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Dielectric and piezoelectric properties of perovskite materials at cryogenic temperatures

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Dielectric and piezoelectric properties of perovskite materials including La modified Pb(Zr, Ti)O_3 (PZT's), (Ba, Sr)TiO_3 (BST) polycrystalline ceramics and Pb($Zn_{1/3}Nb_{2/3}$)O_3-PbTiO_3 (PZN-PT) single crystals were investigated for capacitor and actuator applications at cryogenic temperatures. PZTs were compositionally engineered to have decreased Curie temperatures (T_c) by La and Sn doping in order to compensate for the loss of extrinsic contributions to piezoelectricity at cryogenic temperatures. Enhanced extrinsic contributions resulted in piezoelectric coefficients (d_{33}) as high as 250 pC/N at 30 K, superior to that of conventional DOD Type PZT's ($d_{33} \sim 100$ pC/N). This property enhancement was associated with retuning to the MPB at cryogenic temperatures. 5/95 BST with a dielectric maximum at 57 K was investigated to obtain high electrostrictive properties or E-field induced piezoelectricity. Coupling coefficients (k_{31}) $\sim$ 25% comparable to those of the cryogenic PLZT piezoelectrics were observed at d.c. bias of 1.5 kV/cm and 50 K. Though significantly lower than the room temperature values, PZN-PT rhombohedral single crystals exhibited $d_{33} > 500$ pC/N at 30 K. *© 1999 Kluwer Academic Publishers*

1. Introduction

Piezoelectric materials with the perovskite structure such as $BaTiO_3$ and Pb(ZrTi)O_3 (PZT) have been widely used for capacitor and actuator applications near room temperature. Recently, special devices operational at cryogenic temperatures are required in applications such as actuators for adaptive optics [1] (e.g., next generation space telescope and low temperature capacitors), requiring high coupling (k_{ij}) and piezoelectric coefficients (d_{ij}). Compositionally, La modified lead zirconium titanate (PLZT) ceramics lie near the morphotropic phase boundary (MPB) between the tetragonal and rhombohedral phases [2]. In general, morphotropic phase boundary (MPB) compositions in ferroelectric ceramics exhibit anomalously high dielectric and piezoelectric properties as a result of enhanced polarizibility arising from the coupling between two equivalent energy states (i.e., the tetragonal and rhombohedral phases), allowing optimum domain reorientation during the poling process [3]. To achieve a high piezoelectric coefficient, MPB-based ceramics are further engineered by compositionally adjusting the Curie temperature (T_c) downward relative to room temperature. The effect of the Curie temperature on the piezoelectricity is clearly evident from previous work [4]. Enhanced piezoelectric activity of MPB-based ceramics results in "soft" piezoelectric ceramics. The room temperature properties of PZT ceramics are optimized by using compositions that correspond to the morphotropic phase boundary (MPB). Both undoped and commercially available hard and soft PZT compositions exhibit poor piezoelectric performance at temperatures below 100 K. For example, soft PZT (Navy Type VI) has a $k_{31} \sim 25\%$ and $-d_{31} < 50$ pC/N at 30 K compared to $\sim$35% and $\sim$250 pC/N, respectively, at room temperature [5]. The decrease in properties is attributed to a "freezing out" of extrinsic contributions (i.e., ferroelectric domain wall motion) to piezoelectricity [6]. A second possibility is the loss of domain orientation variants due to a shift in the MPB with decreasing temperature. In this paper, retuning the composition of soft PZT (through Zr/Ti variation) was investigated to determine the shift in MPB with decreasing temperature.

In addition to piezoelectric devices, an electrostrictive actuator has been developed. Electrostrictive materials exhibit strain that is proportional to the square of polarization induced in a material by an electric field [7]. Large electrostrictive strains are obtained in materials undergoing a phase transition between paraelectric to ferroelectric state. Thus, the operating temperature range of electrostrictors tends to be narrow ($\pm 15\,^\circ$C around the transition temperature) [8]. Naturally, an electrostrictor actuating at cryogenic temperatures requires that the paraelectric to ferroelectric transition takes place at cryogenic temperatures. In other words, a large strain can be obtained by compositional engineering to locate a dielectric maximum temperature ($T_{\max}$) at the cryogenic temperatures, resulting in maximum induced polarization and high electrostrictive strain [9]. By changing the Ba/Sr ratio in (Ba, Sr)TiO_3 (BST) ceramics [10], the transition temperature (Curie temperature) can be adjusted from $\sim$0 to 393 K. In this work, 5/95 BST ceramics with $T_{\max} \sim 57$ K was investigated, including electrostrictive behavior below $T_{\max}$ and correspondingly electric field induced piezoelectricity.

Recent developments have shown that relaxor-based ferroelectric single crystals, such as $Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$, exhibit high piezoelectric properties relative to PZT's such as $k_{33} \sim 94\%$ and $d_{33} > 2500$ pC/N at room temperature [4]. The effect results from an engineered domain state not achievable with conventional PZT ceramics. The engineered domain state (rhombohedral phase) shows high stability and very high piezoelectric activity at room temperature. Optimum crystallographic orientation was found to be pseudocubic $\langle 001\rangle$ for rhombohedral crystals such as (1-x)PZN-xPT ($x < 0.09$), exhibiting high strain and low hysteresis behavior due to an electric field induced phase transition [11]. As in the PZT system, there is also an MPB on the PZN-PT phase diagram [12]. However, because of a unique domain structure in single crystals, formulating compositions to lie on this boundary is not critical to room temperature piezoelectric properties [11]. From the room temperature properties of PZN-PT crystals, substantial piezoelectricity can be expected to remain at cryogenic temperatures.

It was the objective of this investigation to explore various materials such as modified PZT, BST ceramics, and PZN-PT single crystals for cryogenic actuators. The cryogenic piezoelectric properties of soft PLZT ceramics will be discussed with respect to temperature dependence of the MPB. Electric field induced piezoelectric properties for BST ceramics were also investigated as a function of temperature. The piezoelectric properties of two representative rhombohedral compositions, PZN-4.5% PT and 8% PT single crystals are discussed at cryogenic temperatures.

2. Experimental procedure

Piezoelectric ceramics investigated in this work were based on a commercially available PLZT (TRS Ceramics Inc., PA, USA) with $T_c \sim 190\,^\circ$C. The base composition was modified with a different Zr/Ti ratio to locate the MPB at cryogenic temperatures. The BST composition consisted of 5 mol% Ba and 95 mol% Sr designed with $T_{\max} \sim 57$ K. To prepare the various materials, stoichiometric amounts of constituent powders were first dispersed into a water slurry and mixed by vibratory milling. The powders were then pan-dried, followed by a high temperature calcination at 950 °C for PLZT and at 1275 °C for BST to form the desired perovskite phase. Phase purity of the calcined powders was verified by XRD. After calcination, the powders were remilled to reduce the particle size for sintering. Three wt % acrylic binders were added to the remilled powders, which were then granulated with an 80 mesh sieve. Sample disks 13 mm in diameter and 1 mm in thickness were pressed at 340 kg/cm^2. The samples were then sintered at 1300 °C for PLZT and at 1425 °C for BST. Gold electrodes were sputtered on all of the samples for dielectric and piezoelectric measurements. The PLZT samples were poled by applying 30 kV/cm at 50 °C for 5 min. All of the properties were measured 24 h after poling.

Single crystals of PZN-PT were grown using the high temperature flux technique. The polarization direction was parallel to the $\langle 001\rangle$ crystallographic direction. Experimental details are reported elsewhere [13].

Room temperature dielectric and piezoelectric coefficients (d_{33}) were measured using a Stanford Research LCR meter and a Berlincourt d_{33} meter, respectively. Dielectric, piezoelectric, and elastic properties as a function of temperature down to 30 K were measured from IEEE standard methods [14]. Paraelectric BST ceramics at room temperature were investigated as a function of electric field at cryogenic temperature ranges, $\pm 15\,^\circ$C $T_{\max}$. For cryogenic measurements, thin rectangular bar samples were used with dimensions appropriate for the d_{31} mode piezoelectric resonance. The d_{31} coefficient relates strain that was induced perpendicular to the polarization direction to an electric field applied parallel to the polarization direction. The samples were placed in an expander module with vacuum sealed electrical connections. A helium cryostat was used to cool the expander module and sample to 30 K. d_{33}'s at low temperature were estimated using the relationship $d_{33} \sim 2 \times |d_{31}|$ [8].

3. Results and discussion

3.1. PLZT piezoelectric ceramics

The dielectric and piezoelectric properties of MPB PLZT compositions at 300 and 30 K are listed in Table I. The Curie temperature (T_c) of the PLZT ceramics synthesized in this study ranged from 175 °C to 200 °C, lower than most commercial PZTs with $T_c > 300\,^\circ$C. Dopants (La and Sn) that shift the Curie point closer to room temperature are often used in PZT ceramics for high strain actuator applications. Lower Curie point materials tend to have a severe temperature dependence of piezoelectric properties and are susceptible to depoling, even though they have relatively high piezoelectric coefficients. However, if the material is used at cryogenic temperatures, the Curie temperature can be shifted well below 200 °C with no detrimental effects. Lower T_c indicates softer piezoelectrics, resulting in increased extrinsic contributions to piezoelectricity. Figs 1 and 2 present dielectric constant and d_{33} as a function of Zr content, respectively. At room temperature, the MPB was located at 57 mol% as evidenced by the peak at this composition. As shown in Figs 1 and 2, there is an apparent shift of 2 mol% in the MPB location on cooling to 30 K. The estimated d_{33} value of 250 pC/N at 30 K approaches the room temperature value for commercial hard PZTs (DOD Type I & III). Thus, the combined effect of a relatively low Curie temperature (180 °C) and cryogenic MPB tuning resulted in significant property improvements compared to conventional soft piezoelectrics ($d_{33} < 100$ pC/N at 30 K). Figs 3 and 4 show the temperature dependence

TABLE I Dielectric and piezoelectric properties of PLZT ceramics and PZN-PT single crystals at 300 K and 30 K

	$K_3^{T a}$		tan δ^a (%)		d_{33} (pC/N)		k_{31} (%)		
Composition	300 K	30 K	300 K	30 K	300 K	30 K	300 K	30 K	T_c^a (°C)
PLZT (300K MPB)	3870	1040	1.8	3.7	760	~220^b	39	32	175
PLZT (30K MPB)	3150	1220	1.4	3.4	570	~250^b	34	30	192
PZN-4.5% PT	4200	675	0.4	1.0	2000	~500^b	48	40	155
PZN-8% PT	4500	605	1.0	2.1	2500	~700^b	69	52	180

^{a} at 1 kHz
^{b}estimated values from d_{31}

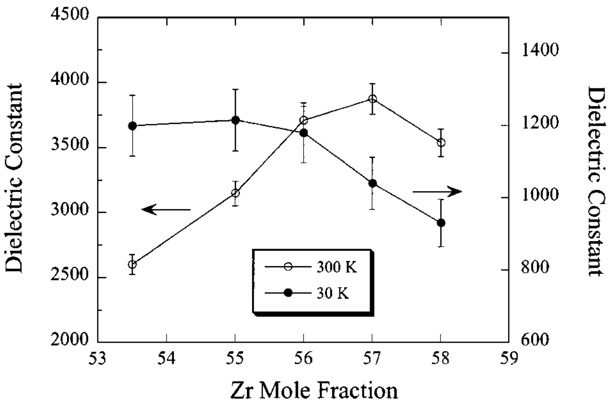

Figure 1 Dielectric constants of PLZT ceramics as a function of Zr content at 300 and 30 K.

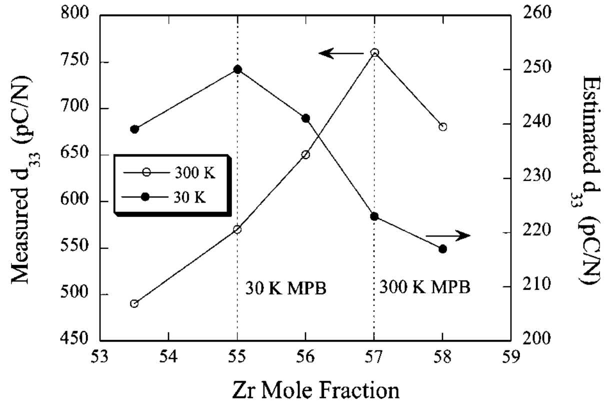

Figure 2 Piezoelectric coefficient (d_{33}) of PLZT ceramics as a function of Zr content at 300 and 30 K.

of dielectric constant, electromechanical coupling factor, and transverse piezoelectric coefficient for several PLZT compositions from 300 to 30 K. As shown in Fig. 3, ceramics close to the cryogenic MPB composition (Zr 55 mol%) had a less severe change in dielectric constant with temperature than did the samples close to the room temperature MPB. Materials compositionally engineered to lie on the MPB at room temperature have both rhombohedral and tetragonal phases coexisting, resulting in maximum polarization. Upon cooling the temperature to 30 K, a phase transition occurs from the mixed phase to rhombohedral phase with a subsequent shift of the MPB into the Ti-rich side of the phase diagram. In addition to MPB tuning, dopants that shift the Curie point closer to room temperature are often used in PZT ceramics for high strain actuator applications.

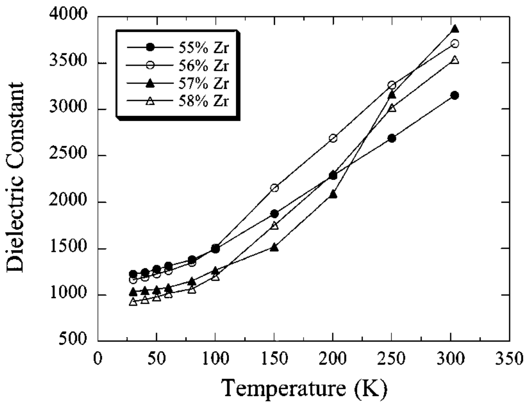

Figure 3 Temperature dependence of dielectric constants for PLZT ceramics.

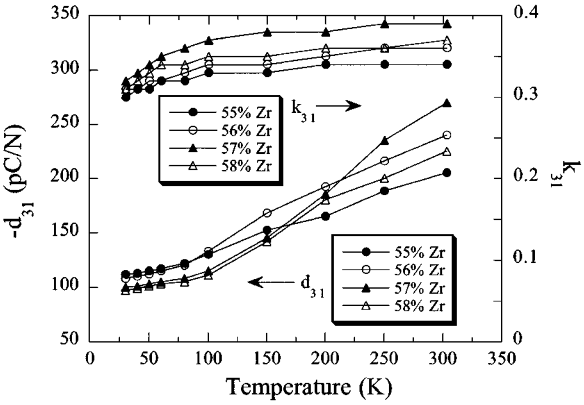

Figure 4 Temperature dependence of piezoelectric properties for PLZT ceramics.

3.2. BST ceramics

The dielectric maximum temperature observed for 5/95 BST was ~57 K. Dielectric constants and piezoelectric properties are shown in Figs 5 through 7 as a function of electric field and temperature. The maximum transverse coupling coefficient (k_{31}) ~ 25% was achieved at 1.5 kV/cm and 50 K, comparable to those of the cryogenic PLZT piezoelectrics. The transverse piezoelectric coefficients (d_{31}) below T_c ranged from ~−100 to −130 pC/N, similar to the cryogenic MPB PLZT composition. For electrostrictive ceramics, the longitudinal piezoelectric coefficient (d_{33}) can be estimated using the relationship $d_{33} \sim 3 \times |d_{31}|$ [8]. From the relationship, BST ceramics exhibited $d_{33} \sim 300$ to 400 pC/N near T_c, higher than the PLZT ceramics. The strain perpendicular to the electric field direction can

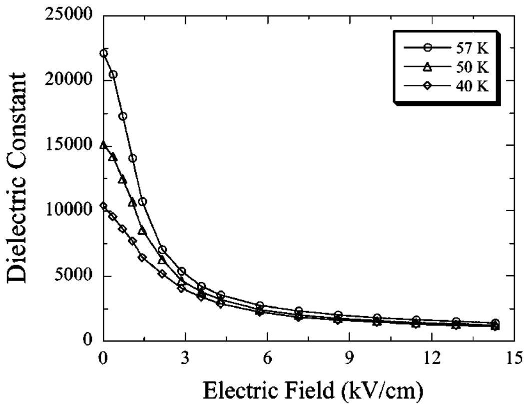

Figure 5 Dielectric constants of BST ceramics as a function of temperature and electric field.

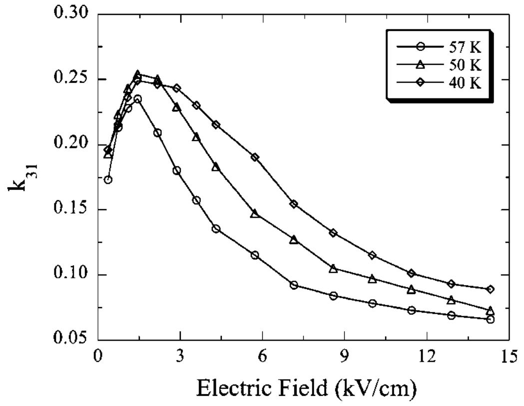

Figure 6 Electromechanical coupling coefficients of BST ceramics as a function of temperature and electric field.

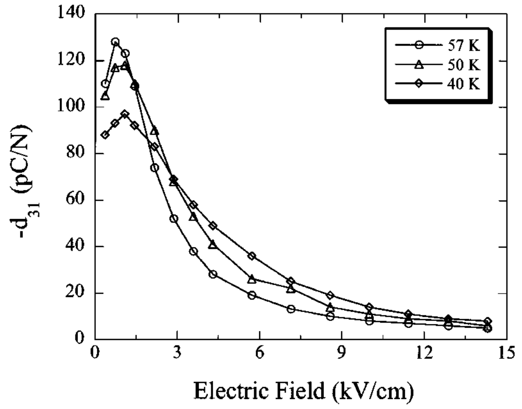

Figure 7 Piezoelectric coefficients of BST ceramics as a function of temperature and electric field.

be calculated by integrating the d_{31} curve as shown in Fig. 8. The calculated transverse strain was ~0.0062% at 14 kV/cm and 50 K. Thus, the longitudinal strain level estimated from the previous relationship was ~0.0186%. Considerably high piezoelectric performance was observed by locating T_c at a cryogenic temperature, but the working temperature range of BST with high piezoelectricity is narrow compared to that of piezoelectric materials. Upon considering electrostrictive behavior, direct strain measurement as a function of electric field is required in the future.

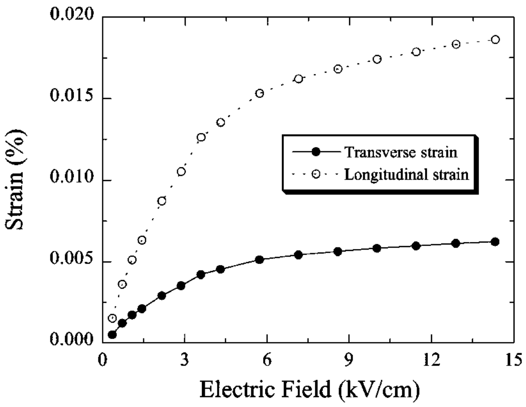

Figure 8 Estimated transverse and longitudinal strains of BST ceramics at 50 K.

3.3. PZN-PT single crystals

The dielectric and piezoelectric properties of rhombohedral PZN-4.5 and 8% PT single crystals are also listed in Table I. Figs 9 and 10 depict dielectric and piezoelectric properties of rhombohedral PZN-PT single crystals measured as a function of temperature from 300 K to 30 K. Large coupling coefficients ($k_{33} > 94\%$) and large piezoelectric coefficients ($d_{33} \sim 2500$ pC/N) were found at room temperature as shown in Table I. PZN-4.5% PT and 8% PT crystals were also found to possess high d_{31} values of ~−800 and ~−1200 pC/N,

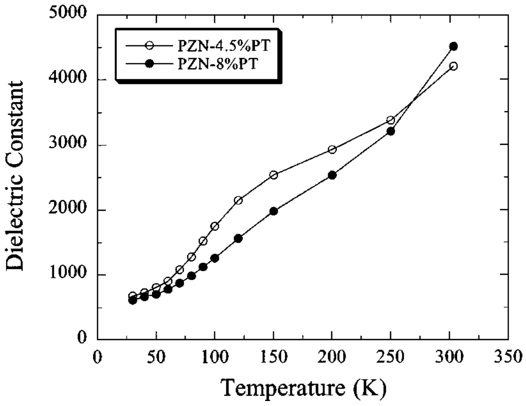

Figure 9 Temperature dependence of dielectric constants for PZN-PT single crystals.

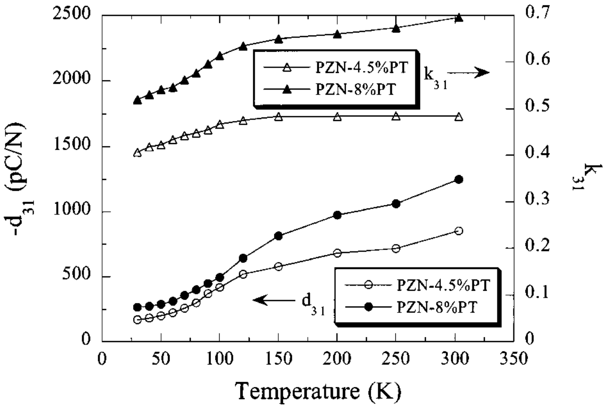

Figure 10 Temperature dependence of piezoelectric properties for PZN-PT single crystals.

respectively, at room temperature. Because the MPB of PZN-PT crystals is more dependent upon temperature, rhombohedral PZN-PT crystals are further away from the MPB at low temperature than is the case for PZT ceramics. Rhombohedral single crystals, therefore, exhibit no phase transition under cooling from room temperature because the low temperature form of crystal is rhombohedral structure. For cryogenic temperatures large decreases in properties were observed for both of compositions compared to the room temperature properties. Despite the decreases, substantial piezoelectricity remains at cryogenic temperatures. Domain reorientation did not occur because neighboring domains must involve an equal amount of induced distortion. The estimated d_{33}'s of $\sim$700 and 500 pC/N for PZN- 8% PT and 4.5% PT crystals, respectively, are substantially larger than those of most room temperature PZT's. These high piezoelectric properties resulted from the unique domain state suggested by Park and Shrout [11]. Although domain wall motion of single crystals was frozen out by cooling, there is still significant piezoelectricity because domain wall motion is not believed to contribute to the piezoelectric effect in the same manner as in PLZT ceramics [15]. High piezoelectric properties of PZN-PT single crystals at cryogenic temperatures are very important in investigating the origin of ultra-high piezoelectricity of engineered rhombohedral PZN-PT single crystals.

4. Conclusion

Compositionally, PZTs were engineered to increase extrinsic contributions to piezoelectricity at cryogenic temperatures by adjusting T_c below 200 °C and returning Zr/Ti ratios to locate the cryogenic MPB. The cryogenic MPB composition (55 mol% Zr) exhibited high piezoelectric properties such as $d_{33} \sim 250$ pC/N, corresponding to hard PZTs at room temperature. BST (5/95) ceramics with $T_{\max} \sim 57$ K exhibited high $d_{33} \sim 400$ pC/N near T_c, approaching the room temperature values for conventional PZT ceramics. Dramatic performance at cryogenic temperatures such as $d_{33} > 500$ pC/N was observed in the PZN-PT single crystals that had domain engineered rhombohedral structure.

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