On the high temperature phase transition in $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ ceramic

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Temperature dependent X-ray diffraction (XRD) and dielectric properties of perovskite $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ ceramic prepared using a standard solid-state reaction process is presented. Along with phase transitions at low temperature, a new phase transition at high temperature (873°C at 20 Hz), diffusive in character has been found where the lattice structure changes from monoclinic (space group: $P2_1/m$) to hexagonal (space group: $P6_3/mmm$). This result places present ceramic in the list of potential candidate for intended high temperature applications. The AC conductivity data followed hopping type charge conduction and supports jump relaxation model. The experimental value of $d_{33} = 98 \text{ pC/N}$ was found. The dependence of polarization and strain on electric field at room temperature suggested that lead-free $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ is a promising material for electrostrictive applications.

Keywords: Lead-free ceramic; structure; dielectric properties; phase transition; AC conductivity; piezoelectric; electrostriction.

1. Introduction

Barium zirconate titanate, $\text{Ba}(\text{Zr,Ti})\text{O}_3$ (BZT) is a well-known stable lead-free ferroelectric material which finds many technological applications such as relaxor,^{1–5} microwave,⁶ high voltage,⁷ high temperature,⁸ actuator,⁹ piezoelectric,^{10–12} energy storage,¹³ magnetoelectric.¹⁴ Investigations have been taken up world-wide with different aims on the solid solutions of BZT with other materials like: $(\text{Ba,Ca})\text{TiO}_3$,^{15–19} $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$,^{20–23} $(\text{K}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$,¹⁰ $\text{Bi}_{0.4871}\text{Na}_{0.4871}\text{La}_{0.0172}\text{TiO}_3$,¹² $\text{Ba}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$,²⁴ BiFeO_3 ,^{9,25} $\text{BiFe}_{0.99}\text{Al}_{0.01}\text{O}_3$,⁸ $\text{Mg}_{0.2}\text{Cu}_{0.3}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$,¹⁴ $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$,²⁶ PbTiO_3 - $(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$,²⁷ MgTiO_3 ,²⁸ Yb_2O_3 ,²⁹ NiO ,³⁰ Ni ,³¹ polyvinyl alcohol,³² epoxy,³³ Portland cement,^{34,35} etc. Further, materials having high dielectric constant (10^3 – 10^6) are considered to be important nowadays keeping in view the growing interest in the fields of aeronautic, aerospace, power plants, automotive industries, oil and natural gas industries, various critical components' evaluation in nuclear industries, hybrid or electrically powered vehicles, thermal and geothermal engineering, etc. implying the use of piezoelectric devices in extreme operating conditions on a wide temperature range.^{36–39} Liu and Ren,¹⁹ showed that there exists a

cubic–rhombohedral–tetragonal triple point at morphotropic phase boundary in a BZT-based ferroelectric system, $(1-x)(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ - $x\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ at $x = 0.50$ with high dielectric constant and piezoelectric coefficient at room temperature which are, respectively, found to be ~ 3060 and $\sim 620 \text{ pC N}^{-1}$. Also, a most recent work of authors' group, it was reported that apart from the phase transitions at low temperature, there exist phase transitions at high temperature too in this ceramic system and was well supported by in situ high temperature X-ray diffraction (XRD) studies.¹⁶ Keeping in view of these,^{10,14–19} $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ (BZT20/80) with tetragonal structure at room temperature is considered to be a promising material. It is observed that, no report, to the authors' knowledge, has so far been made on BZT20/80 at elevated temperatures ($T > 500^\circ\text{C}$). Further, the knowledge of phase transition of a material is of paramount importance from the science and technology point of view. Thus, examining the phase transition behaviour of BZT20/80 at high temperature seems very important and this very fact is the crux of motivation of this work.

Accordingly, in the present work, *in situ* X-ray diffraction and dielectric studies of $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ ceramic up to

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1000°C have been carried out with the aim of getting information about phase transition behavior at high temperature, if at all exist, which will be able to further widen the intended applications' window. Fortunate enough, a new transition phase at 873°C with giant dielectric constant ($\sim 10^6$) has been observed in BZT20/80. The microstructural (SEM and EDX), room temperature electric polarization, electrostrictive strain and piezoelectric studies have also been carried out.

2. Experimental

Ba(Zr_{0.2}Ti_{0.8})O₃ ceramic powder was prepared using standard solid-state reaction technique. The calcination and sintering conditions were, respectively kept to be 1450°C/5 h and 1500°C/3 h in air atmosphere. Polyvinyl alcohol (PVA) was used as binder. The powder high temperature X-ray diffraction (HXRD) data at high temperature for BZT20/80 ceramic were collected from 30°C to 1000°C with CuK α radiation over a wide range of 2θ , i.e., from 10° to 90°. The lattice parameters along with the structures for the measured temperatures were obtained from Rietveld analysis of HXRD data using FullProf software. The energy dispersive X-ray pattern and microstructure of the fractured surface of BZT20/80 were carried out by a field emission scanning electron microscope (JEOL JSM-7600F, Japan). The dielectric characteristics of present ceramic, coated with platinum paste, were measured with an Impedance analyzer (E4990A-120, Keysight Technologies, USA) over a temperature range (25–950°C) and frequency (20–10,00,000 Hz). AC conductivity data were obtained using a relation: $\sigma_{AC} = \omega \epsilon_0 \epsilon' \tan \delta$, where $\omega = 2\pi f$, (f being the operating frequency); $\epsilon_0 (= 8.854 \times 10^{-12} \text{ Fm}^{-1})$ is the permittivity of free space, ϵ' real part of permittivity and $\tan \delta (= \epsilon''/\epsilon')$ is the dielectric loss factor. A DC electric field 15 kV/cm was applied for 30 min at room temperature to pole BZT ceramic. The electric field versus polarization (P) and electrostrictive strain (S) curves at room temperature for poled sample were obtained using a ferroelectric analyzer (TF Analyzer 2000, Aixact, Germany) at 2 Hz. A piezometer PM 3500 (KCF Technologies, USA) was

used to measure the longitudinal piezoelectric charge coefficient (d_{33}) of the poled BZT sample.

3. Results and Discussion

Figure 1 shows the energy dispersive X-ray (EDX) spectrum of BZT20/80. Only the peaks of Ba, Ti, Zr and O are visible, indicating the purity of formation of compound. The micrograph taken using SEM is presented in the inset of Fig. 1. The photograph does not contain any void, suggesting the formation of high density material. The average grain size was estimated to be $\sim 6 \mu\text{m}$.

The frequency variation of the real, ϵ' and imaginary, ϵ'' parts of permittivity at different temperatures, are illustrated in Fig. 2. It is observed that both ϵ' and ϵ'' follows inverse dependence on frequency like that of normal ferroelectric materials. Such nature of the dielectric relaxation suggests that in the measured frequency region, dipolar relaxation is covered up by free charge relaxation.^{40,41} The room temperature (25°C) values of ϵ' and $\tan \delta$ at 1 kHz are respectively, found to be 4198 and 0.04.

Figure 3 displays the variation of ϵ' and $\tan \delta$ with temperature at different frequencies. Apart from two lower temperature dielectric relaxations, which veers towards higher temperature side, a phase transition at high temperature (T_m^H) could clearly be seen at 873°C at 20 Hz (inset Fig. 3) in BZT20/80 whereas ϵ'' - T curves also show similar behavior with the peak positions are occurring at lower temperatures compared to the respective peaks of ϵ' - T curves. Further, the value of T_m^H , diffusive in character, also veers towards higher temperature side with increasing frequency, exhibiting an extremely high relaxor like dielectric behavior and the frequency dispersion is much stronger than the typical relaxor ferroelectrics such as Pb(Mg_{1/3}Nb_{2/3})O₃. The values of the dielectric parameters: T_m^H , ϵ' and $\tan \delta$ are respectively, found to be 873°C, 2.45×10^6 , and 0.19 at 20 Hz. The reason behind displaying giant dielectric constant may not simply be owing to the grain-boundary and grain-size dependent external factors rather an important contribution of the

Fig. 1. EDX pattern and scanning electron micrograph of fractured surface (inset) of Ba(Zr_{0.2}Ti_{0.8})O₃ ceramic.

Fig. 2. Frequency dependence of real and imaginary parts of dielectric constant of $\text{Ba}(\text{Zr}_{0.20}\text{Ti}_{0.80})\text{O}_3$ ceramic at different temperatures.

inherent factors like chemical substitution which induces the modifications of localized electronic structure also plays a crucial role.

With an aim to confirm the observed T_m^H in BZT20/80, *in situ* X-ray diffraction studies were carried out at high temperatures. Accordingly, Rietveld refined HXRD profiles of BZT20/80 ceramic from 700°C to 1000°C are illustrated in Figs. 4(a) and 4(b). It is seen that the XRD patterns at all the temperatures display single phase perovskite structure whose peaks are veering towards left (lower Bragg angle side) with the increasing temperature up to 800°C thereafter they are veering towards right. This confirms that the material has a definite phase transition (change in lattice structure) between 800°C and 900°C. Figure 4(b) displays one of the XRD peaks hived between 30° to 33° and properly magnified to show their shifting with temperature. A small shift in the XRD peak has been noticed. This advocates the increment in d -value which might be due to the thermal expansion during heating. The analyses of XRD data indicated the unit cell structure to be monoclinic (space group $P2_1/m$) up to 800°C and thereafter it becomes hexagonal (space group $P6_3/mmm$). The unit cell structures and their parameters are depicted in Table 1. Hence, the HXRD studies also confirmed that BZT20/80 has a definite phase transition between 800°C and 900°C.

Fig. 3. Temperature dependence of dielectric constant and loss tangent of $\text{Ba}(\text{Zr}_{0.20}\text{Ti}_{0.80})\text{O}_3$ ceramic at different frequencies. Inset: Variation of dielectric constant with temperature at 20 Hz.

The frequency-dependent AC conductivity (σ_{AC}) of BZT20/80 at different temperatures has been shown in Fig. 5. The conductivity spectra show the dispersion throughout the frequency range for all temperatures. Also, the values of σ_{AC} decrease with decreasing frequency and become almost independent (σ_{DC}) of frequency at higher temperatures which could be due to the long-range translational motion of the charge carriers and may be attributed to the existence of space charge in the material. Further, $\sigma_{AC} - f$ data ensue double power law: $\sigma_{AC} = \sigma_{DC} + A\omega^{s_1} + B\omega^{s_2}$, where σ_{DC} is the frequency independent (or DC) part of AC conductivity. The exponent s_1 ($0 \leq s_1 \leq 1$) characterizes the low frequency region, i.e., it resembles to the grain-boundary conductivity corresponding to the translational ion hopping, whereas the exponent s_2 ($0 < s_2 < 2$) characterizes the high frequency region corresponding to the grain conductivity suggesting the presence of localized relaxation/re-orientation process,⁴² the activation energy in such case is ascribed to the reorientation ionic hopping. Also, there is higher probability for an ion to jump back (unsuccessful hop) in case of jump relaxation model (JRM).^{43,44} However, if the neighborhood becomes relaxed with respect to the ion's position, the ion stays in the new site and the conductivity is associated with successful hops in the low frequency region. Beyond this, with the increase in frequency, there will be higher possibility of unsuccessful hops and the change in successful to unsuccessful hops ratio

Fig. 4. XRD patterns of Ba(Zr_{0.20}Ti_{0.80})O₃ ceramic at (a) different temperatures and (b) in the selected regions of 2θ (30°–33°).

results in dispersion in conductivity in the material. In the perovskite type oxide materials, presence of charge traps in the band gap of the insulator is expected. The JRM indicates that different activation energies are related to unsuccessful and successful hopping processes. From the plots, it is manifested that s_1 assumes maximum values ~ 0.9 , while, s_2 assumes maximum values ~ 1.2 and is always greater than 1. Inset of Fig. 5 presents the temperature ($10^3/T$) variation of $\log \sigma_{AC}$ at different frequencies. The activation energy for conduction was obtained using the Arrhenius relationship: $\sigma_{AC} = \sigma_o \exp(-E_a/k_B T)$ in higher temperature region. A linear least-square fit to the conductivity data to this equation gives the value of the apparent activation energy, E_a which are found to increase (from 0.66 eV at 1 kHz to 0.68 eV at 1 MHz) with increment in frequency. Also, increase in

conductivity with increasing temperature can be seen, which may be explained on the basis that within the bulk, the oxygen vacancies due to the loss of oxygen are usually created during sintering and the charge compensation follows the Kröger-Vink equation: $O_o \rightarrow \frac{1}{2} O_2 \uparrow + V_o^{\bullet\bullet} + 2e^-$, which shows that free electrons are left behind in the process, making the material n -type. The temperature as well as frequency dependence of AC conductivity in BZT20/80

Table 1. The crystal data of Ba(Zr_{0.20}Ti_{0.80})TiO₃ ceramic obtained from X-ray powder diffraction data procured at different temperatures.

Parameters	700°C	800°C	900°C	1000°C
Crystal system	Monoclinic	Monoclinic	Hexagonal	Hexagonal
Space group	$P2_1/m(10)$	$P2_1/m(10)$	$P6_{3mm}(191)$	$P6_{3mm}(191)$
a (Å)	4.6409	4.0200	11.4093	9.2287
b (Å)	6.9784	8.0805	11.4093	9.2287
c (Å)	3.9900	2.9275	13.0902	15.7593
β (°)	92.826	91.949	—	—
γ (°)	—	—	120	120
V (Å ³)	129.0631	95.0411	1475.6787	1162.3724

Fig. 5. Frequency dependence of AC conductivity of Ba(Zr_{0.20}Ti_{0.80})O₃ ceramic at different temperatures. Inset: Variation of AC conductivity of Ba(Zr_{0.20}Ti_{0.80})O₃ with temperature at different frequencies.

Fig. 6. The P - E , bipolar S - E and S - P^2 (inset) plots for $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ ceramic at room temperature.

resembles that of hopping type charge conduction and supports JRM.

Figure 6 illustrates the variation of electric polarization (P) and electrostrictive strain (S) with electric field measured at room temperature for BZT20/80 ceramic. P - E plot displays a normal ferroelectric hysteresis loop akin to such system.⁴⁵ The values of remanent polarization P_r and coercive field E_c are observed to be $0.35 \mu\text{C}/\text{cm}^2$ and $0.77 \text{ kV}/\text{cm}$. The strain-field plot exhibits very fine butterfly-shaped strain hysteresis loop, a distinct feature of ferroelectric materials.^{46,47} The maximum value of strain measured at $60 \text{ kV}/\text{cm}$ is found to be 0.04% . Further, a linear variation of S and P^2 without any negative strain at E_c is expected for a normal nonpolar material under external fields.^{47,48} The converse piezoelectric effect is measured for BZT20/80 sample from the ratio of the strain maximum to peak electric field $S_{\text{max}}/E_{\text{max}}$, which was calculated to be $0.08 \text{ nm}/\text{V}$. The value of electrostrictive coefficient Q_{11} was determined using the linear least-square fitting of S - P^2 data (inset Fig. 6) with the formula: $S = Q_{11}P^2$. The value of Q_{11} has been estimated to be $0.03 \text{ m}^4 \text{ C}^{-2}$ which is even larger than that of the well-known electrostrictive material $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ single crystal having Q_{11} of $0.025 \text{ m}^4 \text{ C}^{-2}$ and also notably higher to the recently reported BNT-BT-KN ceramic system with $Q_{11} = 0.0296 \text{ m}^4 \text{ C}^{-2}$.^{49,50} However, the value of electrostrictive coefficient is reported to be $0.04 \text{ m}^4 \text{ C}^{-2}$ in Fe-doped $0.5\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ - $0.5(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ lead-free ferroelectric ceramics^{51,52} which is notably higher compared to the present ceramic. The strain response in such system is believed to be due to an extrinsic contribution comes from ferroelectric non- 180° domain switching and/or an intrinsic contribution due to changes in the crystal lattice dimensions.^{53,54} Furthermore, the S - P^2 curve is observed to be linear with very small hysteresis, moderate strain and converse piezoelectric coefficient measured at low electric field shows the soft-elastic nature of ceramic, which indicates that the BZT20/80 is a favorable lead-free electrostrictive material especially for applications in positioning actuators. The

experimental value of $d_{33} = 98 \text{ pC}/\text{N}$ was found for BZT20/80 ceramic.

4. Conclusions

Ceramics $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ was synthesized using a standard high-temperature solid-state reaction process. Temperature dependence studies on the dielectric properties displayed a phase transition at high temperature (873°C at 20 Hz), diffusive in character, along with usual low temperature phases, which places present ceramic in the list of potential candidate for high temperature applications. The observed phase transition at high temperature in the system were well supported by *in situ* X-ray diffraction studies and the analyses of which showed that the lattice structure changes from monoclinic (space group: $P2_1/m$) to hexagonal (space group: $P6/mmm$). AC conductivity data followed hopping type charge conduction and supported jump relaxation model. The experimental value of $d_{33} = 98 \text{ pC}/\text{N}$ was found. The dependence of polarization and strain on electric field at room temperature suggested that lead-free $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ is a promising material for electrostrictive applications.

References

- P. Sateesh, J. Omprakash, G. S. Kumar and G. Prasad, Studies of phase transition and impedance behavior of $\text{Ba}(\text{Zr,Ti})\text{O}_3$ ceramics, *J. Adv. Dielectr.* **5**, 1550002 (2015).
- F. Moura, A. Z. Simões, C. A. Paskocimas, M. A. Zaghe, J. A. Varela and E. Longo, Temperature dependence on the electrical properties of $\text{Ba}(\text{Ti}_{0.90}\text{Zr}_{0.10})\text{O}_3$:2V ceramics, *Mater. Chem. Phys.* **123**, 772 (2010).
- S. Ke, H. Fan, H. Huang, H. L. W. Chan and S. Yu, Dielectric dispersion behavior of $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ solid solutions with a quasiferroelectric state, *J. Appl. Phys.* **104**, 034108 (2008).
- F. Moura, A. Z. Simões, B. D. Stojanovic, M. A. Zaghe, E. Longo and J. A. Varela, Dielectric and ferroelectric characteristics of barium zirconate titanate ceramics prepared from mixed oxide method, *J. Alloys Compd.* **462**, 129 (2008).
- C. E. Ciomaga, R. Calderone, M. T. Buscaglia, M. Viviani, V. Buscaglia, L. Mitoseriu, A. Stancu and P. Nanni, Relaxor properties of $\text{Ba}(\text{Zr,Ti})\text{O}_3$ ceramics, *J. Optoelectron. Adv. Mater.* **8**, 944 (2006).
- A. Ioachim, M. I. Toacsan, L. Nedelcu, M. G. Banciu, C. A. Duțu, E. Andronescu, S. Jinga, P. Nita and H. V. Alexandru, Dielectric properties of BZT ceramics for microwave applications, *J. Optoelectron. Adv. Mater.* **9**, 1833 (2007).
- J. Q. Qi, B. B. Liu, H. Y. Tian, H. Zou, Z. X. Yue and L. T. Li, Dielectric properties of barium zirconate titanate (BZT) ceramics tailored by different donors for high voltage applications, *Solid State Sci.* **14**, 1520 (2012).
- Z. Cen, C. Zhou, J. Cheng, X. Zhou, W. Li, C. Yan, S. Feng, Y. Liu and D. Lao, Effect of Zr^{4+} substitution on thermal stability and electrical properties of high temperature $\text{BiFe}_{0.99}\text{Al}_{0.01}\text{O}_3$ - $\text{BaTi}_{1-x}\text{Zr}_x\text{O}_3$ ceramics, *J. Alloys Compd.* **567**, 110 (2013).
- J. Chen and J. Cheng, High electric-induced strain and temperature-dependent piezoelectric properties of 0.75BF - 0.25BZT lead-free ceramics, *J. Am. Ceram. Soc.* **99**, 536 (2016).

- ¹⁰A. Zeb and S. J. Milne, 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, *J. Am. Ceram. Soc.* **96**, 3089 (2013).
- ¹¹F. Zhou, L. Wu, N. Liu, Y. Teng, Y. Li, J. Wen and X. Ren, Phase structure and electrical properties of $(0.8-x)\text{BaTiO}_3-0.2\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-x\text{BaZrO}_3$ lead-free piezoceramics, *J. Alloys Compd.* **512**, 52 (2012).
- ¹²P. Kantha, K. Pengpat, P. Jarupoom, U. Intatha, G. Rujijanagul and T. Tunkasiri, Phase formation and electrical properties of BNL-T-BZT lead-free piezoelectric ceramic system, *Curr. Appl. Phys.* **9**, 460 (2009).
- ¹³V. S. Puli, D. K. Pradhan, B. C. Riggs, S. Adireddy, R. S. Katiyar and D. B. Chrisey, Synthesis and characterization of lead-free ternary component BST-BCT-BZT ceramic capacitors, *J. Adv. Dielect.* **4**, 1450014 (2014).
- ¹⁴S. A. Khader, N. V. Giridharan, A. Chaudhuri and T. Sankarappa, Structural, dielectric and magnetic studies of $(x)\text{Mg}_{0.2}\text{Cu}_{0.3}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4+(1-x)\text{Ba}_{0.8}\text{Zr}_{0.2}\text{TiO}_3$ magnetoelectric composites, *AIP Conf. Proc.* **1728**, 020562 (2016).
- ¹⁵L. Zhang, X. Ren and M. A. Carpenter, Influence of local strain heterogeneity on high piezoelectricity in $0.5\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-0.5(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ceramics, *Phys. Rev. B* **95**, 054116 (2017).
- ¹⁶K. P. Chandra, R. Singh, A. R. Kulkarni and K. Prasad, High temperature phase diagram of pseudo binary $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ceramic system: *In situ* x-ray diffraction and dielectric studies, *Ferroelectric* **514** (2017), doi: 10.1080/00150193.2017.1357986.
- ¹⁷K. Brajesh, K. Tanwar, M. Abebe and R. Ranjan, Relaxor ferroelectricity and electric-field-driven structural transformation in the giant lead-free piezoelectric $(\text{Ba,Ca})(\text{Ti, Zr})\text{O}_3$, *Phys. Rev. B* **92**, (2015) 224112.
- ¹⁸Y. Tian, X. Chao, L. Jin, L. Wei, P. Liang and Z. Yang, Polymorphic structure evolution and large piezoelectric response of lead-free $(\text{Ba,Ca})(\text{Zr,Ti})\text{O}_3$ ceramics, *Appl. Phys. Lett.* **104**, 112901 (2014).
- ¹⁹W. Liu and X. Ren, Large piezoelectric effect in Pb-Free ceramics, *Phys. Rev. Lett.* **103**, 257602 (2009).
- ²⁰V. M. Ishchuk, L. G. Gusakova, N. G. Kisel, D. V. Kuzenko, N. A. Spiridonov and V. L. Sobolev, Zr and Sn substituted $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ -based solid solutions, *Mater. Res. Express* **3**, 026301 (2016).
- ²¹B. Parija, T. Badapanda and S. Panigrahi, Morphotropic Phase boundary in BNT-BZT solid solution: A study by Raman spectroscopy and electromechanical parameters, *J. Ceram. Process. Res.* **16**, 565 (2015).
- ²²B. Parija and S. Panigrahi, Impedance and ac conductivity study of $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3-\text{Ba}(\text{Zr}_{0.25}\text{Ti}_{0.75})\text{O}_3$ lead-free ceramics, *Ferroelectr. Lett.* **39**, 38 (2012).
- ²³C.-H. Wang, Physical and electric properties of lead-free $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3-\text{Ba}(\text{Zr}_{0.04}\text{Ti}_{0.96})\text{TiO}_3$ ceramics near the morphotropic phase boundary, *J. Ceram. Soc. Jpn.* **116**, 632 (2008).
- ²⁴H. Maimon, S. Eitssayeam, U. Intatha, T. Tunkasiri and G. Satittada, Phase evolution and physical properties of $(1-x)\text{BZT}-x\text{BFN}$ ceramic system, *Adv. Mater. Res.* **55-57**, 53 (2008).
- ²⁵W. Cai, C. Fu, G. Chen, R. Gao and X. Deng, Dielectric and ferroelectric properties of $x\text{BaZr}_{0.52}\text{Ti}_{0.48}\text{O}_3-(1-x)\text{BiFeO}_3$ solid solution ceramics, *J. Mater. Sci., Mater. Electron.* **26**, 322 (2015).
- ²⁶S.-H. Lee, S.-G. Lee and Y.-H. Lee, Electrical properties of lead-free $0.98(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3-0.02\text{Ba}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ piezoelectric ceramics by optimizing sintering temperature, *Nanoscale Res. Lett.* **7**, 15 (2012).
- ²⁷A. Prasatkhetragarn, A. Ngamjarurojana and R. Yimnirun, Relaxor-like behavior and ferroelectric evolution in $(1-x)[0.5\text{BZT}-0.5\text{PT}]-x\text{BKT}$ ternary system, *Integr. Ferroelectr.* **175**, 81 (2016).
- ²⁸X. Chou, J. Zhai and X. Yao, Relaxor behavior and dielectric properties of MgTiO_3 -doped $\text{BaZr}_{0.35}\text{Ti}_{0.65}\text{O}_3$ composite ceramics for tunable applications, *J. Am. Ceram. Soc.* **90**, 2799 (2007).
- ²⁹Y. Li, Z. Cui, R. Sang and X. Ma, Microstructure and dielectric behavior of ytterbium doped $\text{BaZr}_{0.1}\text{Ti}_{0.9}\text{O}_3$ ceramics, *Mater. Res.* **19**, 1376 (2016).
- ³⁰P. Jarupoom, S. Eitssayeam, K. Pengpat, T. Tunkasiri, D. P. Cann and G. Rujijanagul, Effects of NiO nanoparticles on the magnetic properties and diffuse phase transition of BZT/NiO composites, *Nanoscale Res. Lett.* **7**, 59 (2012).
- ³¹W. Cai, J. Gao, C. Fu and L. Tang, Dielectric properties, microstructure and diffuse transition of Ni-doped $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ ceramics, *J. Alloys Compd.* **487**, 668 (2009).
- ³²T. Badapanda, V. Senthil, S. Anwar, L. S. Cavalcante, N. C. Batista and E. Longo, Structural and dielectric properties of polyvinyl alcohol/barium zirconium titanate polymer-ceramic composite, *Curr. Appl. Phys.* **13**, 1490 (2013).
- ³³F. G. Garcia, C. R. Foschini, J. A. Varela, E. Longo, F. Moura and A. Z. Simões, Structural and functional characterization of barium zirconium titanate/epoxy composites, *Process. Appl. Ceram.* **5**, 205 (2011).
- ³⁴R. Potong, R. Rianoyi, A. Ngamjarurojana and A. Chaipanich, Dielectric and piezoelectric properties of 1-3 non-lead barium zirconate titanate-portland cement composites, *Ceram. Int.* **39**, S53 (2013).
- ³⁵R. Potong, R. Rianoyi, A. Ngamjarurojana, R. Yimnirun, R. Guo, A. S. Bhalla and A. Chaipanich, Effect of particle size on dielectric properties and hysteresis behavior of 0-3 barium zirconate titanate-portland cement composites, *Integr. Ferroelectr.* **148**, 131 (2013).
- ³⁶X. Jiang, K. Kim, S. Zhang, J. Johnson and G. Salazar, High-temperature piezoelectric sensing, *Sensors* **14**, 144 (2014).
- ³⁷S. K. Roy, S. N. Singh, S. K. Mukherjee and K. Prasad, $\text{Ba}_{0.06}(\text{Na}_{1/2}\text{Bi}_{1/2})_{0.94}\text{TiO}_3-\text{Ba}(\text{Fe}_{1/2}\text{Ta}_{1/2})\text{O}_3$: Giant permittivity lead-free ceramics, *J. Mater. Sci., Mater. Electron.* **28**, 4763 (2017).
- ³⁸S. Zhang and F. Yu, Piezoelectric materials for high-temperature sensors, *J. Am. Ceram. Soc.* **94**, 3153 (2011).
- ³⁹D. Damjanovic, Materials for high-temperature piezoelectric transducers, *Curr. Opin. Solid State Mater. Sci.* **3**, 469 (1998).
- ⁴⁰A. Molak, M. Paluch, S. Pawlus, J. Klimontko, Z. Ujma and I. Gruszka, Electric modulus approach to the analysis of electric relaxation in highly conducting $(\text{Na}_{0.75}\text{Bi}_{0.25})(\text{Mn}_{0.25}\text{Nb}_{0.75})\text{O}_3$ ceramics, *J. Phys. D, Appl. Phys.* **38**, 1450 (2005).
- ⁴¹K. P. Chandra, R. Singh, A. R. Kulkarni and K. Prasad, High temperature phase transition in $(\text{Ba}_{0.76}\text{Ca}_{0.24})(\text{Zr}_{0.04}\text{Ti}_{0.96})\text{O}_3$ ceramic, *Ferroelectric* **502**, 231 (2016).
- ⁴²C. R. Bowen and D. P. Almond, Modelling the 'universal' dielectric response in heterogeneous materials using microstructural electrical networks, *Mater. Sci. Technol.* **22**, 719 (2006).
- ⁴³K. Funke, Jump relaxation in solid electrolytes, *Prog. Solid State Chem.* **22**, 111 (1993).
- ⁴⁴S. R. Elliot, AC conduction in amorphous chalcogenide and pnictide semiconductors, *Adv. Phys.* **36**, 135 (1987).

- ⁴⁵J. P. Praveen, T. Karthik, A. R. James, E. Chandrakala, S. Asthana and D. Das, Effect of poling process on piezoelectric properties of sol-gel derived BZT-BCT ceramics, *J. Euro. Ceram. Soc.* **35**, 1785 (2015).
- ⁴⁶Y. M. Chiang, G. W. Farrey and A. N. Soukhojak, Lead-free high-strain single-crystal piezoelectrics in the alkaline-bismuth-titanate perovskite family, *Appl. Phys. Lett.* **73**, 3683 (1998).
- ⁴⁷L. Jin, F. Li and S. Zhang, Decoding the fingerprint of ferroelectric loops: Comprehension of the material properties and structures, *J. Amer. Ceram. Soc.* **97**, 1 (2014).
- ⁴⁸J.-S. Lee, K.-N. Pham, H.-S. Han, H.-B. Lee and V. D. N. Tran, Strain enhancement of lead-free $\text{Bi}_{1/2}(\text{Na}_{0.82}\text{K}_{0.18})_{1/2}\text{TiO}_3$ piezoelectric ceramics by Sn doping, *J. Korean Phys. Soc.* **60**, 212 (2012).
- ⁴⁹K. Uchino, S. Nomura, L. E. Cross, S. J. Jang and R. E. Newnham, Electrostrictive effect in lead magnesium niobate single crystals, *J. Appl. Phys.* **51**, 1142 (1980).
- ⁵⁰J. M. Li, F. F. Wang, X. M. Qin, M. Xu and W. Z. Shi, Large electrostrictive strain in lead-free $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-BaTiO}_3\text{-KNbO}_3$ ceramics, *Appl. Phys. A* **104**, 117 (2011).
- ⁵¹F. Li, L. Jin and R. Guo, High electrostrictive coefficient Q_{33} in lead-free $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3\text{-x}(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ piezoelectric ceramics, *Appl. Phys. Lett.* **105**, 232903 (2014).
- ⁵²L. Jin, R. Huo, R. Guo, F. Li, D. Wang, Y. Tian, Q. Hu, X. Wei, Z. He, Y. Yan and G. Liu, Diffuse phase transitions and giant electrostrictive coefficients in lead-free Fe^{3+} -doped $0.5\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3\text{-0.5}(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ferroelectric ceramics, *ACS Appl. Mater. Interfaces* **8**, 31109 (2016).
- ⁵³J. L. Jones, M. Hoffman, J. E. Daniels and A. J. Studer, Direct measurement of the domain switching contribution to the dynamic piezoelectric response in ferroelectric ceramics, *Appl. Phys. Lett.* **89**, 092901 (2006).
- ⁵⁴H. Kungl, R. Theissmann, M. Knapp, C. Baecht, H. Fuess, S. Wagner, T. Fett and M. J. Hoffmann, Estimation of strain from piezoelectric effect and domain switching in morphotropic PZT by combined analysis of macroscopic strain measurements and synchrotron X-ray data, *Acta Mater.* **55**, 184 (2007).