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**Published article:**

Zeb, A and Milne, SJ (2013) *Dielectric and Piezoelectric Properties of (1-x)K<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub>-xBa(Ti<sub>0.8</sub>Zr<sub>0.2</sub>)O<sub>3</sub> Ceramics*. *Journal of the American Ceramic Society*, 96 (10). 3089 - 3093. ISSN 0002-7820

<http://dx.doi.org/10.1111/jace.12425>

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## **Dielectric and Piezoelectric Properties of $(1-x)\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-x\text{Ba}(\text{Ti}_{0.8}\text{Zr}_{0.2})\text{O}_3$ Ceramics**

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### **Abstract**

The properties of relaxor ceramics in the compositional series  $(1-x)\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-x\text{Ba}(\text{Ti}_{0.8}\text{Zr}_{0.2})\text{O}_3$  have been investigated. Values of  $T_m$ , the temperature of maximum relative permittivity, decreased from 380 °C at  $x = 0.0$  to below room-temperature for  $x > 0.7$ . Compositions  $x = 0.1$  and  $0.2$  were piezoelectric and ferroelectric. The maximum value of  $d_{33}$  piezoelectric charge coefficient, 130 pC/N, and strain, 0.14 %, occurred at  $x = 0.1$ . Piezoelectric properties of  $x = 0.1$  were retained after thermal cycling from room temperature to 220 °C, consistent with results from high-temperature x-ray diffraction indicating a transition to single-phase cubic at  $\sim 300$  °C.

## Introduction

Health and environmental concerns surrounding the use of lead oxide have stimulated extensive research into lead-free electroceramics [1-5]. A wide variety of possible alternative lead-free solid solutions to the market leading lead zirconate titanate (PZT) have been reported, many of which are based on the same perovskite  $ABO_3$  crystal structure. A common theme is to attempt to engineer a temperature-insensitive morphotropic phase boundary (MPB) between ferroelectric phases of differing symmetry in order to maximize ferroelectric and piezoelectric coefficients, in an analogous manner to the PZT system [6,7].

Examples of lead-free piezoelectrics include solid solutions of sodium niobate and potassium niobate,  $Na_{1-x}K_xNbO_3$ . At a composition,  $x \sim 0.5$  (abbreviated NKN),  $d_{33}$  values reach  $\sim 100$  pC/N [8]; NKN forms an end-member for a number of other solid solutions which have been investigated as potential lead-free piezoelectrics [8-14]. Binary solid solutions include NKN-LiTaO<sub>3</sub> with  $d_{33} \sim 200$  pC/N at compositions 5-6 % LiTaO<sub>3</sub> [4, 8]; similar properties exist in NKN-LiNbO<sub>3</sub> [10]. In both of these systems, the maximum  $d_{33}$  and coupling coefficient,  $k_p$ , values at 20 °C occur for levels of LiTaO<sub>3</sub> or LiNbO<sub>3</sub> substitution where the temperature of the polymorphic phase transition (PPT) between orthorhombic/monoclinic and tetragonal phases is lowered to  $\sim 20$  °C [4]. Phase coexistence at the PPT creates enhanced piezoelectric coefficients, but values degrade on heating the samples above room-temperature, due to disruption of the polar domain structure on cycling through the PPT [4]. This limits implementation as a working piezoelectric for device applications in which stable properties are required over a range of temperatures, although improved stability may be achieved by a slight increase in LiTaO<sub>3</sub> content [4]. **Textured ceramics based on (K, Na)NbO<sub>3</sub>-LiTaO<sub>3</sub>-LiSbO<sub>3</sub> have been reported using complex reactive template grain growth techniques;  $d_{33}$  values are around 400 pC/N [15].**

Compositionally modified BaTiO<sub>3</sub> ceramics have attracted interest as lead-free piezoelectrics and relaxor dielectrics [16-25]. High d<sub>33</sub> values, ~ 600 pC/N at 20°C have been reported for a composition, 0.5Ba(Zr<sub>0.2</sub>Ti<sub>0.8</sub>)O<sub>3</sub> - 0.5(Ba<sub>0.7</sub>Ca<sub>0.3</sub>)TiO<sub>3</sub> [22], competitive with PZT. The Ca<sup>2+</sup> and Zr<sup>4+</sup> substituents modify the temperature of the various polymorphic phase transitions in BaTiO<sub>3</sub> such that a boundary between rhombohedral and tetragonal phase develops at this composition [22]. Rietveld refinement of high resolution x-ray diffraction indicated mixed tetragonal and rhombohedral phases at 20 °C, and single phase cubic at 100 °C [23]. The high d<sub>33</sub> values have been interpreted on the basis of a combination of polarisation rotation and extension, the latter arising from the relatively low Curie point, T<sub>c</sub> ≤ 100 °C, at which the paraelectric cubic phase forms [21]. The replacement of BZT with Ba(Sn<sub>0.12</sub>Ti<sub>0.88</sub>)O<sub>3</sub>, gave a d<sub>33</sub> of ~ 530 pC/N with a T<sub>c</sub> of ~ 70 °C [24]; comparable properties were reported for Ba(Hf<sub>0.2</sub>Ti<sub>0.8</sub>)O<sub>3</sub>- Ba<sub>0.7</sub>Ca<sub>0.3</sub>)TiO<sub>3</sub> [25].

Similarities in the electronic structures of Pb<sup>2+</sup> and Bi<sup>3+</sup> ions have attracted interest in Bi-based perovskites. Systems include Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub> - BaTiO<sub>3</sub> with d<sub>33</sub> = 125 pC/N and k<sub>p</sub> = 0.55 at a phase boundary between rhombohedral and tetragonal phases [26]. Although T<sub>c</sub> at the optimum composition is ~ 280 °C, a depolarising transition at ~ 150 °C limits the temperature range of operation [1, 27]. Solid solutions Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub>- K<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub> offer maximum d<sub>33</sub> values of ~ 200 pC/N for ~20 mol % KBT at a rhombohedral-tetragonal phase boundary, but again a depolarising transition occurs at ~ 150 °C [2, 28].

This paper reports the properties of a novel compositional series, (1-x)K<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub>- xBa(Ti<sub>0.8</sub>Zr<sub>0.2</sub>)O<sub>3</sub>, (KBT-BZT). The KBT end-member is tetragonal at room-temperature and a relaxor dielectric, with T<sub>m</sub> ~ 380 °C [28, 29]. The BZT end-member composition is cubic at room-temperature, and lies close to the ‘pinch - point’ where the temperatures of cubic-tetragonal, tetragonal-orthorhombic, and orthorhombic–rhombohedral phase transitions coincide [30].

## Experimental

Ceramics in the KBT-BZT system  $(1-x)\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-x\text{Ba}(\text{Ti}_{0.80}\text{Zr}_{0.20})\text{O}_3$ , were fabricated by a solid state processing route. The starting powders were  $\text{BaCO}_3$  (Alfa Aesar, 99 %),  $\text{TiO}_2$  (Sigma Aldrich, 99.9 %),  $\text{ZrO}_2$  (Sigma Aldrich, 99%),  $\text{Bi}_2\text{O}_3$  (Sigma Aldrich, 99.9%) and  $\text{K}_2\text{CO}_3$  (Sigma Aldrich, 99%). The powders were dried overnight in an oven at 200 °C and then weighed according to the stoichiometric ratios. All batches were mixed by ball milling with zirconia grinding media in isopropanol for 24 h. After drying and sieving through a 300  $\mu\text{m}$  mesh nylon sieve, powders were calcined at 1000 °C for 4 h in closed alumina crucibles with a heating ramp rate of 300 °C/h. The calcined powders were re-milled for 24 h with addition of 1wt% binder (Ciba Glascol HA4). Powders were compacted into pellets, 10 mm diameter and 1.5 mm thickness by uniaxial pressing in a steel die at 65 MPa, followed by cold isostatic pressing at 300 MPa. During sintering, the pellets were embedded in calcined powder of the same chemical composition; sintering was conducted in closed alumina crucibles at dwell temperatures ranging from 1060 °C-1350 °C for 4-6 h.

An X-ray diffractometer (Bruker D8,  $\text{Cu-K}\alpha \sim 1.5406\text{\AA}$ ) was used to determine phase content of powders obtained by crushing and grinding sintered pellets; the powders were annealed at 500 °C to reduce strain introduced by the grinding process. For electrical characterization, the pellets were ground to reduce thickness to 0.8 mm, and silver paste (Agar scientific) was applied to parallel polished surfaces; electroded pellets were fired to 550 °C for 15 min with heating rate of 15 °C/min. Measurements of dielectric relative permittivity,  $\epsilon_r$ , and loss tangent,  $\tan \delta$ , as a function of temperature (25 °C - 600 °C) and frequency (1 kHz - 1 MHz) were performed using an impedance analyzer (HP Agilent, 4192 Hewlett Packed) linked to a computerized data acquisition system. Piezoelectric  $d_{33}$  charge coefficients were measured on poled samples using the Berlincourt technique (Piezotest

meter PM 300). The samples were poled in a silicon oil bath at 50 °C for 10 min with an applied electric field of ~ 4 kV/mm. Strain – field measurements (S-E) were performed at room-temperature using a Precision LC analyzer (Radiant Technologies Inc.). Polarisation-electric field response was measured using a triangular waveform (1s duration pulse). The densities of sintered ceramic pellets were 90-92 % of theoretical, as determined from geometric measurements using values of theoretical density obtained by least square refinement of XRD data.

## Results and discussion

X-ray diffraction patterns of the  $(1-x)\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-xBa}(\text{Ti}_{0.80}\text{Zr}_{0.2})\text{O}_3$  compositional series are shown in Figure 1a. The KBT end-member ( $x = 0$ ) was tetragonal [28] and BZT ( $x = 1$ ) cubic perovskite [30]. The tetragonal lattice parameters changed from  $a = 3.907 \text{ \AA}$  and  $c = 3.997 \text{ \AA}$  at  $x = 0$ , to  $a = 3.926 \text{ \AA}$  and  $3.997 \text{ \AA}$  for  $x = 0.05$ . The KBT-BZT solid solutions,  $0.5 \leq x \leq 1$  had single-phase cubic XRD patterns, with lattice parameter  $a$  increasing to  $4.033 \text{ \AA}$  at  $x = 1$ , Figure 2. Faint additional reflections appeared either side of the 100 and 200 cubic XRD peaks for  $0.1 \leq x \leq 0.4$ , as highlighted in Figure 1b. Comparisons of diffraction patterns in terms of trends in positions of the peaks in the 200<sub>c</sub> region, and their relative intensity, infer that the extra reflections signify a phase coexistence region of tetragonal and pseudo-cubic phases for  $0.1 \leq x \leq 0.4$ .

Plots of relative permittivity,  $\epsilon_r$ , versus temperature indicated that KBT-BZT solid solutions were relaxor dielectrics, Figure 3. The  $\epsilon_r$  - T plot for KBT ( $x = 0$ ) showed diffuse peaks, with a temperature of maximum dielectric constant,  $T_m$ , ~380 °C, (1 kHz), and only a slight variation in  $T_m$  with changing radio frequency ( $T_m(1 \text{ kHz}) - T_m(1\text{MHz}) = 20 \text{ }^\circ\text{C}$ ), consistent with literature reports [28]. The  $\epsilon_r$  - T plot for  $x = 0.05$  was similar to KBT, but

$T_m$  was slightly lower, 370 °C. A much stronger frequency-dependence in  $T_m$  values was observed for compositions  $x \geq 0.1$ , Figure 4. This, together with the relaxation in  $\tan \delta$  at temperatures around  $T_m$ , is typical of a relaxor dielectric. The change in frequency-dependence of  $T_m$  as the BZT constituent increased from  $x = 0.05$  to 0.1 correlates to the emergence of the pseudo-cubic phase as the dominant phase in XRD patterns (Figure 1b).

Room temperature relative permittivity was  $\sim 700$  for  $x = 0.1$ , and  $\sim 1000$  for  $x = 0.2$  (1 kHz); with  $\tan \delta$  (20 °C) values of 0.06 - 0.07 (1 kHz) for  $x = 0.1 - 0.2$ , higher values,  $\tan \delta \sim 0.1$ , were recorded for compositions  $0.3 \leq x \leq 0.6$  due to the effects of the loss tangent peak as  $T_m$  decreased. Peak values of relative permittivity decreased from  $\epsilon_{r \max} \sim 4000$  (1 kHz) for  $x \leq 0.2$ , to  $\sim 3000$  for  $0.2 < x \leq 0.5$ , and to  $\leq 1500$  at  $x \geq 0.6$ , Figure 3. The trend of falling  $T_m$  with increasing  $x$  was such that  $T_m$  decreased to below room temperature for  $x > 0.7$ , Figure 5 (and relaxor behaviour was not investigated).

Various models have been proposed to account for relaxor behaviour; it is generally considered to arise from chemical or structural disorder associated with the existence of polar nanoregions [31-34]. Relaxor properties of BaTiO<sub>3</sub>-BaZrO<sub>3</sub> solid solutions have been studied by several groups [16, 17, 35-38]: a change from normal ferroelectric to relaxor behaviour occurs as the Zr content in Ba(Ti<sub>1-y</sub>Zr<sub>y</sub>)O<sub>3</sub> increases to  $0.25 \leq y \leq 0.5$ . Unlike classic relaxors such as Pb(Mg,Nb)O<sub>3</sub> both B-site ions in Ba(Ti<sub>1-y</sub>Zr<sub>y</sub>)O<sub>3</sub> are of the same valence. An EXAFS study (extended x-ray absorption fine structure) of Ba(Ti<sub>1-y</sub>Zr<sub>y</sub>)O<sub>3</sub> compositions identified aggregation of non-polar ZrO<sub>6</sub> units inferring relaxor behaviour was due to random elastic fields created by BaZrO<sub>3</sub> inclusions [38].

In the present KBT - BZT solid solutions, a combination of mixed valence substitution on the A sites, and isovalent substitution on the B sites of the perovskite ABO<sub>3</sub> lattice may be anticipated from the basic solid solution mechanism: (K<sub>0.5-0.5x</sub>Bi<sub>0.5-0.5x</sub>Ba<sub>x</sub>) (Ti<sub>1-</sub>

$x\text{Zr}_x\text{O}_3$ . Relaxor behaviour may relate to  $\text{ZrO}_6$  ordering in the manner reported for BZT [38], but with an additional contribution arising from mixed valence A-site occupancy. The changeover in dielectric properties as composition approaches KBT to a weak frequency dependence suggests the level of  $\text{Zr}^{4+}$  substitution is insufficient at  $x \leq 0.05$  to form  $\text{ZrO}_6$  clusters of sufficient size or number to give a classic relaxor response.

Only compositions  $x = 0.1- 0.2$  were ferroelectric, as evidenced by the polarisation-electric field responses shown in Figure 6. Remanent polarization,  $P_r$ , values were 12 -14  $\mu\text{C}/\text{cm}^2$  and coercive fields,  $E_c \sim 30 \text{ kVcm}^{-1}$  and  $\sim 20 \text{ kV/cm}$  for  $x = 0.1$  and  $0.2$  respectively. Broadening of the ferroelectric P-E hysteresis loops was consistent with the relatively high  $\tan \delta$  values.

Strain-electric field responses of  $x = 0.1$  and  $0.2$  compositions are shown in Figure 7. Maximum strains were  $\sim 0.14 \%$  at  $x = 0.1$ , with  $d_{33}^* \sim 200 \text{ pC/N}$ , Figure 7. Negative strains recorded for  $x = 0.1$  and  $0.2$  samples were consistent with piezoelectric behaviour. Remaining compositions were non-piezoelectric, with electrostrictive strains of  $< 0.08 \%$ . Trends in measured  $d_{33}$  values from composition  $x = 0$  to  $x = 0.5$  are shown in Figure 8; values increased from  $44 \text{ pC/N}$  for KBT to a maximum of  $130 \text{ pC/N}$  at  $x = 0.1$ , decreasing to  $\sim 100 \text{ pC/N}$  for  $x = 0.2$  and then dropping sharply at  $x > 0.2$ , Figure 8. Hence the optimum ferroelectric and piezoelectric properties in KBT-BZT occur around the changeover in phase content from tetragonal to mixed phase (tetragonal and pseudocubic) at  $x = 0.1$ . A future detailed crystallographic study would clarify the symmetry of the ferroelectric phase(s) in this region.

As discussed in the Introduction, few lead-free piezoelectrics retain their properties on thermal cycling to  $> 200 \text{ }^\circ\text{C}$  in the manner of PZT. The thermal stability of  $d_{33}$  for  $x = 0.1$  was investigated by measuring  $d_{33}$  before and after heating a poled sample. The  $d_{33}$  value

after heating to 220 °C was within 10 % of the original value, whereas significant depolarisation occurred after heating to 250 °C. Analysis of a powdered sample of the  $x = 0.1$  ceramic by *in-situ* high-temperature x-ray diffraction indicated a transition from mixed phase to single phase cubic at  $\sim 300$  °C, Figure 9, similar to the temperature  $T_m$  recorded from permittivity plots. Hence depolarization occurs  $\sim 80$  °C below  $T_m$  (PZT depolarizes well below its  $T_c$  of  $\sim 390$  °C).

The  $d_{33}$  value of  $x = 0.1$ , at a ceramic density of only 92 % theoretical, is higher than a number of other KBT-based perovskites such as KBT- BiScO<sub>3</sub> or KBT-BiFeO<sub>3</sub> [39, 40];  $d_{33}$  values are comparable to NBT-BaTiO<sub>3</sub> but lower than NKN-LT with  $d_{33} \sim 200$  pC/N [4, 41]. The new material exhibits a higher depolarization temperature than NBT-BT and NBT-KBT which depolarize at  $\sim 150$  °C [2,27,28], or BaTiO<sub>3</sub> with a  $T_c$  of  $\sim 130$  °C [6]. Although KBT-BZT has much lower  $d_{33}$  values than BCT-BZT ceramics, the latter depolarise at  $< 100$  °C [22]. Overall, the results infer that this region of the  $K_{0.5}Bi_{0.5}TiO_3$ -BaTiO<sub>3</sub>- BaZrO<sub>3</sub> phase diagram offers promise in the search for lead-free piezoelectrics which retain piezoelectric activity to elevated temperatures.

## Conclusions

Ceramics in the system  $(1-x)K_{0.5}Bi_{0.5}TiO_3$ - $xBa(Ti_{0.8}Zr_{0.2})O_3$  were fabricated by conventional mixed oxide processing. Dielectric measurements showed typical relaxor behaviour for  $x > 0.05$ . The temperature of peak relative permittivity,  $T_m$ , decreased with increasing levels of  $Ba(Ti_{0.8}Zr_{0.2})O_3$ , with  $T_m \sim 380$  °C at  $x = 0$ , decreasing to  $T_m < 20$  °C for  $x > 0.7$ . A narrow range of compositions,  $x = 0.1$  and  $0.2$ , were ferroelectric. The maximum piezoelectric charge coefficient  $d_{33}$  occurred at  $x = 0.1$ , with  $d_{33} = 130$  pC/N and maximum

piezoelectric-field strain 0.14 % ( $d^*_{33} = 200$  pC/N). Unlike a number of other lead-free piezoelectrics, the piezoelectric properties were retained after thermal cycling to  $>200$  °C.

### **Acknowledgements.**

A Zeb wishes to thank the Pakistan government for a scholarship. Both authors wish to thank T. Comyn, T. Stevenson and A. Qasir for advice with electrical measurements.

## List of Figure Captions

Figure 1. (a) X-ray diffraction patterns for  $(1-x)\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-x\text{Ba}(\text{Ti}_{0.8}\text{Zr}_{0.2})\text{O}_3$  at room temperature; (b) highlighted  $002_c$  region, arrows indicate trends in peaks attributed to a tetragonal phase coexisting with a pseudo-cubic phase for  $0.1 \leq x \leq 0.5$ .

Figure 2. Lattice parameters for  $(1-x)\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-x\text{Ba}(\text{Ti}_{0.8}\text{Zr}_{0.2})\text{O}_3$  as a function of  $x$ .

Figure 3. Relative permittivity and loss tangent versus temperature at different radio frequencies for: (a)  $x=0$ ; (b)  $x=0.05$ ; (c)  $x=0.1$ ; (d)  $x=0.4$ .

Figure 4. Temperature of maximum permittivity,  $T_m$ , versus log frequency for  $x=0$  to  $x=0.4$ .

Figure 5. Temperature of maximum relative permittivity ( $T_m$ ) as function of BZT content ( $x$ ).

Figure 6. Polarisation – electric field response for  $x = 0.05, 0.1, 0.2, 0.3$ .

Figure 7. Strain-electric field (S-E) response for  $x = 0.1$  and  $0.2$ .

Figure 8. Charge coefficient  $d_{33}$  for  $x = 0$  to  $0.5$ .

Figure 9. Temperature-variable X-ray diffraction data for  $x=0.1$  showing transition to single-phase cubic pattern at  $\geq 300$  °C.

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