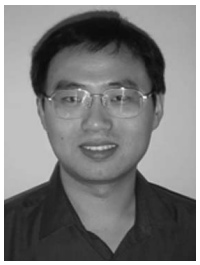

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