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High temperature piezoelectric ceramics in the $Bi(Mg_{1/2}Ti_{1/2})O_3$-$BiFeO_3$-$BiScO_3$-$PbTiO_3$ system

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Abstract Compositons in the pseudoquaternary system, $1\text{-}\times(0.35Bi(Mg_{1/2}Ti_{1/2})O_3\text{-}0.30BiFeO_3\text{-}0.35BiScO_3)\text{—}\times PbTiO_3$ were fabricated and characterised at the morphotropic phase boundary (MPB) between ferroelectric rhombohedral and tetragonal phases. The MPB occurred at $\times\approx0.48$ at which composition the ferreoelectric to paraelectric phase transition, T_C=450°C, the piezoelectric constant, d_{33}=328 pC/N and electromechanical coupling factor, k_p=0.44. The piezoelectric properties are viable for actuator applications but lower than equivalent high T_C piezoelectrics such as $0.36BiScO_3$–$0.64PbTiO_3$ (d_{33}= 450 pC/N, T_C=450°C). However, the relative reduction in the Sc_2O_3 content gives a significant cost saving which may prove a commercial advantage.

Keywords Piezoelectrics · Morphotropic phase boundary · High curie temperature · BS-PT · BMTFS-PT

1 Introduction

Lead zirconate titanate (PZT) based piezoelectric ceramics have dominated the transducer and actuator industries since their development in the early 1950's [1]. Typically, transducers and actuators make use of morphotropic phase boundary (MPB) compositions between rhombohedral (R) and tetragonal (T) phases in the PZT phase diagram at ~48 mol% $PbTiO_3$[1]. However, environmental restrictions on the usage of lead and the depoling and ageing of PZT at temperatures above 200°C have focussed the attention of researchers worldwide to look for alternative materials [2]. In 2001, Eitel *et al* [3] reported a ceramic based on the solid solution, $BiScO_3$–$PbTiO_3$ (BS-PT) which had a lower concentration of PbO, higher Curie temperature, T_C=450°C compared with <380°C for PZT and a similar piezoelectric constant, d_{33}=450 pC/N. However, the high cost of Sc_2O_3 currently restricts its usage in commercial applications. Other $Bi(Me)O_3$–$PbTiO_3$ systems have been studied extensively but the majority have shown either limited solid solubility, eg: $BiInO_3$–$PbTiO_3$ [4], $BiGaO_3$–$PbTiO_3$ [5] or inferior properties eg: $Bi(Mg_{1/2}Ti_{1/2})O_3$–$PbTiO_3$ [6], $Bi(Mg_{1/2}Zr_{1/2})O_3$–$PbTiO_3$ [7]. The only notable success in decreasing costs whilst sustaining usable piezoelectric activity was described in the work of Sterianou *et al* [8, 9] who substituted Sc_2O_3 with up to 80% Fe_2O_3 in the solid solution $(1\text{-}\times)Bi(Sc_{1-y}Fe_y)O_3\text{–}\times PbTiO_3$ (BSF-PT). However, piezoelectric properties significantly deteriorated for $y>0.5$ due to partially immiscibility of the two perovskite compositions [9].

To overcome the problems of immiscibility encoutered by Sterianou *et al* [9], the pseudoternary system BSF-PT has been expanded in this work to include $Bi(Mg_{1/2}Ti_{1/2})O_3$. To simplify the search for MPB compositions the ratio of $BiMg_{1/2}Ti_{1/2}O_3$:$BiFeO_3$:$BiScO_3$ has been initially fixed at 0.35:0.3:0.35. The objective of the work reported here is therefore to characterise compositions near the MPB in the solid solution $(1\text{-}\times)(0.35Bi(Mg_{1/2}Ti_{1/2})O_3\text{-}0.3BiFeO_3\text{-}0.35BiScO_3)\text{—}\times PbTiO_3$, $(1\text{-}\times)BMTFS\text{—}\times PT$ and determine whether such complex sytems yield

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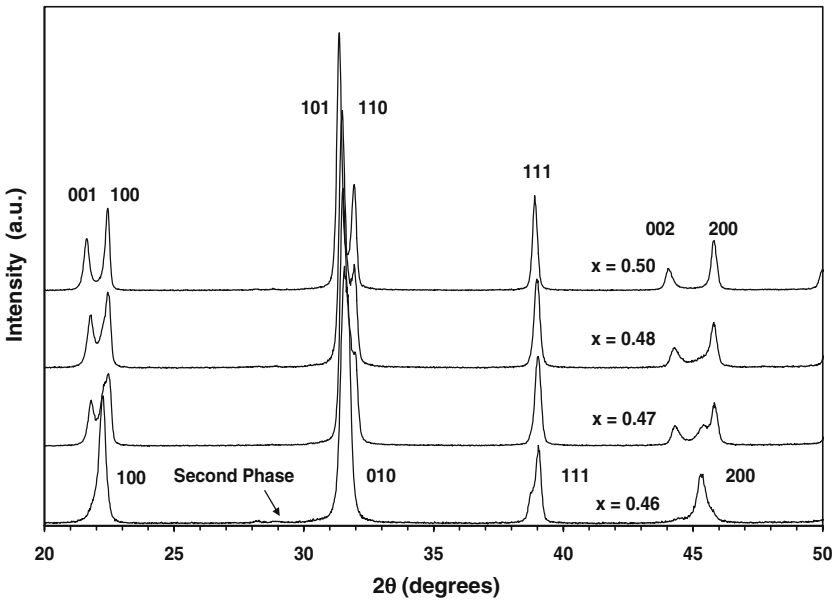

Fig. 1 X-ray diffraction traces of sintered pellets of (1-×)BMTFS-× PT for x=0.46, 0.47, 0.48 and 0.50. Peaks are indexed based on pseudo cubic cell

piezoelectric coefficients suitable for commercial applications whilst retaining $T_C \geq 450°C$.

2 Experimental

Polycrystalline samples in the solid solution (1-×) BMTFS—×PT, $0.50 \geq x \geq 0.46$ were prepared using the solid state mixed oxide route. Bi_2O_3 (99.9%, Acros Organics, Geel, Belgium), PbO (99.9%, Acros Organics, Geel, Belgium), $Mg(OH)_2$ (95%, Fisher Scientific, Loughborough, U.K), TiO_2 (99.9%, Sigma-Aldrich, Dorset, U.K), Fe_2O_3 (99% Aldrich Chemical company Inc. Milkwauee, U.S.A), Sc_2O_3 (99.99%, Stanford Materials Corporation, U.S.A) were weighed out in stoichiometric amounts in ~100 g batches to an accuracy of ~0.01 g and attrition milled using 3 mm diameter Y_2O_3 stabilised zirconia for 1 hour in distilled water. The milling media were removed and the remaining slurry was dried in an oven for 48 hours at 80°C. The dried sample was crushed using a mortar and pestle until it passed completely through a 355 μm mesh sieve. Powder was reacted at 900°C for 2 h in a lidded alumina crucible using a ramp rate of 2° per minute. The reacted powders were attrition milled for 1 hour in distilled water using yttria stabilised ZrO_2 milling media. The slurry was dried, crushed and sieved as before. Dried samples were pressed into 10 mm diameter pellets using a uniaxial press at ~1 tonne for ~1 min. Pellets and a small amount of powder of the same composition as that of pellet were placed on platinum foil and covered with a lid and sintered. The sacrificial powder was used to create a vapour pressure of the volatile species (PbO and Bi_2O_3) within the vicinity of the pellet. Sintering was carried out in air at 1,000°C for 5 h at a ramp rate of 5° per minute.

X-ray diffraction was performed on a D500 Siemens diffractometer using Cu Kα (λ=1.540598 Å) radiation to examine the phase purity of the system. Reflections were measured in steps of 0.02° at a speed of 0.1° per minute across the 2θ range 20 to 70° and data were analysed using 'STOE WinXPow' software. Surface morphology was examined using Scanning electron microscopy (SEM), (JEOL JSM6400) on thermally etched samples polished to 1 μm.

Prior to measuring the dielectric, ferroelectric and piezoelectric properties, pellets were electroded with gold paste and fired at 800°C for 2 hours. Dielectric properties were measured between room temperature and 600°C using an inductance/capacitance/resistance (LCR) meter (4284A, HP). Relative dielectric permittivity (ε_r) and dielectric loss (tan δ) were measured at frequencies of 1, 10, 100 and

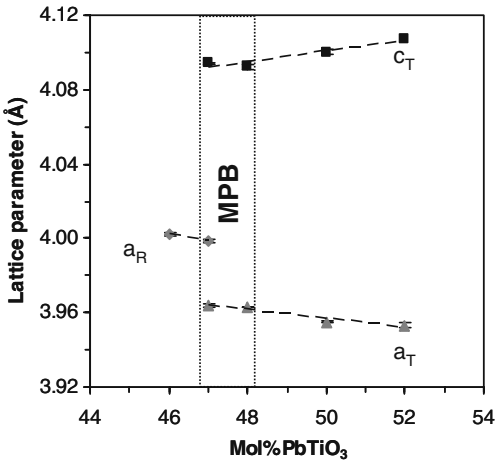

Fig. 2 Room temperature lattice parameters of (1-×)BMTFS-×PT for x=0.46, 0.47, 0.48, 0.50 and 0.52 ceramics obtained from refinement of XRD data

Table 1 Piezoelectric properties of (1-×)BMTFS-×PT, compared with known reported ceramics.

Material	T_C (°C)	tan δ	d_{33} (pC/N)	k_p	c_T/a_T	Reference
Undoped PZT	386	0.012	223	0.53	1.022	[1]
Navy type II (PZT)	365	0.017	374	0.60		[1]
$0.36BiScO_3$–$0.64PbTiO_3$	450	0.027	460	0.56	1.023	[3]
$0.63Bi(Mg_{1/2}Ti_{1/2})O_3$–$0.37PbTiO_3$	478	0.079	225	-	1.034	[6]
$0.45Bi(Sc_{1/2}Fe_{1/2})O_3$–$0.55PbTiO_3$	440	0.033	298	0.49	1.021	[8]
Current work						
0.54BMFTS-0.46PT	440	0.033	183	0.18		
0.53BMTFS-0.47PT	443	0.025	226	0.27	1.0328	
0.52BMTFS-0.48PT	450	0.036	328	0.44	1.0327	
0.50BMFTS-0.50PT	463	0.019	270	0.31	1.0367	

250 kHz. Polarization-electric field (P-E) measurements were conducted in a heated silicone oil bath at a temperature of 100°C and a frequency of 2 Hz using a ferroelectric test system based on a HP33120A function generator in combination with a high voltage (+/- 5 kV) amplifier and a current amplifier. The piezoelectric constant, d_{33}, was measured using a Berlincourt meter (IAAS ZJ-2) on a pellet poled at 150°C in a silicone oil bath under optimum field (60 kV/cm) for 5 min. The electromechanical coupling factor, k_p was measured using an impedance analyzer (Agilent 4294A) based on IEEE standards [10]. Strain (S) was measured using a non—contact fibre-optic displacement probe (10 μm.V^{-1} sensitivity, Philtec Inc) to generate strain—electric field loops.

3 Results and discussion

3.1 Phase stability and microstructure

Figure 1 shows the XRD traces of pellets of all compositions sintered for 5 h. All major peaks could be attributed to perovskite-structured phases but minor unidentified second phase peaks appear at approximately 29° 2θ for $x \leq 0.46$ compositions. Rhombohedral symmetry, characterised by splitting of the $\{111\}_p$ perovskite peak, was observed at room temperature for $x=0.46$. For $x>0.47$ splitting of the $\{110\}_p$ peak show evidence of a structural phase transition to a tetragonally distorted perovskite structure. $\{200\}_p$

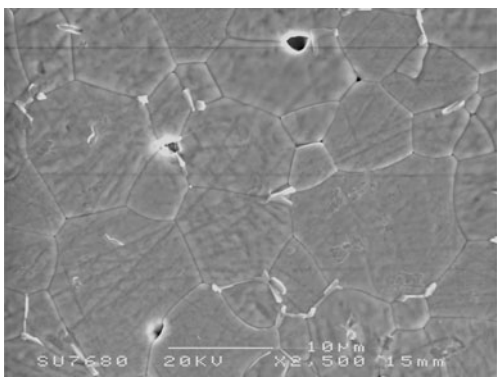

Fig. 3 SEM image showing the grain structure of BMTFS-PT, $x=0.50$

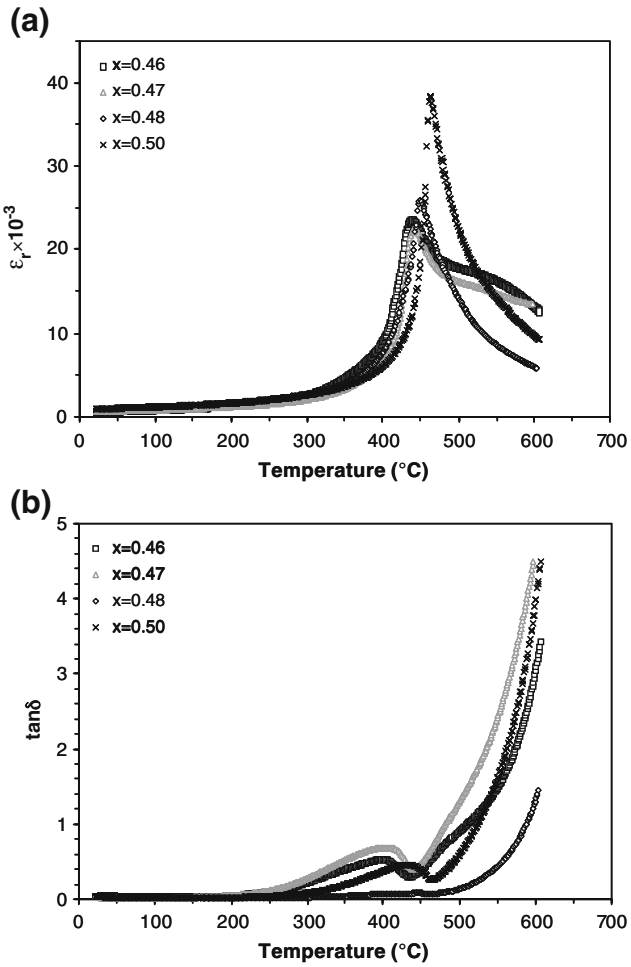

Fig. 4 (**a**) Relative permittivity and (**b**) dielectric loss for sintered pellets of (1-×)BMTFS—×PT for $x=0.46$, 0.47, 0.48 and 0.50, at 10 kHz

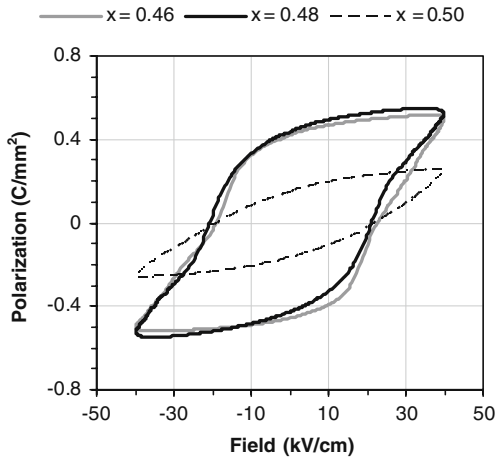

Fig. 5 Hysteresis curves obtained at 100°C for sintered pellets of (1-×)BMTFS—×PT for x=0.46, 0.48 and 0.50 at a frequency of 2 Hz

perovskite peaks show a clear evidence of structural transformation from rhombohedral to tetragonal phase with both phases co-existing at x=0.47, peaks at 2θ values 44.197°, 45.744° corresponding to tetragonal phase and at 45.304° corresponding to rhombohedral phase. It was concluded therefore that an MPB occurred in the BMTFS-PT system at 0.48≥×≥0.46. Figure 2 presents room temperature lattice parameters for this system. The lattice parameters of tetragonal 0.52BMTFS—0.48PT were obtained as a=3.9630(10) and c=4.0925(13). The degree of tetragonal distortion denoted by (c_T / a_T) for various Bi(Me)O_3—$PbTiO_3$ systems is shown in Table 1. The c/a ratio at MPB of the current system (~ 3%) is relatively high when compared to other systems. SEM images of thermally etched pellets across the MPB for 0.50≥×≥0.46 revealed the grain size to be~6-7 μm for all samples with no second phase, as typified by Fig. 3.

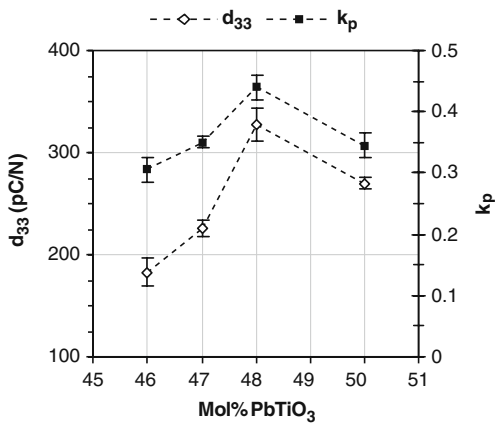

Fig. 6 Piezoelectric constant, d_{33} and electromechanical coupling factor, k_p near morphotropic phase boundary in (1-×)BMTFS—×PT, showing enhanced values at MPB

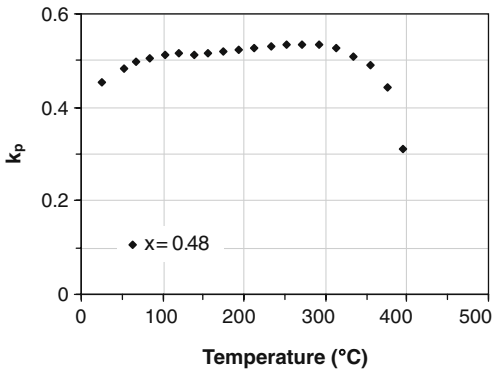

Fig. 7 Planar electromechanical coupling factor, k_P, versus temperature for a poled 0.52 BMTFS- 0.48 PT ceramic

3.2 Electrical characterisation

Relative permittivity and dielectric loss versus temperature for unpoled samples at 10 kHz for 0.50≥×≥0.46 are plotted in Fig. 4. All samples had T_C≥440°C, considerably higher than that of PZT and equivalent to 0.63BS—0.37PT with dielectric loss <0.04 at room temperature. However, a second anomaly was observed for x=0.46 at 550°C. Similar high temperature anomalies have been previously attributed to the immiscibility of perovskite phases, one of which is rich in $PbTiO_3$/$BiFeO_3$ with a high T_C [9]. The precise composition of these regions may only be determined by energy dispersive X-ray analysis of thin sections utilising transmission electron microscopy. This work is underway and will be presented elsewhere in a more detailed study of the ceramic microstructure. In the (1-×)$BS_yF_{(1-y)}$—xPT system second high temperature phase transitions were encountered for y<0.5 and for all values of x across the

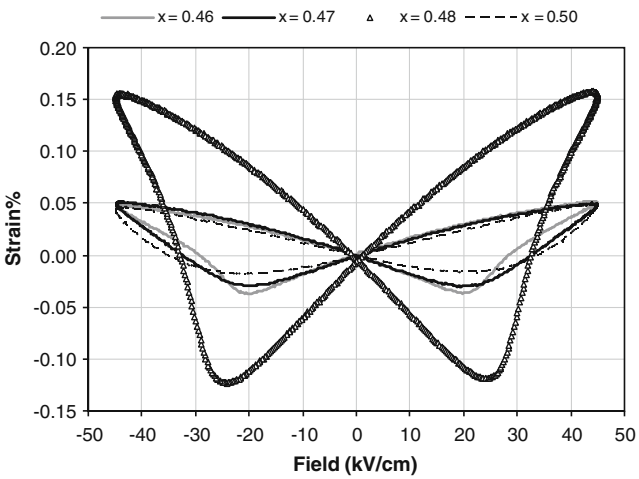

Fig. 8 Bipolar strain—electric field curves obtained at room temperature for sintered pellets of (1-×)BMTFS—×PT for x=0.46, 0.47, 0.48 and 0.50, at a frequency of 0.1 Hz

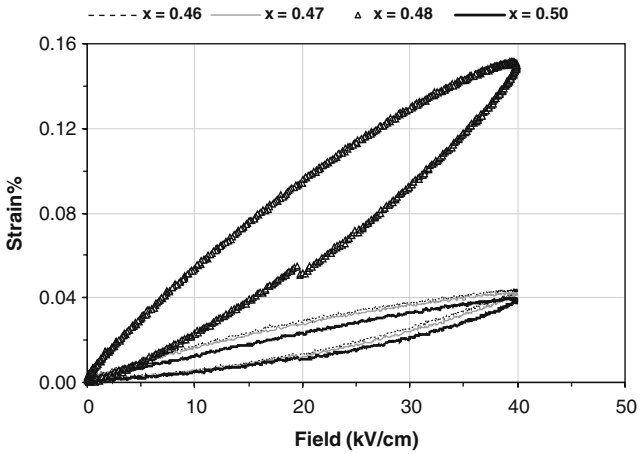

Fig. 9 Unipolar strain—electric field curves obtained at room temperature for sintered pellets of (1-×)BMTFS—×PT for x=0.46, 0.47, 0.48 and 0.50, at a frequency of 0.1 Hz

MPB [9]. The immiscibility presented a thermodynamic barrier to ceramic homogeneity and prevented optimisation of the piezoelectric properties at the MPB. In contrast, in the BMTFS—PT system, the high temperature phase transition is absent for $x \geq 0.47$ and the addition of $BiMg_{1/2}Ti_{1/2}O_3$ to form a quaternary system has had the desired effect of suppressing immiscibility across the MPB.

Figure 5 shows the P-E hysteresis loops for x=0.46, 0.48 and 0.5 obtained at 100°C. Optimum $P_r \approx 43$ μC/cm^2 and coercive field $E_c \approx 21$ kV/cm was achieved for x=0.48. The non-saturated P-E loop for x=0.5 is attributed to an increase in the coercive field associated with increased tetragonality, Fig. 2.

Figure 6 shows the d_{33} and k_p for $0.50 \geq \times \geq 0.46$. d_{33} (328 pC/N) and k_p (0.44) values are optimised in the tetragonal phase (Fig. 1) at x=0.48. In PZT, the piezoelectric response is also optimised in the tetragonal phase field in the vicinity of the MPB [1]. Figure 7 illustrates the thermal stability of the piezoelectric ceramic by measuring the variation of k_p as a function of temperature. It retains the room temperature k_p (~ 0.44) up to ~375°C, considerably higher than PZT. Table 1 compares T_C, tanδ, d_{33}, k_p and c_T/a_T of BMTFS—PT compositions with the reported values for various piezoelectric compounds. d_{33} compares well with Navy type I ceramics but exhibits a higher T_C. However, ceramics in the solid solution BS-PT still show superior d_{33} for equivalent T_C although their higher Sc_2O_3-content makes them commercially less appealing.

Figure 8 represents S-E response of compositions $0.50 \geq \times \geq 0.46$ under bipolar drive for a maximum field of 45 kV/cm and at a frequency of 0.1 Hz. Ceramics with x=0.48 exhibit the maximum strain (~ 0.37% at 55 kV/cm). Figure 9 shows the unipolar S-E curves for $0.50 \geq \times \geq 0.46$ under the same conditions as the bipolar measurements. The maximum unipolar strain is exhibited by x=0.48 (~0.15) with a slope that gives an effective d_{33} of ~380 pC/N.

4 Conclusions

(1-×)BMTFS—×PT compositions have been fabricated in the search for a low cost commercially viable $Bi(Me)O_3$–$PbTiO_3$ piezoelectric ceramic. The MPB occurs at $0.48 \geq \times \geq 0.46$ and for x=0.48, d_{33}=328 pC/N with T_C=450°C. To date, d_{33} is considerably higher for $0.36BiScO_3$—$0.64PbTiO_3$ (450 pC/N) systems which have an equivalent T_C but the content of highly expensive Sc_2O_3 is significantly reduced in BMTFS-PT which may offer a commercial advantage. BMTFS-PT shows a cost reduction of about 45% compared to BS-PT, based on the laboratory scale production. Moreover, there is considerable potential in this quaternary system for a range of MPB compositions by altering the $BiMg_{1/2}Ti_{1/2}O_3$:$BiFeO_3$:$BiScO_3$ ratio. Future studies may therefore yield superior piezoelectric ceramics than reported here.

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