Full length article

A complex lead-free (Na, Bi, Ba)(Ti, Fe)O₃ single phase perovskite ceramic with a high energy-density and high discharge-efficiency for solid state capacitor applications

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ABSTRACT

We have investigated a series of compositions in the pseudo-ternary lead-free alloy system Na_{1/2}Bi_{1/2}TiO₃-BaTiO₃-BiFeO₃ with regard to its energy storage density and discharge efficiency. A composition 0.4(Na_{0.5}Bi_{0.5}TiO₃)-0.225BaTiO₃-0.375BiFeO₃ of this series was identified to give the best energy density and discharge efficiency. While conventional sintering gave energy density of 0.77 J/cm³ and discharge efficiency of 67%, we achieved a remarkable increase in energy storage density (~1.4 J/cm³) and discharge efficiency (~90%) by using spark plasma sintering of this composition. Our results suggest that this alloy system can be a potential lead-free candidate for high electric energy storage and discharge efficiency.

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1. Introduction

The progress of human civilization in this modern age requires newer sources of energy generation. Developing non polluting techniques for energy generations and finding efficient materials for energy storage are the most discussed topics in this century among the scientific community and global leaders. With active research going on to find new sources of energy, environment friendly energy storage materials also need to be developed [1]. Researchers working in the field of ferroelectrics have off late shown interest in the energy storage aspects of their materials. Lead based ferroelectric materials have shown good energy density and discharge efficiency. However lead is toxic and carcinogenic in nature and has adverse effect on human health and environment. Hence countries are now seriously looking into the aspect of banning the use of lead and laws are being framed for doing so. So there is an increasing pressure on the research community and the industry to find suitable lead free materials which can be used as an alternative to lead based ones in energy storage devices [2–5]. Till date the lead free ferroelectric materials have not shown prop-

erties comparable to the lead based ones. Anti-ferroelectric and relaxor category of materials are being actively probed for potential applications in energy storage devices owing to their low remnant polarization and coercive field leading to good energy storage capabilities and high discharge efficiency. Research groups from across the world are now in the search of suitable lead free materials which can be sintered at low temperature, for better utilization in multilayer ceramic capacitor (MLCC) applications and which displays a good energy density and discharge efficiency [6–8]. A few anti-ferroelectric systems have been reported which have shown good energy storage capabilities and good temperature stability [9,10]. However they lack a high discharge efficiency [11]. Hence a lead free system is required which has both a good energy density and discharge efficiency. Na_{0.5}Bi_{0.5}TiO₃ (NBT) based system are being seen as the most suitable lead free replacements for the lead based systems. However they have major drawbacks like high dielectric loss, high conductivity and large coercive field which limit their applications [12–15]. Our research was primarily guided by the motivation to find suitable composition in the lead-free category. In this paper we report the results of a pseudo-ternary lead-free alloy Na_{1/2}Bi_{1/2}TiO₃-BiFeO₃-BaTiO₃. First we identified the optimal composition with best properties by following the conventional ceramic synthesis method. We then investigated the effect of K_{0.5}Na_{0.5}NbO₃ (KNN) doping in dilute concentration and also compare the results vis-à-vis the specimens prepared by spark plasma

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sintering (SPS). Our strategy resulted in achieving an extraordinarily large energy density ($\sim 1.3 \text{ J/cm}^3$) and discharge efficiency ($\sim 90\%$) in this lead-free material system.

2. Experimental procedure

In this study we started with two pseudo-binary alloys $0.8(\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3)-0.2(\text{BaTiO}_3)$ which we refer to as NBTBT and $0.75\text{BiFeO}_3-0.25\text{BaTiO}_3$ is referred to as BFBT. NBTBT and BFBT were mixed in different molar ratios and the resultant compound was prepared by conventional solid state synthesis technique. Ultra-high pure chemicals Na_2CO_3 (99.9%, SRL), Bi_2O_3 (99%, SRL), TiO_2 (99.8%, Alfa Aesar), BaCO_3 (99.8%, Alfa Aesar), Fe_2O_3 (99.5%, Alfa Aesar), K_2CO_3 (99%, Alfa Aesar) and Nb_2O_5 (99.9%, Alfa Aesar) were dried in hot air oven for 2 h at 150°C . The dried chemicals were weighed according to their stoichiometric proportions and were ball milled in acetone medium in Agate vials (FRITSCH, P5) at 200 rpm for 8 h. After ball milling, the agate vials were taken out and dried under IR lamp for 12 h to remove acetone. The dried ball milled powders were collected and calcined at 850°C for 2 h in muffle furnace in covered alumina crucibles. $0.1 \text{ wt}\%$ MnO_2 was sprinkled on the calcined powders. Poly-Vinyl Alcohol (5 wt%) was added as a binder to the calcined powder and the powder was mixed thoroughly in agate mortar and pestle till the binder dried off and green pellets were prepared from the resultant powder by uniaxial pressing. Cold Isostatic pressing (CIP) of the green pellets was done at 300 MPa using a custom made setup in a hydraulic oil medium. The pellets were sintered in muffle furnace at 1125°C for 5 h by placing them on a platinum foil and covering them in a base and cone arrangement using alumina cone and plates. The density of the sintered pellets was measured using Archimedes principle. Two compositions were also synthesised by spark plasma synthesis (SPS) technique using a graphite die under a pressure of 50 MPa at a temperature of 800°C for 15 min. The residual carbon in the spark plasma sintered pellets that came from the graphite die, were removed by annealing the pellets at 800°C for 3 h. The sample was then heated at 1125°C for 2 h to increase the grain size. Microstructure of the sintered pellets was recorded by Scanning Electron Microscopy (ESEM, Quanta) after gold sputtering the pellets for 6 min. Prior to that the sintered pellets were given a mirror surface finish by diamond polishing and were thermally etched at 1025°C for 15 min. Sintered pellets were gently crushed using mortar and pestle for 2 mins followed by annealing at 500°C for 1 h to remove stress effect. The X-Ray Diffraction scan was performed on the resultant annealed powder using $\text{Cu-K}\alpha$ radiation in the θ - 2θ scan mode (Rigaku, Smart Lab) so as to have a texture free and stress free pattern. The ferroelectric hysteresis of the sintered pellets was obtained using a ferroelectric test system (RADIANT Technologies, Premier Precision II).

3. Results and discussion

Fig. 1 shows the X-Ray Diffraction (XRD) pattern of 0.5NBTBT-0.5BFBT, 0.25NBTBT-0.75BFBT, 0.75NBTBT-0.25BFBT, 0.5NBTBT-0.49BFBT-0.01KNN and 0.5NBTBT-0.48BFBT-0.02KNN annealed powder. The XRD pattern revealed a single perovskite phase without any secondary phases for all the compositions. All the Bragg peaks appeared as singlets suggesting a cubic-like perovskite structure for these compositions. Research groups in the past have reported $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ -based solid solutions with a similar cubic-like structure [16–19]. The bulk density of the sintered pellets of the five ceramic compounds of the NBTBT-BFBT series was measured by Archimedes principle. All the sintered pellets showed a density of more than 96%. The SPS pellets of the two compositions 0.5NBTBT-0.5BFBT and 0.5NBTBT-0.49BFBT-0.01KNN were more than 99%

Fig. 1. X-ray powder diffraction patterns of the annealed powders of the different compositions of NBTBT-BFBT.

dense. The microstructure of the sintered pellets was recorded by Scanning Electron Microscope (ESEM, Quanta). A visual overview of the SEM micrographs in Fig. 2 showed that 0.75NBTBT-0.25BFBT had a smaller average grain size as compared to 0.5NBTBT-0.5BFBT and 0.25NBTBT-0.75BFBT. This could be a possible reason (see Fig. 3) for the lower polarization of 0.75NBTBT-0.25BFBT compared to the other two compositions [20]. Doping of KNN did not cause any significant changes in grain size as 0.5NBTBT-0.49BFBT-0.01KNN and 0.5NBTBT-0.48BFBT-0.02KNN have similar grain sizes to 0.5NBTBT-0.5BFBT. Absence of visible porosity in the SEM micrographs confirms the high density obtained using the Archimedes method.

Fig. 3 shows the ferroelectric hysteresis behaviour of 0.5NBTBT-0.5BFBT (0.1 wt% MnO_2 doped), 0.25NBTBT-0.75BFBT (0.1 wt% MnO_2 doped) and 0.75NBTBT-0.25BFBT (0.1 wt% MnO_2 doped) as a function of field at 1 Hz at room temperature. The addition of 0.1 wt% MnO_2 to the compositions was done with the view to reduce the leakage current [21,22]. All the specimens suffered dielectric breakdown in the electric field range of 55 kV/cm to 60 kV/cm. Hence, for the sake of comparison, in this paper we will report ferroelectric loops, energy density and discharge efficiency upto a field of 50 kV/cm. The energy density (W) of the compositions are calculated by taking the integration of the area between the polarization axis and the discharge curve of the monopolar ferroelectric hysteresis loop. The formulae used for computing the

energy density is $W = \int_{P_r}^{P_{\max}} E.dP$. The area under the monopolar

hysteresis loop (W_{loss}) is calculated. The formulae used to calculate the discharge efficiency (η) is $\eta = \left(\frac{W}{W+W_{\text{loss}}} \times 100 \right)$ [23]. It is clearly evident that 0.5NBTBT-0.5BFBT has a double pinched loop indicating an anti-ferroelectric like behaviour. It shows a maximum polarization of $41.70 \mu\text{C/cm}^2$ at a field of 50 kV/cm at 1 Hz at room temperature. Among the other compositions in the series 0.75NBTBT-0.25BFBT has the most antiferroelectric like behaviour indicated by slim and slant loop with a distinct pinch in the middle. 0.25NBTBT-0.75BFBT, on the other hand, has a reduced pinching effect indicating a decrease in anti-ferroelectric nature as we go towards the BFBT rich side. However 0.75NBTBT-0.25BFBT has a lower polarization of $24.04 \mu\text{C/cm}^2$ at 50 kV/cm at 1 Hz as compared to 0.5NBTBT-0.5BFBT. 0.25NBTBT-0.75BFBT has a maximum polarization of $36.55 \mu\text{C/cm}^2$ at 50 kV/cm. The energy densities of 0.25NBTBT-0.75BFBT, 0.50NBTBT-0.50BFBT and

Fig. 2. SEM micrographs of the different compositions of NBTBT-BFBT. All the compositions were sintered at 1125 °C for 5 h. (a) 0.5NBTBT-0.5BFBT, (b) 0.25NBTBT-0.75BFBT, (c) 0.75NBTBT-0.25BFBT, (d) 0.50NBTBT-0.49BFBT-0.01KNN and (e) 0.50NBTBT-0.48BFBT-0.02KNN. Adjacent to the micrographs are the plots of the respective grain size distributions.

0.75NBTBT-0.25BFBT at 50 kV/cm are 0.57, 0.77 and 0.46 J/cm³, respectively. The corresponding discharge efficiencies are 60.3%, 67.0% and 73.0%, respectively.

When we added a third compound $K_{0.5}Na_{0.5}NbO_3$ (KNN) in a small amount to 0.5NBTBT-0.5BFBT, as per the nominal formula 0.5NBTBT-0.49BFBT-0.01KNN, the loops became extraordinarily slim, Fig. 4. This led to a dramatic increase in the discharge efficiency from 67.0% to 90.3%, as shown in Fig. 5. However due to decrease in the polarization the energy density is compromised. On increasing KNN doping to 2 mol percent the loop loses its slim character and becomes slightly wider. Though this led to a minor improvement in maximum polarization and energy density as compared to the 1% KNN doped sample, the increased hysteresis led to a significant decrease in its discharge efficiency. A comparison of the energy density and discharge efficiency of all the five compositions as a function of field at room temperature is shown in Fig. 5.

The ferroelectric behaviour of the composition 0.5NBTBT-0.5BFBT which exhibits the maximum energy density was also analysed as a function of temperature, Fig. 6. We observed that the energy density and the discharge efficiency of the 0.5NBTBT-0.5BFBT peaked at 75 °C with an energy density of 0.854 J/cm³ and a discharge efficiency of 71.5%. These values slightly decreased at 100 °C where an energy density of 0.80 J/cm³ and a discharge efficiency of 57.8% was obtained. The decrease in the discharge efficiency above 100 °C can be attributed to the loops became lossy in

Fig. 3. Ferroelectric hysteresis loop of different compositions of NBTBT-BFBT at room temperature. (a) 0.5NBTBT-0.5BFBT, (b) 0.25NBTBT-0.75BFBT and (c) 0.75NBTBT-0.25BFBT. The numbers inside the frames indicate the amplitudes of the field in kV/cm.

Fig. 4. Ferroelectric hysteresis loop of KNN doped 0.5NBTBT-0.5BFBT material at room temperature. (a) 0.5NBTBT-0.49BFBT-0.01KNN and (b) 0.5NBTBT-0.48BFBT-0.02KNN. The numbers inside the frames show the amplitudes of the ac field in kV/cm .

nature, presumably due to the thermally activated leakage [24]. This limits the applications of this material above 100°C .

We also carried out energy density and discharge efficiency study of 0.5NBTBT-0.5BFBT and 0.5NBTBT-0.49BFBT-0.01KNN by fabricating using spark plasma sintering technique, the details of which is given in the experimental section. The high densification achieved by SPS, as evidenced from the dense microstructure,

Fig. 5. Variation of (a) energy density and (b) discharge efficiency as a function of the maximum field amplitude for the different compositions of NBTBT-BFBT.

shown in Fig. 7, led to more than 1.5 times increase in the dielectric breakdown strength. For example, the pellets prepared by conventional synthesis were able to sustain a field of 50–55 kV/cm , whereas the pellets prepared by SPS were able to sustain up to a field of 80 kV/cm . Fig. 8 shows polarization-field hysteresis loop, energy density, and discharge efficiency of both the SPS samples. As compared to the conventionally sintered specimen, the energy density of 0.5NBTBT-0.5BFBT increased from 0.77 to $1.37 \text{ J}/\text{cm}^3$ and the discharge efficiency increased from 67.0% to

Fig. 6. (a) Polarization-field hysteresis loops of 0.5NBTBT-0.5BFBT at four different temperatures. (b) and (c) shows energy density and discharge efficiency at a field of 50 kV/cm (1 Hz) as a function of temperature. (d) shows polarization-field loops at 125 $^\circ\text{C}$ and 150 $^\circ\text{C}$.

Fig. 7. SEM micrographs of SPS pellets of (a) 0.5NBTBT-0.5BFBT and (b) 0.5NBTBT-0.49BFBT-0.01KNN. Adjacent to the micrograph is the plot of the grain size distribution.

Fig. 8. Polarization field hysteresis loop of SPS samples (a) 0.5NBTBT-0.5BFBT, (b) 0.5NBTBT-0.49BFBT-0.01KNN at four different field amplitudes. The corresponding energy densities and discharge efficiencies as a function of field are shown in (c) and (d), respectively.

75.6%. The energy density of SPS 0.5NBTBT-0.49BFBT-0.01KNN increased from 0.38 to 1.27 J/cm³. The corresponding discharge efficiency slightly decreased from 90.3% to 79.7%. These values are among the highest reported for lead free ferroelectrics till date in bulk polycrystalline ceramics.

One of the key aspects a material ought to possess in order to be industrially viable from a capacitor point of view is a low sintering temperature, a high energy density and discharge efficiency. Most studies in the past have used conventional sintering for processing of the ceramics. Zannen et al. [25] reported the energy storage properties of Gd doped NBT systems. They obtained an energy density of 0.45 J/cm³ at room temperature and of 0.85 J/cm³ at 140 °C for 2% Gd doped NBT system. An investigation by Wang et al. [9] into the energy storage capabilities of La doped NBT-BZT system yielded an encouraging value of 1.58 J/cm³ at a field of 83.4 kV/cm. However one of the drawbacks of the above mentioned systems is the use of rare earth elements as dopants which will render the energy storage device expensive. Gao et al. [26] have reported an energy density of 0.59 J/cm³ at a field of 56 kV/cm for 0.89NBT-0.06BT-0.05KNN system. The system was sintered at 1200 °C for 3 h. When compared with the system of Gao et al. our conventionally sintered 0.5NBTBT-0.5BFBT yields a higher energy density of 0.77 J/cm³ at a comparatively lower field of 50 kV/cm. The sintering temperature of our system (1125 °C) is also lower than that of Gao et al. A study by Xu et al. [10] on the NaNbO₃ modified NBT system revealed an energy density of 0.71 J/cm³ with a discharge efficiency of 66% at a field of 70 kV/cm. In contrast, our system shows a slightly higher energy density (0.77 J/cm³) at a lower field (50 kV/cm). Our SPS specimens show energy density of about 1.3 J/cm³ which is significantly higher than any other values reported in the lead-free category. We believe that this value can be further improved by mechanical confinement [23]. Our study reveals that the complex system (Na, Bi, Ba)(Ti, Fe)O₃ is a potential candidate for lead-free solid state capacitor applications. We however also feel that there could be other potential lead-free systems with good ferroelectric properties [27,28], which when modified with KNN and fabricated

using spark plasma sintering technique may also lead to improvement in their energy storage density and discharge efficiency.

4. Conclusion

The solid solutions of 0.5NBTBT-0.5BFBT, 0.25NBTBT-0.75BFBT, 0.75NBTBT-0.25BFBT, 0.50NBTBT-0.49BFBT-0.01KNN and 0.50NBTBT-0.48BFBT-0.02KNN with 0.1 wt% MnO₂ doping were prepared by the traditional solid state synthesis technique. The XRD analysis of the compositions revealed a pure perovskite phase. The ferroelectric characterization of the compositions showed that 0.5NBTBT-0.5BFBT possessed the highest energy density of 0.77 J/cm³ with a discharge efficiency of 67% at room temperature at an electric field strength of 50 kV/cm at 1 Hz. The composition 0.5NBTBT-0.49BFBT-0.01KNN showed a highly encouraging discharge efficiency of 90.3% with an energy density of 0.38 J/cm³ at 50 kV/cm field at room temperature. The ferroelectric behaviour of 0.5NBTBT-0.5BFBT at 50 kV/cm as a function of temperature showed the peak performance at 75 °C where an energy density of 0.85 J/cm³ and a discharge efficiency of 71.5% was noted. At 100 °C there was a slight decrease in energy density and discharge efficiency. Since the compositions prepared by the conventional sintering technique suffered dielectric breakdown relatively early in the field ranges of 55–60 kV/cm, this limited their energy density. When the composition showing the highest energy density was densified further by Spark Plasma Sintering (SPS) technique we found the energy storage density to be nearly doubled (1.3 J/cm³). The value of energy density obtained by us for 0.5NBTBT-0.5BFBT is among the highest reported till date for lead free ferroelectrics in the form of bulk ceramics.

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References

- [1] P. Poizat, F. Dolhem, Clean energy new deal for a sustainable world: from non- CO_2 generating energy sources to greener electrochemical storage devices, *Energy Environ. Sci.* 4 (2011) 2003–2019.
- [2] E. Cross, Materials science: lead-free at last, *Nature* 432 (7013) (2004) 24–25.
- [3] Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, M. Nakamura, Lead-free piezoceramics, *Nature* 432 (7013) (2004) 84–87.
- [4] J. Rödel, W. Jo, K.T. Seifert, E.M. Anton, T. Granzow, D. Damjanovic, Perspective on the development of lead-free piezoceramics, *J. Am. Ceram. Soc.* 92 (6) (2009) 1153–1177.
- [5] J. Parui, S.B. Krupanidhi, Enhancement of charge and energy storage in sol-gel derived pure and La-modified PbZrO_3 thin films, *Appl. Phys. Lett.* 92 (19) (2008) 2901.
- [6] H. Ogihara, C.A. Randall, S. Trolrier-McKinstry, High-Energy density capacitors utilizing 0.7 BaTiO_3 –0.3 BiScO_3 ceramics, *J. Am. Ceram. Soc.* 92 (8) (2009) 1719–1724.
- [7] R.B. Amin, H.U. Anderson, C.E. Hodgkins, San Fernando Electric Manufacturing Company, Low Temperature Fired Ceramic Capacitors, 1978, U.S. Patent 4,082,906.
- [8] G.H. Haertling, Ferroelectric ceramics: history and technology, *J. Am. Ceram. Soc.* 82 (4) (1999) 797–818.
- [9] Y. Wang, Z. Lv, H. Xie, J. Cao, High energy-storage properties of $[(\text{Bi}_{1/2}\text{Na}_{1/2})_{0.94}\text{Ba}_{0.06}]\text{La}_{(1-x)}\text{Zr}_x\text{TiO}_3$ lead-free anti-ferroelectric ceramics, *Ceram. Int.* 40 (3) (2014) 4323–4326.
- [10] Q. Xu, T. Li, H. Hao, S. Zhang, Z. Wang, M. Cao, Z. Yao, H. Liu, Enhanced energy storage properties of NaNbO_3 modified $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ based ceramics, *J. Eur. Ceram. Soc.* 35 (2) (2015) 545–553.
- [11] L. Zhao, Q. Liu, S. Zhang, J.F. Li, Lead-free AgNbO_3 anti-ferroelectric ceramics with an enhanced energy storage performance using MnO_2 modification, *J. Mater. Chem. C* 4 (36) (2016) 8380–8384.
- [12] I. Levin, I.M. Reaney, E.M. Anton, W. Jo, J. Rödel, J. Pokorny, L.A. Schmitt, H.J. Kleebe, M. Hinterstein, J.L. Jones, Local structure, pseudosymmetry, and phase transitions in $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ – $\text{K}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ ceramics, *Phys. Rev. B* 87 (2) (2013) 024113.
- [13] B.N. Rao, R. Ranjan, Electric-field-driven monoclinic-to-rhombohedral transformation in $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$, *Phys. Rev. B* 86 (13) (2012) 134103.
- [14] B.N. Rao, A.N. Fitch, R. Ranjan, Ferroelectric-ferroelectric phase coexistence in $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$, *Phys. Rev. B* 87 (6) (2013) 060102.
- [15] R. Garg, B.N. Rao, A. Senyshyn, P.S.R. Krishna, R. Ranjan, Lead-free piezoelectric system $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ – BaTiO_3 : Equilibrium structures and irreversible structural transformations driven by electric field and mechanical impact, *Phys. Rev. B* 88 (1) (2013) 014103.
- [16] J.E. Daniels, W. Jo, J. Rödel, J.L. Jones, Electric-field-induced phase transformation at a lead-free morphotropic phase boundary: case study in a 93% $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ –7% BaTiO_3 piezoelectric ceramic, *Appl. Phys. Lett.* 95 (3) (2009) 032904.
- [17] S.T. Zhang, A.B. Kouna, E. Aulbach, H. Ehrenberg, J. Rödel, Giant strain in lead-free piezoceramics $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ – BaTiO_3 – $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ system, *Appl. Phys. Lett.* 91 (11) (2007) 112906.
- [18] Y. Hiruma, H. Nagata, T. Takenaka, Detection of morphotropic phase boundary of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – $\text{Ba}(\text{Al}_{1/2}\text{Sb}_{1/2})\text{O}_3$ solid-solution ceramics, *Appl. Phys. Lett.* 95 (5) (2009) 2903.
- [19] R. Ranjan, A. Dwiwedi, Structure and dielectric properties of $(\text{Na}_{0.50}\text{Bi}_{0.50})_{1-x}\text{Ba}_x\text{TiO}_3$: $0 \leq x \leq 0.10$, *Solid State Commun.* 135 (6) (2005) 394–399.
- [20] C.A. Randall, N. Kim, J.P. Kucera, W. Cao, T.R. Shrout, Intrinsic and extrinsic size effects in fine-grained morphotropic-phase-boundary lead zirconate titanate ceramics, *J. Am. Ceram. Soc.* 81 (3) (1998) 677–688.
- [21] K. Chen, G. Xu, D. Yang, X. Wang, J. Li, Dielectric and piezoelectric properties of lead-free 0.95 $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ –0.05 LiNbO_3 crystals grown by the Bridgman method, *J. Appl. Phys.* 101 (4) (2007) 4103.
- [22] Q. Zhang, Y. Zhang, F. Wang, Y. Wang, D. Lin, X. Zhao, H. Luo, W. Ge, D. Viehland, Enhanced piezoelectric and ferroelectric properties in Mn-doped $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ – BaTiO_3 single crystals, *Appl. Phys. Lett.* 95 (10) (2009) 102904.
- [23] A. Chauhan, S. Patel, R. Vaish, Mechanical confinement for improved energy storage density in BNT–BT–KNN lead-free ceramic capacitors, *AIP Adv.* 4 (8) (2014) 087106.
- [24] S.T. Zhang, A.B. Kouna, E. Aulbach, Y. Deng, Temperature-dependent electrical properties of 0.94 $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ –0.06 BaTiO_3 ceramics, *J. Am. Ceram. Soc.* 91 (12) (2008) 3950–3954.
- [25] M. Zannen, A. Lahmar, H. Khemakhem, M. El Marssi, Energy storage property in lead free gd doped $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ ceramics, *Solid State Commun.* 245 (2016) 1–4.
- [26] F. Gao, X. Dong, C. Mao, W. Liu, H. Zhang, L. Yang, F. Cao, G. Wang, Energy-storage properties of 0.89 $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ –0.06 BaTiO_3 –0.05 $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ lead-free anti-ferroelectric ceramics, *J. Am. Ceram. Soc.* 94 (12) (2011) 4382–4386.
- [27] Y.F. Wang, X.J. Yi, W. Pan, G.Z. Zang, J. Du, Dielectric and piezoelectric properties of lead free $(1-x)\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ – $x\text{BaTiO}_3$ – $y\text{BiFeO}_3$ piezoelectric ceramics, *Key Eng. Mater.* 492 (2012) 194–197, Trans Tech Publications.
- [28] I. Fujii, Y. Ito, T. Suzuki, T. Wada, Ferroelectric and piezoelectric properties of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – BiFeO_3 ceramics, *J. Mater. Res.* 31 (01) (2016) 28–35.