Piezoelectric activity of (1-x)[0.35Bi(Mg$_{1/2}$Ti$_{1/2}$)O$_3$-0.3BiFeO$_3$-0.35BiScO$_3$] - xPbTiO$_3$ ceramics as a function of temperature

Tutu Sebastian · Iasmi Sterianou · Ian M. Reaney ·
Thorsten Leist · Wook Jo · Jürgen Rödel

Abstract The piezoelectric and ferroelectric properties of ceramics in the (1-x)[0.35Bi(Mg$_{1/2}$Ti$_{1/2}$)O$_3$-0.3BiFeO$_3$-0.35BiScO$_3$] - xPbTiO$_3$ (0.46≤x≤0.50) solid solution have been studied as a function of temperature with a view to establishing their potential for commercial usage as high T$_C$ actuators and sensors. The polarisation, unipolar and bipolar strain, piezoelectric coefficient d$_{33}$ and coupling factor k$_p$ all increased with temperature consistent with softening of extrinsic and intrinsic contributions to piezoactivity as T$_C$ is approached. Small signal d$_{33}$ and k$_p$ increased from 328 pm/V and ~0.45 at room temperature to >1100 pm/V and ~0.5, respectively, until depoling occurred at ~400°C, illustrating a significant improvement in operating temperature over PZT (~200°C) and demonstrating great potential for high temperature sensor applications. Bipolar (bi) and unipolar (uni) measurements (large signal, d$^*_{33}$) normally used to demonstrate potential for actuation, revealed extremely promising values, d$^*_{33(bi)}$=940 pm/V and d$^*_{33(uni)}$=600 pm/V, up to 180°C, the limit of the experimental apparatus.

Keywords Piezoelectrics · High curie point · Temperature stability · High temperature actuators

T. Sebastian · I. Sterianou (✉) · I. M. Reaney
Department of Materials Science and Engineering,
University of Sheffield,
Mappin Street,
S1 3JD Sheffield, UK
e-mail: I.Sterianou@sheffield.ac.uk

T. Leist · W. Jo · J. Rödel
Institute of Materials Science, Technische Universität Darmstadt,
64287 Darmstadt, Germany

1 Introduction

Technological advancements in the field of materials engineering and systems integration have led to the need for piezoelectric actuators and sensors that operate in extreme conditions, especially within the aerospace, automotive and energy industries. National Aeronautical Space Agency's decadal mission of exploring Venus illustrates the potential requirement of high temperature actuators to exert efficiently high strokes, torques and forces while operating at 450°C and ~ 9 MPa [1]. However, conventional piezoelectric materials based on PbZr$_{1-x}$Ti$_x$O$_3$ with a Curie temperature, T$_C$= 386°C are limited to less than 200°C due to de-poling under high mechanical stress and electric fields [2].

The search for alternative high temperature piezoelectrics based on Bi(*Me*)O$_3$ – PbTiO$_3$ gained prominence after the synthesis of BiScO$_3$ – PbTiO$_3$ system (BS – PT) in which there is a morphotropic phase boundary (MPB) between rhombohedral and tetragonal ferroelectric polymorphs, similar to that in PZT [3]. In these systems, *Me* represents a generic, suitably sized cation with a valence 3+ or a mixture of cations with an average valence of 3+ (Sc, Fe, Mg$_{1/2}$Ti$_{1/2}$, Ni$_{2/3}$Nb$_{1/3}$, etc.). Eitel et al. proposed that a number of MPB systems should exist with higher T$_C$ than PZT based on the concept of the 'end-member tolerance factor' in which the MPB Curie point increases as the so-called 'rhombohedral end-member' tolerance factor decreases [3]. Although BS – PT shows high temperature stability and improved properties compared to PZT, the high cost of Sc$_2$O$_3$ currently restricts commercial exploitation.

In a previous contribution, Sebastian et al. [4] reported a high T$_C$ (~450°C) pseudoquaternary system, (1-x)[0.35Bi(Mg$_{1/2}$Ti$_{1/2}$)O$_3$-0.3BiFeO$_3$-0.35BiScO$_3$] – xPbTiO$_3$, (BMTFS – PT) in which at room temperature the small signal d$_{33}$ ~ 328 pC/N, strain under bipolar field is ~0.28%

and $k_p=0.44$ for compositions with $x=0.48$. Most importantly, the raw material costs were reduced by ~ 47% compared to BS–PT [4]. However, to be considered as a genuine candidate for use in high temperature applications, the piezoelectric and ferroelectric responses must be established close to the potential operating temperatures (250–450°C). Although the ferroelectric and piezoelectric properties of many Bi(Me)O$_3$ – PbTiO$_3$ materials have been reported at room temperature, only select piezoelectric properties of a few systems have been demonstrated at high temperature [5–8]. In this contribution, therefore, the temperature dependence of ferroelectric and piezoelectric properties, is evaluated. Both large signal properties (polarisation and strain to 180°C) and small signal properties (piezoelectric coefficient and coupling factor to 500°C) are assessed to establish whether the BMTFS – PT system has genuine potential for high temperature sensor and actuator applications.

2 Experimental

The sample preparation of the $(1-x)$BMTFS – xPT ceramics was described by the authors in their previous contribution

[4]. Four compositions were chosen with $x=0.46$ (primary rhombohedral structure), $x=0.50$ (primary tetragonal structure, and $x=0.47$ and 0.48 (both MPB regime). High temperature polarisation – electric field (P-E), strain – electric field (S-E) measurements and small signal d_{33} measurements were performed on the samples at the Institute of Materials Science, Technical University of Darmstadt, Germany. The polarisation and strain response was measured using the aixPES system (aixACCT Systems, GmbH, Aachen, Germany). A commercial TF Analyser 2000 was used to apply the excitation signal and record the current response of the device. A triangular wave form at a frequency of 1 Hz was applied using a Sawyer-Tower circuit equipped with a strain gauge to measure the temperature dependence of polarisation and field induced strain. Pellets were immersed in silicone oil to prevent break down along the edges. The measurements were performed from room temperature to 180°C. Before taking each measurement the pellets were left at the desired temperature for 30 min to achieve thermal stabilisation.

The temperature variation of the small signal d_{33} coefficient using the converse piezoelectric effect was determined on poled samples by applying a small AC signal of 10 V at

Fig. 1 Temperature dependence of P-E loops for $(1-x)$BMTFS – xPT ceramics, at 25°C, 50°C, 100°C, 150°C and 180°C, measured at 50 kV/cm, (a) $x=0.46$, (b) $x=0.47$, (c) $x=0.48$ and (d) $x=0.50$
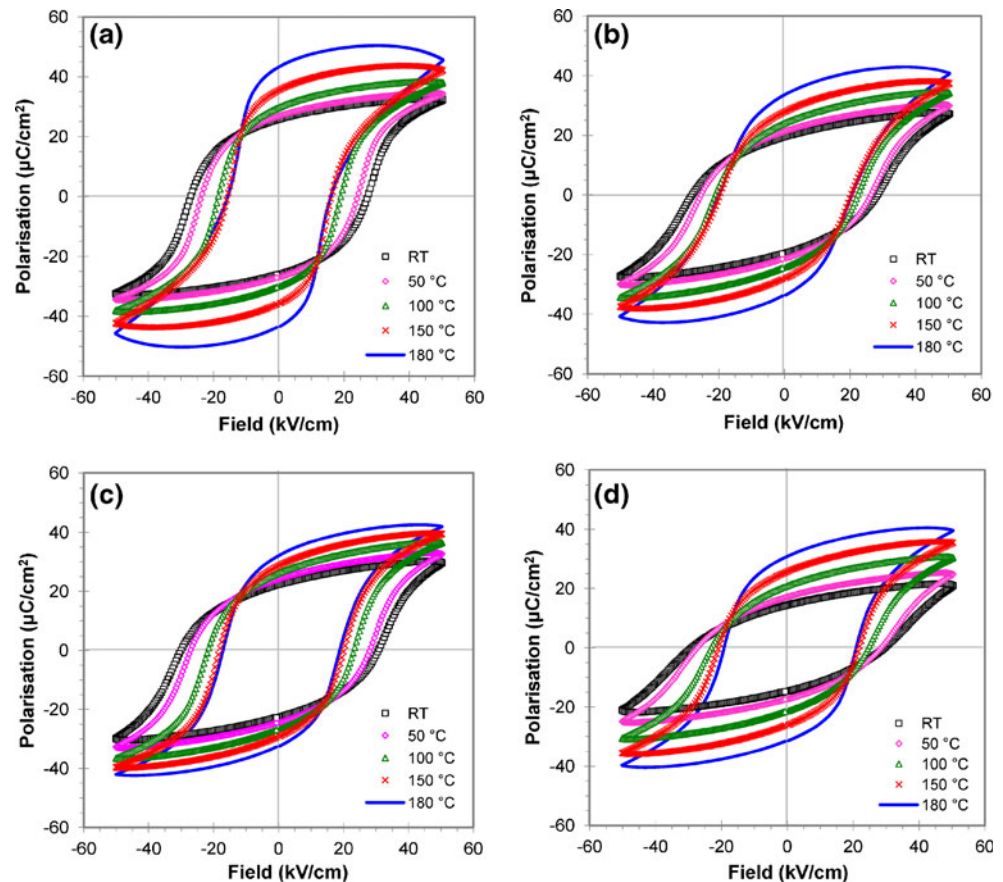
1 kHz and measuring the resulting longitudinal displacement with a single beam laser interferometer, while the sample was being heated. The temperature was obtained from a thermocouple positioned very close to the sample [9].

The temperature dependence of planar coupling coefficient (k_p) was calculated from resonance and antiresonance frequencies obtained using an impedance analyser (Agilent 4294A) with an accuracy of 50 Hz (IEEE standards) [10]. The k_p was determined by attaching the poled specimen to a conductivity jig connected to a non–inductively wound tube furnace. The sample was held by platinum wires and placed horizontally without disturbing its vibration at resonance. The resonance spectrum was obtained at each temperature after allowing sufficient time for the sample to achieve thermal equilibrium.

3 Results and discussion

The temperature dependence of P-E loops from room temperature to 180°C for $(1-x)$BMTFS – xPT is plotted in Fig. 1. All compositions show the hysteretic behaviour of a normal ferroelectric and all display saturated loops either at room temperature or with increase in temperature. As shown in Fig. 2, P_r increases and E_c decreases with increase in temperature which is attributed to an increase in domain switching as the motion of domain walls becomes easier as T_C is approached. This general behaviour can be compared to a related study in $Bi(Mg_{1/2}Ti_{1/2})O_3 – PbTiO_3$ (BMT – PT) piezoceramics which display higher remanent polarisation and higher coercive fields, but exhibit a very similar increase in remanent polarisation and decrease in coercive field with temperature [5]. The rhombohedral composition, x=0.46, provides the highest P_r and lowest E_c for all equivalent temperatures up to ~45 µC/cm^2 at 180°C. Adjacent to the MPB, the rhombohedral and tetragonal lattice strains, obtained from least squares refinements of the XRD data, are ~0.2% and ~3.2%, respectively. The internal stress imparted by the rhombohedral structure is consequently lower than the tetragonal structure and therefore non-180° domain walls are relatively free to move, resulting in a lower E_c and increase in P_r. The high internal strain exerted by the tetragonal structure makes the switching of domain walls more difficult and E_c increases and P_r decreases within the tetragonal phase [2]. However, the loops obtained above 100°C for compositions with x=0.46 show evidence of pinching close to the maximum field and higher conductivity than at room temperature. Pinching of loops in the R phase of PZT is often attributed to the presence of Me-V_O defect dipoles associated with V_O migration [11].
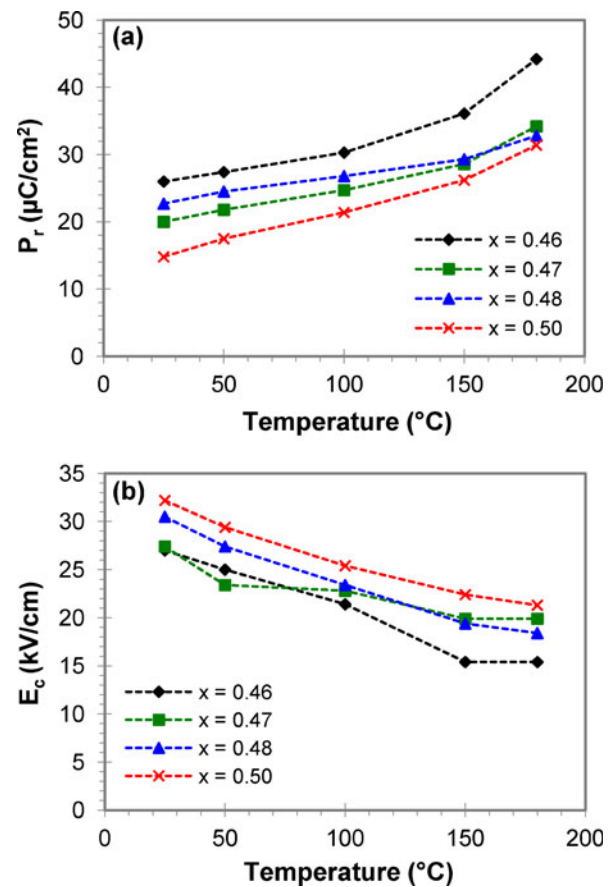

Fig. 2 (a) P_r and (b) E_c of $(1-x)$BMTFS – xPT, at different temperatures at 50 kV/cm

The migration of V_O under applied field may also explain why the maximum polarisation is greater than the saturated polarisation for compositions with x=0.46 above 100°C [12].

Figure 3 displays the temperature dependent bipolar strain hysteresis loops of $(1-x)$BMTFS – xPT for $0.46 \leq x \leq 0.50$ with a maximum field of 50 kV/cm from room temperature to 180°C. The increase in total strain behaves in a similar manner to that of polarisation. The loops appear to be more saturated and the total strain exhibited by all samples (plotted in Fig. 4(a)) increases with temperature. A decrease in coercive field is also observed with increase in temperature. The high field $d^*_{33(bi)}$, calculated as S_{max}/E_{max}, is shown in Fig. 4(b). A dramatic increase in polarisation, total strain and $d^*_{33(bi)}$ is observed for the rhombohedral composition x=0.46 above 100°C as shown in Figs. 2(a) and 4. This could be due to the increase in concentration of domain walls or their mobility. In each case, it suggests that the composition is closer to the MPB above 100°C than at room temperature, implying that the MPB curves towards the $Bi(Me)O_3$ end member on heating. Similar behaviour in

Fig. 3 Temperature dependence of S-E bipolar loops for (1-*x*)BMTFS – *x*PT ceramics, at 25°C, 50°C, 100°C, 150°C and 180°C, measured at 50 kV/cm, (**a**) *x*=0.46, (**b**) *x*=0.47, (**c**) *x*=0.48 and (**d**) *x*=0.50
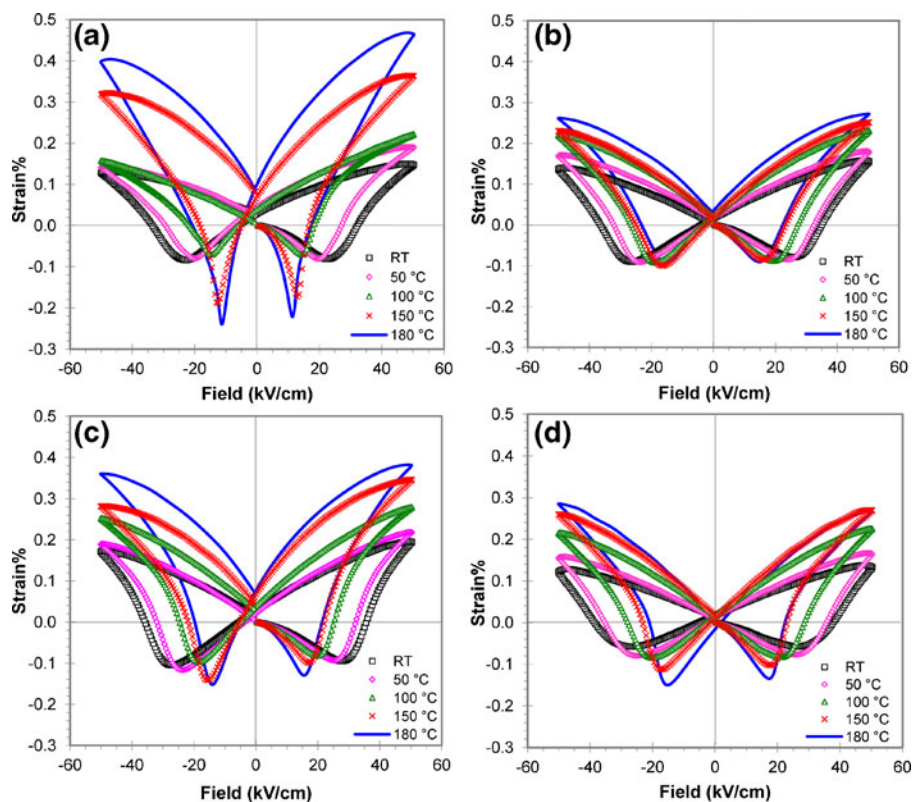
unipolar strain data has been reported for BMT – PT compositions close to the MPB [5] and in some PZT-based compositions [13].

Figure 5 presents the % strain vs. electric field from room temperature to 180°C exhibited by poled (1-*x*) BMTFS – *x*PT ceramics with 0.46≤*x*≤0.50 at 50 kV/cm under unipolar drive. At a given field, the strain displayed by the sample approaching E_{max} was lower than the strain departing E_{max} due to strain hysteresis [14]. Figure 6 shows the temperature dependence of % strain and high field piezoelectric coefficient under unipolar drive, $d^*_{33(uni)}$ for compositions with 0.46≤*x*≤0.50. A linear increase in strain and $d^*_{33(uni)}$ was observed in all compositions up to 100°C. The highest strains (~0.3%) were obtained in the tetragonal phase (*x*=0.5) at 180°C even though at room temperature, the rhombohedral composition (*x*=0.46) exhibits a greater % strain. This discrepancy may be explained by considering lattice strain for *x*=0.5 (3.2%) compared with *x*=0.46 (0.2%) [4]. At room temperature, more non-180° domains are piezoelectrically active due to lower internal stress in the rhombohedral composition (*x*=0.46) than for tetragonal compositions (*x*=0.5) and hence the % strain is greater in the former. However, as temperature increases, the barrier to domain wall motion decreases and the non-180° domains in *x*=0.5 become increasingly piezoelectrically active. The larger lattice strain associated with *x*=0.5

compared with *x*=0.46, therefore results in a larger % strain [15, 16].

Figure 7 provides the small signal d_{33} coefficient as a function of temperature for poled (1-*x*)BMTFS – *x*PT compositions, *x*=0.46, 0.48 and 0.50 at 10 V. The d_{33} of all compositions increases with temperature. The increase is initially linear but becomes non-linear as T_C is approached. As shown in Fig. 7, samples with *x*=0.48, 0.50 and 0.46 exhibited maximum d_{33} of 1168 pm/V at 418°C, 854 pm/V at 442°C and 509 pm/V at 422°C, respectively. In comparison, none of the prior investigated BMT-PT and BS-PT systems displayed maximum d_{33} values beyond 800 pm/V and all the maximum temperatures were determined to lie below 400°C [9]. The maximum temperatures noted here are 20–30°C lower than the corresponding T_Cs determined from the permittivity maxima. Such differences between the depolarisation and ferroelectric transition temperature have been observed in Bi(*Me*)O₃ – PT [9] and lead free systems [17]. An anomaly is observed in d_{33} for *x*=0.46 at 200°C. Its origin is not yet understood but may be related to the curvature of the MPB towards the Bi(*Me*)O₃ end member. Figure 8 shows k_p as a function of temperature for poled (1-*x*) BMTFS – *x*PT ceramics, 0.46≤*x*≤0.50, obtained by performing impedance analysis on samples at various frequencies. The resonance and antiresonance frequencies decrease with increasing temperature due to the
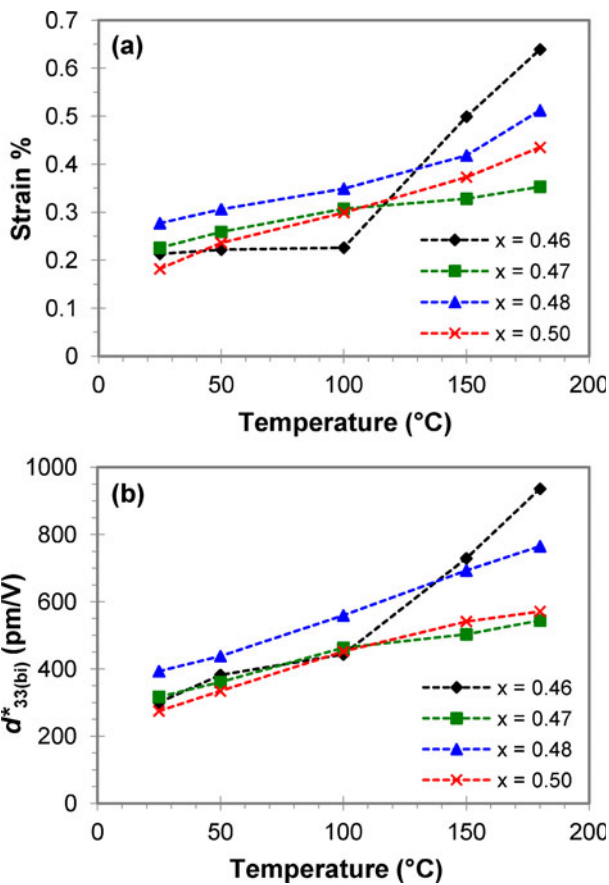
Fig. 4 (**a**) Total strain (%) and (**b**) high field $d^*_{33(bi)}$ of $(1-x)$BMTFS – xPT ceramics obtained from bipolarly driven S-E loops measured at different temperatures at 50 kV/cm
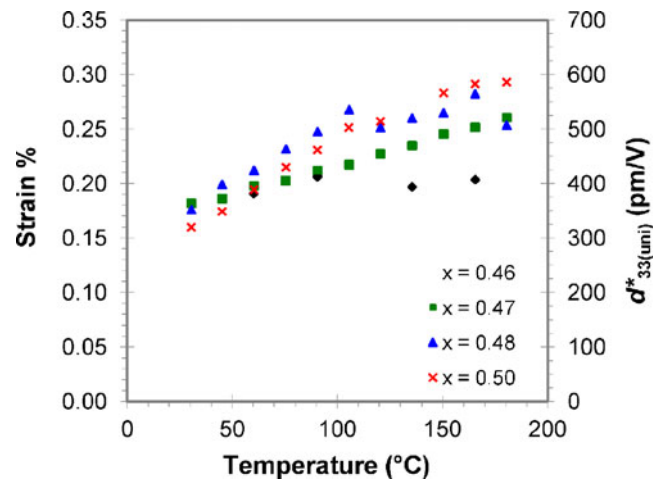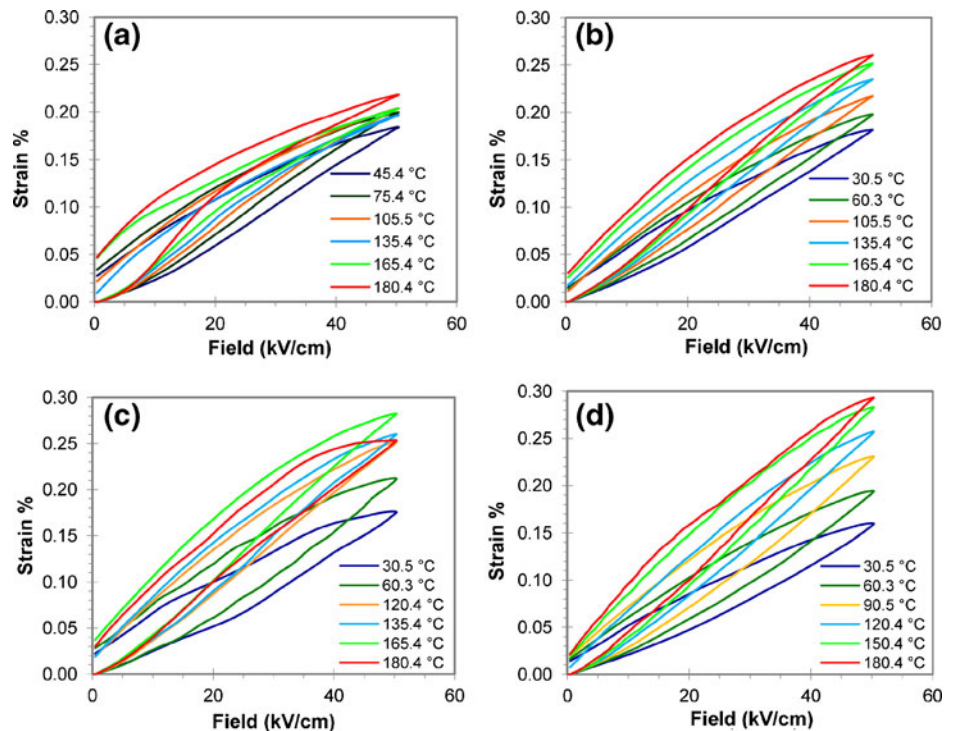

Fig. 6 Strain (%) and high field $d^*_{33(uni)}$ of $(1-x)$BMTFS – xPT ceramics obtained from unipolarly driven S-E loops measured at different temperatures at 50 kV/cm. Note that points for strain (%) and $d^*_{33(uni)}$ are identical since $d^*_{33(uni)}=(S_{max}/E_{max})$

thermal expansion of the sample. Most notably, the coupling coefficient of the MPB composition ($x=0.48$) increases with temperature until ~375°C, above which it markedly decreases as T_C is approached. Note that the coupling coefficient ($k^2=d^2/s^E \varepsilon^X$) [18] does not display a maximum before the phase transition unlike the piezoelectric coefficient, compliance and permittivity. PZT shows higher room temperature k_p (~0.65) but this value decreases steadily with increase in temperature and reduces drastically above 200°C [2]. The presence
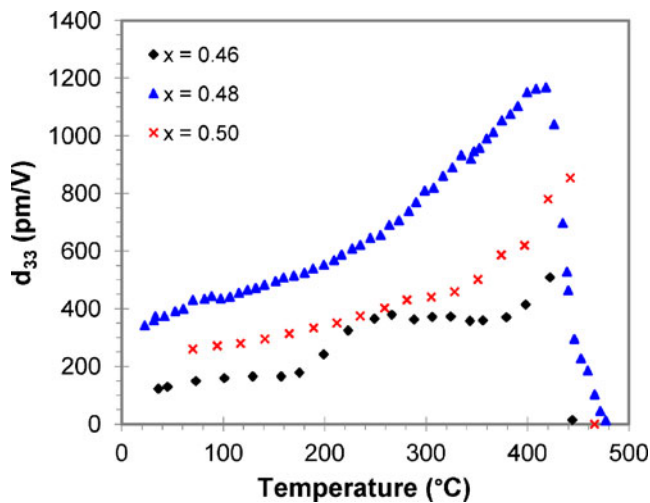
Fig. 5 Temperature dependence of S-E unipolar loops for (1-x)BMTFS – xPT ceramics, measured at 50 kV/cm, (**a**) x=0.46, (**b**) x=0.47, (**c**) x=0.48 and (**d**) x=0.50

Fig. 7 Temperature dependence of small signal d_{33} coefficient of $(1-x)$ BMTFS – xPT ceramics, x=0.46, 0.48 and 0.50

of high k_p values above 200°C illustrates clearly the potential for BMTFS–PT compositions in the fabrication of high temperature sensors and actuators.

4 Conclusions

The temperature dependence of ferroelectric and piezoelectric properties of BMTFS – PT ceramics in the vicinity of the MPB was investigated. Polarisation, unipolar and bipolar strain, d_{33} and k_p increased but E_c decreased with temperature which is explained in terms of thermal softening of dipoles and increased domain wall motion as T_C is approached. The rhombohedral composition, x=0.46 shows a dramatic enhancement in polarisation and strain behaviour above 100°C. To explain this behaviour, it is postulated that
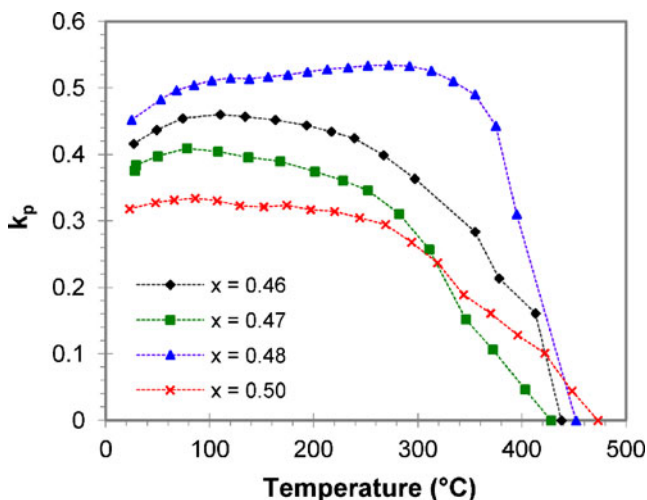
the MPB in the BMTFS-PT solid solution is curved towards the $Bi(Me)O_3$ end member as temperature increases. The MPB composition, x=0.48 displays a small signal d_{33} value of >1000 pm/V recorded up to ~ 400°C and room temperature k_p maintained as high as 375°C. Although these values are comparable to BS–PT [19], the 50% reduction in raw materials costs, coupled with the enhanced high temperature stability in comparison to PZT, makes 0.52BMTFS – 0.48PT a promising candidate for high temperature piezoelectric applications. Further material improvements may be envisaged by employing the enhanced tetragonality embodied by adding $Bi(Zn_{1/2}Ti_{1/2})O_3$ (BZT) as recently demonstrated with high Curie temperatures in the system PT-BMT-BZT [20].

References

1. S. Sherrit, X.Q. Bao, Y. Bar-Cohen, Z.S. Chang, Proc. SPIE **5387**, 411 (2004)
2. B. Jaffe, W.R. Cook, H. Jaffe, Piezoelectric Ceramics, (University of Michigan: R.A.N Publishers, 1971).
3. R.E. Eitel, C.A. Randall, T.R. Shrout, P.W. Rehrig, W. Hackenberger, S.E. Park, Jpn. J. Appl. Phys. Part 1 **40**, 5999 (2001)
4. T. Sebastian, I. Sterianou, D.C. Sinclair, A.J. Bell, D.A. Hall, I.M. Reaney, J. Electroceram. **25**, 130 (2010)
5. J. Chen, X.L. Tan, W. Jo, J. Rödel, J. Appl. Phys. **106**, 034109 (2009)
6. A. Dwivedi, C.A. Randall, Mater. Lett. **65**, 1308 (2011)
7. A. Moure, M. Alguero, L. Pardo, E. Ringgaard, A.F. Pedersen, J. Eur. Ceram. Soc. **27**, 237 (2007)
8. Q.A. Zhang, Z.R. Li, F. Li, Z. Xu, X. Yao, J. Am. Ceram. Soc. **93**, 3330 (2010)
9. T. Leist, J. Chen, W. Jo, E. Aulbach, J. Suffner, J. Rödel, J. Am. Ceram. Soc. (2011). doi:10.1111/j.1551-2916.2011.04848.x
10. IEEE Standard on Piezoelectricity. ANSI/IEEE Std. 176-1987 (1987).
11. K. Carl, K.H. Hardtl, Ferroelectrics **17**, 473 (1978)
12. I.W. Kim, D.S. Lee, S.H. Kang, C.W. Ahn, Thin Solid Films **441**, 115 (2003)
13. H. Kungl, M.J. Hoffmann, Acta Mater. **55**, 5780 (2007)
14. H. Kungl, T. Fett, S. Wagner, M.J. Hoffmann, J. Appl. Phys. **101**, 044101 (2007)
15. D.A. Hall, A. Steuwer, B. Cherdhirunkorn, T. Mori, P.J. Withers, J. Appl. Phys. **96**, 4245 (2004)
16. H. Kungl, R. Theissmann, M. Knapp, C. Baehtz, H. Fuess, S. Wagner, T. Fett, M.J. Hoffmann, Acta Mater. **55**, 1849 (2007)
17. E.M. Anton, W. Jo, D. Damjanovic, J. Rödel, J. Appl. Phys. **110**, 094108 (2011).
18. D. Damjanovic, Rep. Prog. Phys. **61**, 1267 (1998)
19. R.E. Eitel, Novel piezoelectric ceramics: Development of high temperature, high performance piezoelectrics on the basis of structure, Department of Materials Science and Engineering, (The Pennsylvania State University: State College, 2003).
20. D.M. Stein, I. Grinberg, A.M. Rappe, P.K. Davies, J. Appl. Phys. **110**, 074110 (2011)

Fig. 8 Temperature dependence of k_p for $(1-x)$BMTFS – xPT ceramics. All samples were poled for 1 h at 150°C