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Lead-free Piezoelectric $K_{0.5}Bi_{0.5}TiO_3$ - $Bi(Mg_{0.5}Ti_{0.5})O_3$ Ceramics with Depolarisation Temperatures up to ~ 220 °C.

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Abstract

The properties of $K_{0.5}Bi_{0.5}TiO_3$ -rich ceramic solid solutions in the system $(1-x)K_{0.5}Bi_{0.5}TiO_3$ - $xBi(Mg_{0.5}Ti_{0.5})O_3$ are reported. The highest values of piezoelectric charge coefficient, d_{33} , and field-induced strains are found in compositions located close to a compositional boundary between single-phase tetragonal and mixed tetragonal + cubic perovskite phases. Maximum d_{33} values were ~ 150 pC/N for $x = 0.03$, with positive strains of ~ 0.25 %; the $x = 0.04$ composition had a $d_{33} \sim 133$ pC/N and strain of 0.35 % (bipolar electric field, 50 kV/cm, 1Hz). Depolarisation temperature T_d is an important selection criterion for any lead-free piezoelectric for actuator or sensor applications. A T_d of ~ 220 °C for $x = 0.03$ is ~ 100 °C higher than for the widely reported $Na_{0.5}Bi_{0.5}TiO_3$ - $BaTiO_3$ system, yet d_{33} values and strains are similar, suggesting the new material is worthy of further attention as a lead-free piezoceramic for elevated temperature applications.

Introduction

In the search for lead-free piezoelectric materials, considerable attention has been directed toward solid solutions based on sodium bismuth titanate $Na_{0.5}Bi_{0.5}TiO_3$ (NBT),

notably, $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-BaTiO}_3$ (NBT-BT) and $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT-KBT) [1-6].

Large electromechanical strains, in the range 0.3-0.45 % at electric field amplitudes of 80 kV/cm (bimodal) have been reported for NBT-based binary solid solutions, and hence these materials have been the subject of intense research activity [7, 8]. The maximum values of piezoelectric charge coefficient d_{33} are reported to be in the range 122-176 pC/N for NBT-BT near its morphotropic phase boundary (MPB). For the related NBT-KBT system, $d_{33} \sim 140\text{-}190$ pC/N [9]. Both NBT-BT and NBT-KBT display inflections in plots of relative permittivity-temperature ($\epsilon_r\text{-T}$) well below the dielectric peak temperature: these inflections are associated with depolarisation and loss of piezoelectric activity. For example, NBT-BT loses its piezoelectric properties at a depolarisation temperature, T_d , ~ 100 °C [3,9]. Numerous piezoelectric applications require operating temperatures above 100 °C, for example actuators for injection valves in diesel engines operate at ~ 150 °C [10]. The practical upper working temperature of a piezoelectric (including PZT) lies some way below its T_d due to a sharp decline in piezoelectric activity as T_d is approached. Therefore there is a need to pursue research into new high-strain lead-free piezoelectrics with depolarisation temperatures and practical operating limits higher than those of existing NBT-based ceramics. Indeed, temperature stability of properties is considered to be one of the most important issues for the development of new lead-free piezoelectric ceramics [10].

In an earlier investigation of $\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ -based solid solutions we found $(1-x)\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-xBa}(\text{Ti}_{0.8}\text{Zr}_{0.2})\text{O}_3$ (KBT-BZT) to exhibit piezoelectric activity, with a maximum d_{33} piezoelectric charge coefficient of 130 pC/N and corresponding positive strains of 0.14 % (bipolar, 60 kV/cm, 1 Hz) [11]. Interestingly, the piezoelectric properties were retained after thermal cycling from room temperature to 220 °C, although definitive analysis of T_d by in-situ measurements at elevated temperatures was unavailable [11].

Here we summarise the dielectric, ferroelectric and piezoelectric properties of a very promising alternative KBT-based solid solution: $(1-x)\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-x\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ [12]. The KBT and BMT end-members have recently been demonstrated to be key components in the fabrication of relaxor dielectrics that offer high-temperature, stable performance in relative permittivity to ≥ 300 °C [13-16]. Thus the upper operating temperature of the dielectric is far higher than for traditional ferroelectric BaTiO_3 - based ‘high-temperature’ capacitor materials. In the present communication we concentrate on the $\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ -rich region of the binary $\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ - $\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ system. The materials have d_{33} values comparable to NBT-BT or NBT-KBT at their MPB regions. A distinctive feature of the new piezoelectric is the finding that depolarisation temperatures T_d are ~ 100 °C higher than for NBT-BT, and ~ 50 °C higher than for NBT-KBT piezoceramics, making the new material of interest for actuator and sensor applications at elevated temperatures.

Experimental procedure

Ceramic samples in the binary system $(1-x)\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3-x\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ [KBT-BMT] $0 \leq x \leq 0.12$ were fabricated by conventional solid state processing. The initial raw powders: K_2CO_3 (Sigma Aldrich, 99% purity, St. Louis, MO), Bi_2O_3 (Sigma Aldrich, 99.9%), MgO (Alfa Aesar, 99.9%) and TiO_2 (Sigma Aldrich, 99.9%) were dried overnight at 250 °C and cooled to room temperature in a desiccator under reduced pressure, and subsequently weighed in the stoichiometric ratios. The powders were mixed using ball milling with zirconia grinding media in isopropanol for 24 h. The dried mixed powders were sieved through a 300 μm mesh nylon sieve and calcined at 850 °C for 3 h in closed alumina crucibles with heating and cooling ramp rates of 5 °C/min. The calcined powders were sieved and milled again for 24 h, and 1 wt% binder was introduced (Ciba Glascol HA4: Ciba speciality Chemicals, Bradford, UK). The sieved powders were pressed into pellets of 10 mm diameter and ~ 1.5 mm thickness in a steel die at a uniaxial pressure of ~ 100 MPa, followed by cold isostatic pressing at 200

MPa. For sintering, the pellets of each composition were embedded in a powder of their respective composition in a closed alumina crucible. Before reaching sintering temperatures, the binder was burn out by slowly heating at 50 °C/h to 550 °C; then the samples were heated at a ramp rate 300 °C/h to sintering temperatures which were optimised to: 1050 °C ($x = 0-0.02$); 1065 °C ($x = 0.03-0.04$); 1070 °C ($x = 0.06-0.08$); 1100 °C (0.1-0.12). Each composition exhibited a narrow temperature range for densification (close to its melting temperature).

The phase content was determined by using X-ray powder diffraction (XRD, Bruker D8, Cu, $K\alpha \sim 1.5406 \text{ \AA}$): crushed sintered pellets were analysed (scan speed, $1^\circ/\text{min}$). Unit cell lattice parameters were obtained by least square refinement using d-spacings obtained by peak fitting (X'pert Highscore Plus software). To form the electrodes for electrical testing, the sintered pellets were ground to $\sim 1 \text{ mm}$ thickness and silver paste (Agar Scientific) was applied to opposite parallel faces; the pellets were then heated in a furnace at 550 °C for 10 min. Microstructural information on polished and thermally etched samples was obtained by scanning electron microscopy (Hitachi SU 8230 cold FESEM, Japan). Average grain size was estimated by the linear intercept method. Density was measured geometrically and relative densities were calculated based on theoretical densities estimated from unit-cell lattice parameters and assumed cell contents. Relative permittivity and loss tangent were recorded as a function of temperature using an impedance analyser (HP Agilent, 4192A Hewlett Packard, Santa Clara, CA), from 25 °C to 600 °C. For piezoelectric testing, all samples were poled in silicone oil by applying a dc field of 40-60 kV/cm at a temperature of $\sim 80 \text{ }^\circ\text{C}$ for 20 min. The piezoelectric charge coefficient, d_{33} was measured 24 h after poling, using the Berlincourt technique (Piezotest meter PM 300; Piezotest, London, UK). Strain-electric field and polarisation-electric field data at room temperature were obtained using a Radiant Technologies LC precision analyser (Radiant Technologies Inc., Albuquerque, New Mexico) (frequency = 1 Hz). The electromechanical planar coupling factor, k_p , was determined by the

resonance-anti-resonance method using an electrical impedance analyser (Agilent 4192A) on poled discs (diameter: thickness ratio of 10:1). Thermal depolarisation characteristics were investigated by measuring the electric charge released during heating of a poled specimen (dc field = 60 kV/cm, 80 °C for 20 min) at a ramp rate of 2 °C/min, using a Keithley 6512 electrometer.

Results and discussion

Grain size (estimated average) increased from ~ 0.5 μm for $x = 0$ (KBT) to ~ 1 μm for solid solutions $x \geq 0.02$. The geometric densities were 5.1 g/cm^3 for KBT, and ~5.6-5.8 g/cm^3 for the $x = 0.03$ -0.08 samples, Table 1 (the approximate relative densities were 90 to 94 % theoretical). Figure 1 shows representative SEM micrographs for sintered (1-x)KBT-xBMT pellets.

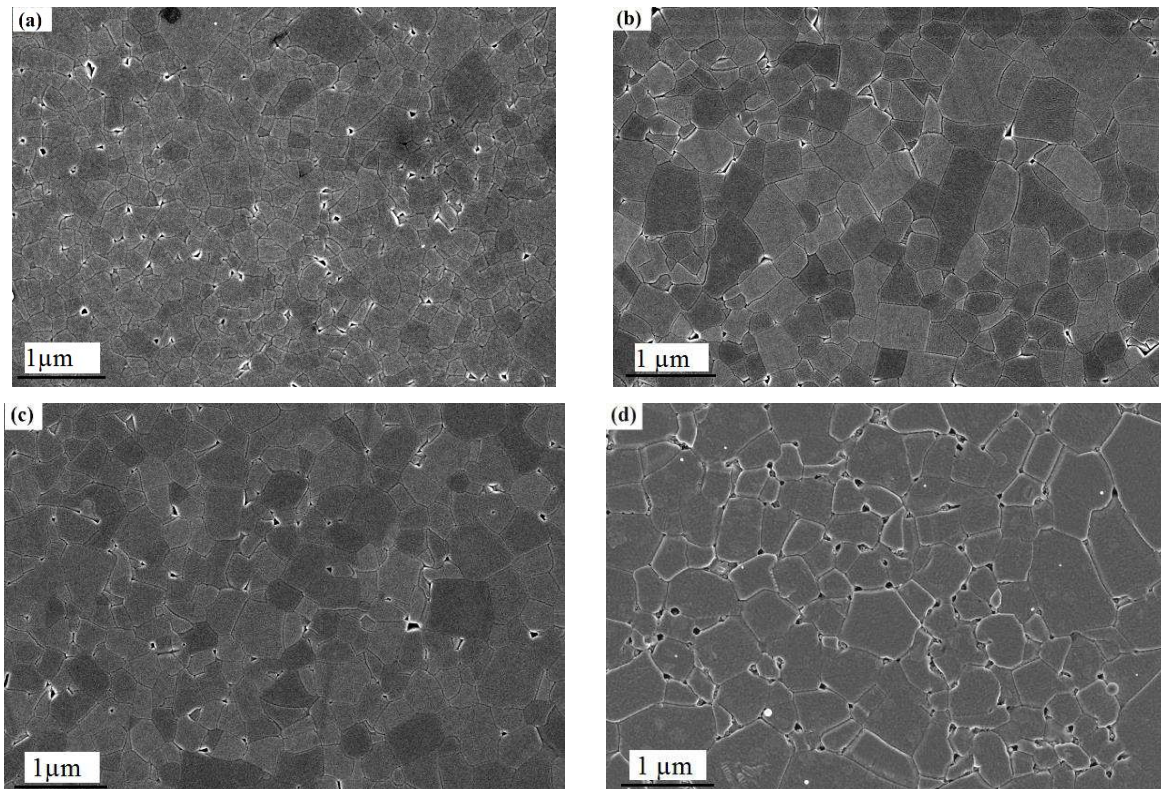


Figure 1 SEM micrographs for polished and thermally etched surfaces of (1-x) KBT-xBMT: (a) $x = 0$, (b) $x = 0.04$, (c) $x = 0.06$ and (d) $x = 0.08$

Table 1. Summary of geometrical density for (1-x)KBT-xBMT ceramic system

Composition(x)	Density (g/cm ³)
x = 0	5.13
x = 0.02	5.52
x = 0.03	5.64
x = 0.04	5.78
x = 0.06	5.86
x = 0.07	5.80
x = 0.08	5.84

Room temperature XRD patterns for crushed sintered pellets are presented in Figure 2. A single-phase perovskite pattern was obtained for samples $x \leq 0.08$. Compositions $x \leq 0.03$ were tetragonal, changing to mixed phase (tetragonal + cubic) for compositions $0.04 \leq x \leq 0.07$. A cubic single-phase perovskite was identified at $x = 0.08$, i.e. with no evidence of 200 peak splitting, Figure 2b. However, the ferroelectric polarisation-electric field response of $x = 0.08$ (see below) suggests the globally cubic phase identified by normal laboratory XRD is non-cubic on a localised scale, or the ceramic undergoes a phase transformation on application of an electric field. Increases in the BMT content to $x = 0.1$ and 0.2 led to a minor amount of secondary $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase, co-existing with the main cubic KBT-BMT phase [12]. The phase boundary region is temperature-insensitive, and comparable to a MPB. This aspect will be reported in detail in a separate publication.

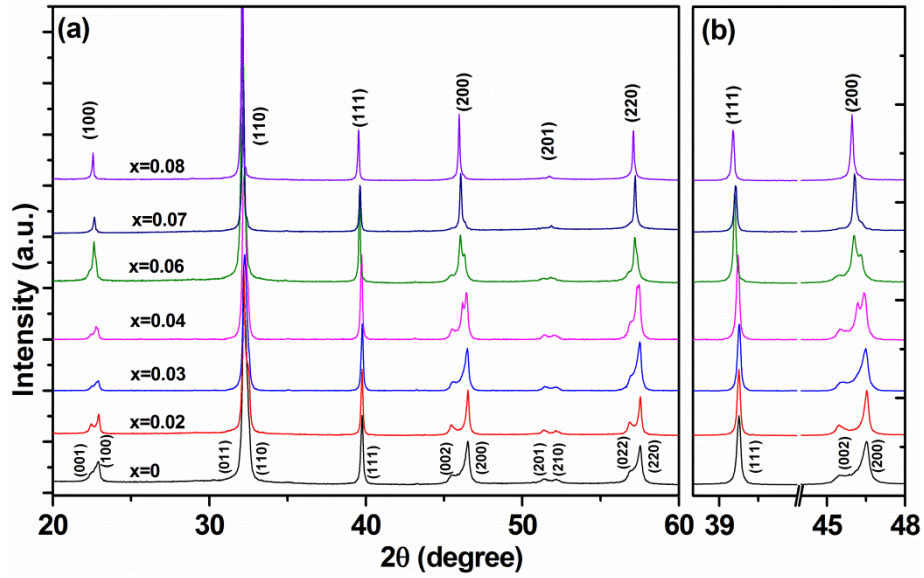


Figure 2. Room temperature XRD patterns for crushed sintered pellets of (1-x)KBT-xBMT system.

A summary of dielectric, ferroelectric and piezoelectric parameters is presented in Table 2.

Figure 3 shows the temperature dependence of relative permittivity, ϵ_r , and loss tangent, $\tan\delta$, measured from room temperature to 600 °C at various single frequencies (1 kHz-1MHz). The dielectric data for KBT ($x = 0$) and all of the KBT-BMT compositions ($x > 0$) revealed frequency-dependent, broad dielectric peaks, and corresponding dispersions in $\tan\delta$ indicating the relaxor nature of the materials [12]. Values of peak temperatures, T_m , decreased from ~ 380 °C (1 kHz) at $x = 0$ to ~ 308 °C at $x = 0.08$. The values of maximum relative permittivity $\epsilon_{r \max}$ (1 kHz) increased from 4080 for $x = 0$ to a limiting value of 6250 for $x = 0.04$, then decreased to 5220 for $x = 0.08$. Only unmodified KBT ($x = 0$) showed a ϵ_r inflection (at temperatures below T_m) as highlighted by an arrow in Figure 3a. It is noted that both NBT-BT and NBT-KBT are reported to show strong inflections well below the peak temperature and the former are associated with depolarisation phenomena. This feature is absent in KBT-BMT.

Dielectric losses increased sharply above ~ 400 °C. This may signify loss of some bismuth and potassium oxide during calcination/sintering, and consequent changes to defect chemistry

resulting in ionic or electronic conduction at these temperatures which gives rise high measured dielectric loss [17-20].

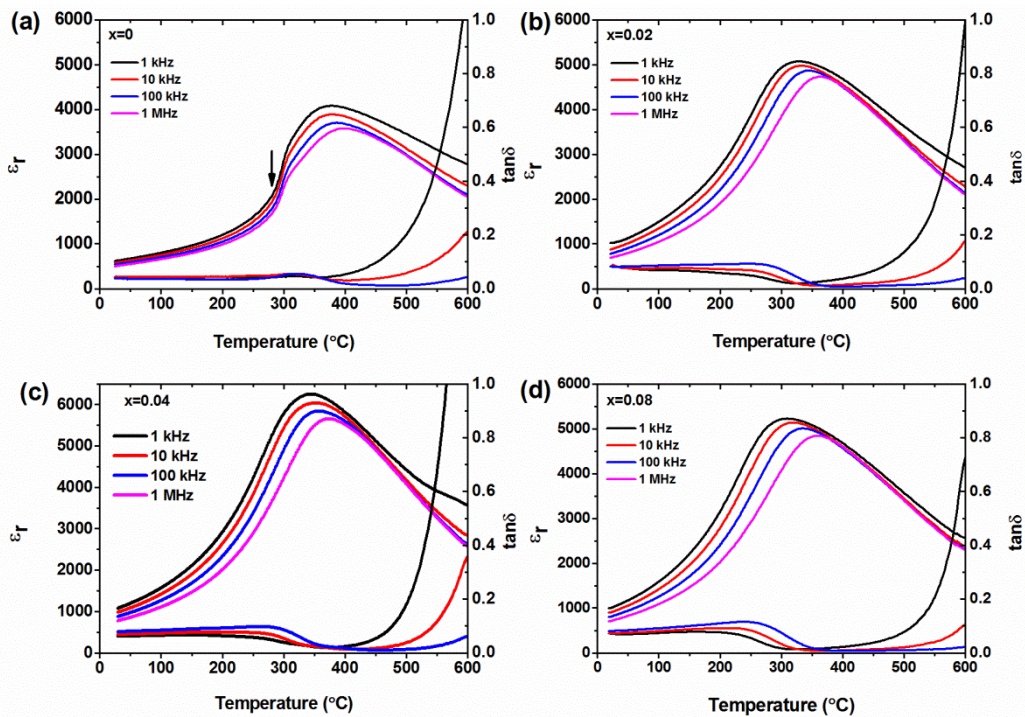


Figure 3. Relative permittivity and $\tan\delta$ values versus temperature for $(1-x)\text{KBT}-x\text{BMT}$: (a) $x = 0$, (b) $x = 0.02$, (c) $x = 0.04$ and (d) $x = 0.08$. The arrow in Figure 3a indicates the onset temperature (heating) of the inflection discussed in the text.

Electric field induced polarisation loops (P-E) are shown in Figure 4. Sample compositions $x \geq 0.03$ displayed ferroelectric P-E loops, with values of remnant polarisation, $P_r \sim 14 \mu\text{C}/\text{cm}^2$ for $x = 0.03$, increasing to $\sim 18 \mu\text{C}/\text{cm}^2$ for $x = 0.04$ and 0.06 . Coercive fields were $\sim 25 \text{ kV}/\text{cm}$ and $28 \text{ kV}/\text{cm}$ for $x = 0.03$ and 0.04 respectively, decreasing to $23 \text{ kV}/\text{cm}$ for $x = 0.06$ and $18 \text{ kV}/\text{cm}$ for $x = 0.08$.

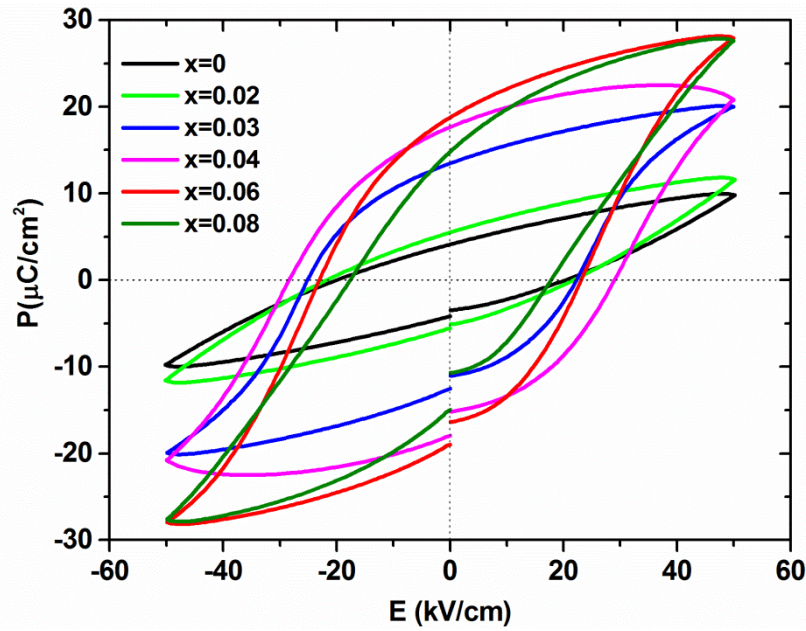


Figure 4. Electric induced polarisation loops (P-E) for the system (1-x)KBT-xBMT

Piezoelectric measurements on unmodified KBT ($x = 0$) indicated a piezoelectric charge coefficient, d_{33} , of 44 pC/N. The d_{33} values increased to peak values of 150 pC/N for $x = 0.03$ and 133 pC/N for $x = 0.04$. These compositions had been identified by XRD to be close to a phase boundary between single-phase tetragonal and mixed tetragonal + cubic phases (Figure 2). The d_{33} value fell to 60 pC/N for composition $x = 0.08$ (this sample gave a single-phase cubic XRD pattern).

Bipolar positive strains of $\sim 0.25\%$ at 50 kV/cm were measured for sample $x = 0.03$, and $\sim 0.35\%$ for $x = 0.04$: the $x = 0.06$ sample also gave high gauge strains, $\sim 0.3\%$, Figure 5, Table 2. The form of the S-E butterfly loops (i.e the negative strains) confirms the samples were ferroelectric; the effective d_{33}^* values (S_{\max}/E_{\max}) were 760 pm/V for $x = 0.04$, and 520 pm/V for $x = 0.03$. At room temperature, the planar coupling coefficient, k_p , was 0.18 for $x = 0.03$ and 0.15 for $x = 0.04$, Table 2. These values of k_p are comparable to a number of other KBT-based ceramics $K_{0.5}Bi_{0.5}TiO_3$ - $Bi(Ni_{0.5}Ti_{0.5})O_3$ ($k_p = 0.18$, $d_{33} = 126$ pC/N) [21] and $K_{0.5}Bi_{0.5}TiO_3$ - $LiNbO_3$ ($k_p = 0.18$, $d_{33} = 75$ pC/N) [22], but lower than for $Na_{0.5}Bi_{0.5}TiO_3$ -

BaTiO₃ ($k_p \sim 0.21-0.36$, $d_{33} = 122-176$ pC/N) [9] and Na_{0.5}Bi_{0.5}TiO₃-K_{0.5}Bi_{0.5}TiO₃ ($k_p \sim 0.27-0.35$, $d_{33} = 140-190$ pC/N) [9, 23].

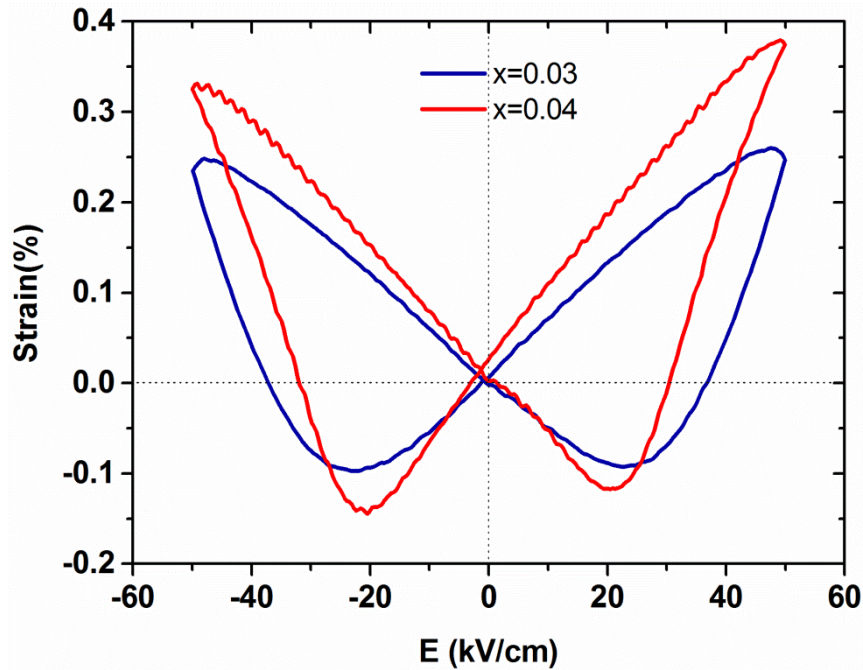
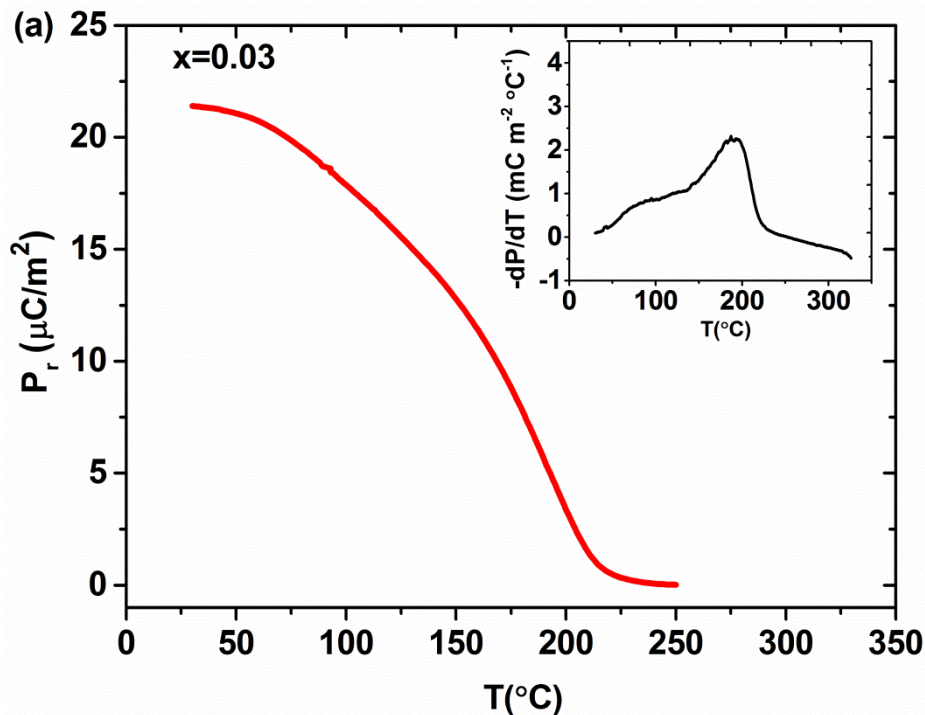


Figure 5 Field induced electromechanical strains for (1-x)KBT-xBMT: $x = 0.03$ and 0.04 (field amplitude 50 kV/cm, 1 Hz)

Thermal depolarisation measurements for $x = 0.03$ and $x = 0.04$ (i.e. compositions with maximum d_{33}) are shown in Figure 6. These samples had been poled under a static electric field of 60 kV/cm, at a temperature of 80 °C for a period of 20 min and hence P_r values were higher than the values from P-E measurements (Figure 4). The latter refer to measurements conducted at room temperature under a maximum electric field of 50 kV/cm at a frequency of 1 Hz (for a single sinusoidal waveform). The pre-poled $x = 0.03$ sample (Figure 6) lost all polarisation by ~ 220 °C (T_d). For $x = 0.04$ the T_d value was slightly lower, ~ 200 °C. The depolarisation temperatures reported for (1-x)NBT-xBT piezoelectrics at the MPB ~ 6 mol % BT (corresponding to maximum piezoelectric properties) can vary widely depending on the measurement technique employed. Anton et al., investigated a number of techniques, reporting

that figures based on the ϵ_r -T inflection temperature overestimate the true T_d . More accurate values were obtained by thermal depolarisation measurements similar to the approach used in the present study, or from k_p -T measurements [10]. Although some research groups report T_d for NBT-BT as high as 150 °C (from ϵ_r -T data), the more accepted T_d range is 90-105 °C [3, 9], as confirmed by thermally stimulated charge decay measurements [24]. This temperature is over 100 °C lower than the T_d for the present KBT-BMT piezoceramics $x = 0.03$ and 0.04 obtained from charge decay measurements. It is relevant to highlight that unlike NBT-BT or NBT-KBT no ‘low-temperature’ depolarising inflection is observed in ϵ_r -T plots for the KBT-BMT materials (Figure 3).

The maximum rate of temperature-induced depolarisation dP/dT for $x = 0.03$ occurred at ~ 190 °C, Figure 6a (inset) but by this temperature the sample had lost ~ 75 % of its original polarisation. The corresponding maximum rate of thermal de-poling occurred at ~ 160 °C for sample $x = 0.04$, Figure 6b (inset). Preliminary experiments based on d_{33} values measured after thermal annealing and cooling back to room-temperature infer a working temperature limit of ~ 170 °C, as d_{33} values remain within 15 % of the base value after heating to ≤ 170 °C.



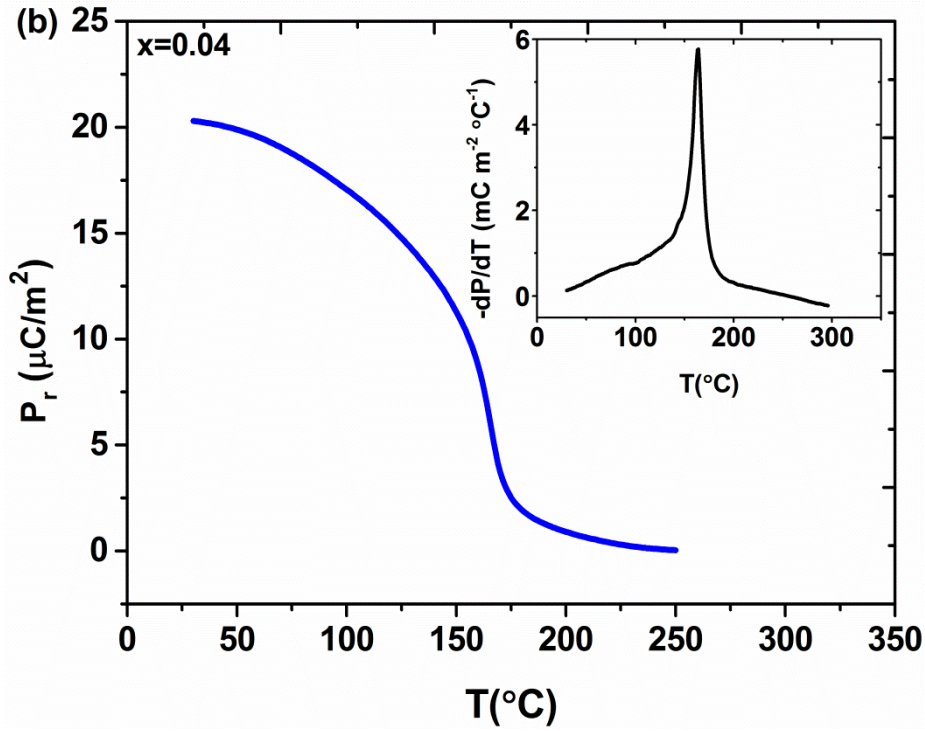


Figure 6. Thermal depolarisation plot for (1-x)KBT-xBMT sample compositions: (a) $x = 0.03$ and (b) $x = 0.04$

Conclusions

The novel solid solution system, $(1-x)\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-x\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$, KBT-BMT, offers favourable piezoelectric properties, and has the benefit of a high depolarisation temperature. A piezoelectric d_{33} charge coefficient of ~ 150 pC/N is obtained for composition $x = 0.03$, with high values of bipolar field-induced strains, $S \sim 0.25\%$ (at 50 kV/cm); corresponding values for $x = 0.04$ are 133 pC/N and 0.35%. Hence, KBT-BMT has comparable piezoelectric properties to the widely cited $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-\text{BaTiO}_3$ system, but has the important practical advantage of a much higher depolarisation temperature, T_d , and projected upper operating temperature. The $x = 0.03$ samples lose polarisation at $T_d \sim 220$ °C, whilst for the $x = 0.04$ samples, $T_d \sim 200$ °C: these depolarisation temperatures are ~ 100 °C higher than for the

optimum NBT-BT morphotropic phase boundary ceramics, and $\sim 50^\circ\text{C}$ higher than for an alternative $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ lead-free piezoceramic. The improved high temperature limit is of potential significance for the development of actuator and sensor devices.

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List of Figures

Table 2. Summary of dielectric and piezoelectric properties of KBT-xBMT system.

Measured Parameters	x = 0	0.02	0.03	0.04	0.06	0.08
T_m ($^\circ\text{C}$)	380	330	334	336	333	308
ϵ_r (20 $^\circ\text{C}$, 1 kHz)	620	1020	1050	1050	1190	1015
$\epsilon_{r \text{ max}}$ (1 kHz)	4080	5070	5970	6250	5840	5220

$\tan\delta$ (20 °C, 1 kHz)	0.04	0.07	0.06	0.06	0.07	0.07
P_r ($\mu\text{C}/\text{cm}^2$) at RT	-	-	13.5	18	18	15
E_c (kV/cm)	-	-	25	28	23	18
d_{33} (pC/N)	44	59	150	133	100	60
k_p	0.16	0.16	0.18	0.15	0.11	-
Bipolar Strain (% , 50 kV/cm)	0.04	0.07	0.25	0.35	0.32	0.23
d_{33}^* (pm/V)-bipolar	87	137	520	760	660	490
Depolarisation Temperature (T_d^{\S} , °C)	-	-	220	200	-	-

T_d^{\S} -based on the thermally stimulated charge decay measurement

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