



Ferroelectric, pizeoelectric and magnetoelectric properties of Sm modified 0.75BiFeO₃-0.25PbTiO₃ binary solid solution

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Abstract

0.75Bi_{1-x}Sm_xFeO₃-0.25PbTiO₃ i.e. (BSFPT)_x solid solutions with $x = 0.05$ and 0.10 were successfully synthesized by solid state reaction method. The effect of Sm doping on ferroelectric, pizeoelectric and magnetoelectric properties has been investigated. Rhombohedral (R_{3c}) and tetragonal (P_{4mm}) phases are present in the produced solid solutions as a result of BiFeO₃ and PbTiO₃ compounds respectively. Ferroelectric study reveals the saturated ferroelectric loops with low remnant polarization (P_r) for prepared solid solutions. The pizeoelectric analysis shows the increase in the converse piezoelectric coefficient (d^*_{33}) with increase in Sm doping. Magnetoelectric coupling investigation reveals that the magnetoelectric coupling coefficient (α_{ME}) improves with Sm doping and reaches a maximum value of 1.616mV/cmOe. These enhanced features make the material attractive contender for possible applications.

Keywords: (BSFPT)_x, PbTiO₃, Tetragonal, Magnetoelectric coupling coefficient, Remnant polarization.

1. Introduction:

The development of multiferroic materials, which demonstrate the coexistence of ferroelectric and ferromagnetic ordering in the same phase, has received a lot of attention in the recent year [1,2]. These materials could be used for a variety of applications, such as spintronics, EMI filters, data storage, multiple state memory, transducers etc[3,4]. Magnetoelectric multiferroic systems have sparked research interest in the last decade due to the coexistence of ferromagnetism and ferroelectricity in a single phase, as well as the coupling between two ferroic orders [5-7]. More study of multiferroic materials has been stimulated by the discovery of magnetoelectric interaction in systems like BiFeO₃ and TbMnO₃ [8,9]. Because composites have a significantly stronger magnetoelectric (ME) effect than single phase materials, multiferroic composites with a magnetoelectric effect at room temperature have attracted researchers' interest for a variety of device applications [10].

BiFeO₃ (BFO) is one of the multiferroic materials that has been investigated the most in recent years and is the only one that is known to display both magnetic order ($T_N = 643$ K) and ferroelectric order (ferroelectric transition temperature $T_C = 1103$ K) at ambient temperature [11-13]. BFO is a single-phase multiferroic compound with distorted rhombohedral perovskite structure and $R3c$ space group symmetry, which exhibits ferroelectricity as well as G-type antiferromagnetism rhombohedral structure and permits the coupling between magnetism and ferroelectricity [10,14]. Magnetism is produced by the magnetic spins of unpaired Fe³⁺ ions, while ferroelectricity is produced by the displacement of Bi³⁺ ions from central-symmetric positions in relation to the oxygen ions around them [15]. BFO exhibits a very weak magnetoelectric coupling as a result of suppressed linear magnetoelectric coupling brought on by cycloidal spin modulation [16,17]. Weak ME coupling in BFO is predicted by theoretical calculations to be caused by a considerable discrepancy between the transition temperatures T_C and T_N [18]. In addition to these drawbacks, BFO also exhibits secondary phase development, low magnetization, high leakage current, poor ferroelectric reliability, and high dielectric loss [19-21]. The poor ferroelectric behavior was caused by the presence of secondary phase development, which caused substantial leakage current. Several efforts, including a doping at the Bi/Fe site, were performed to improve the magnetoelectric coupling, decrease the leakage current, and increase the dielectric constant in BiFeO₃.

Several studies have been conducted to explore the influence of rare earth (La, Eu, Gd, and Nd) modified BFO [22-24]. To improve thermal stability and reduce leakage and volatility of BFO, room-temperature ferroelectric PbTiO₃ (PTO) with tetragonal symmetry ($P4mm$) and $T_C = 490$ °C was added to BFO. In their discussion of the phase transition in the compounds, Correas et al. asserted that a combination of two solid solutions with different symmetry may result in an unstable morphotropic phase boundary known as an MPB, which is thought to have increased piezoelectric and dielectric properties [25]. Comyn et al. observed the tetragonal and rhombohedral phases coexisting in 70% BFO-30%PT. It should be noted that the morphotropic phase boundary (MPB) is a notion; it is a phase transition zone where a massive reaction can be detected in the presence of an external stimulus, such as an electric field or mechanical force [26]. This can be accomplished by fine-tuning the compositional variation of the ABO₃ perovskite systems by substituting rare earths or ions at the A or B-site. The stability, sinterability, lattice parameter, bulk, grain boundary, and total conductivity of ABO₃ type materials are influenced by the various B-site dopants (Al, Sc, In, Lu, Tm, Y, Gd, Sm, Nd, and La). The oxygen ion vacancy and ferroelectric transition temperature (T_C) can both be controlled by substitution [27]. According to Singh et al., substitution of La³⁺ in BFO supports collinear antiferromagnetic spin configuration and results in better dielectric and magnetoelectric properties of 0.50(Bi_{1-x}La_xFeO₃)-0.50(PbTiO₃) compounds [28]. The rare-earth (Ga³⁺, La³⁺ and Mn³⁺) co-modified 0.6BFO-0.4PTO was explored by a number of researchers. The effect of the Nd³⁺ modified MPB system (0.7BFO-0.3PTO) was investigated by N. Kumar et al. They found that the transition temperature decreased as Nd³⁺ ion concentration increased. The conductivity of the sample was lowered when Dy³⁺ was substituted in 0.6BFO-0.4 PTO [29,30].

In recent years, various literary works have discussed the development of composites with perovskite-type materials such as BaTiO₃, which improve optical and multiferroic properties [31]. Pradhan et al. measured ferroelectric loops and magnetoelectric coefficients to study the multiferroic characteristics of a La-modified (BiFeO₃)_{1-x}(PbTiO₃)_x system [32]. In earlier research, the structural, magnetic, piezoelectric, and optical properties of other binary multiferroic perovskites were investigated, and it was found that the multiferroic properties had significantly improved [33]. PTO is used in this work because of its high polarisation and dielectric constant ferroelectric material, which settles the perovskite phase of the composite and also produces an MPB with BFO due to the difference in crystal symmetry between PTO and BFO. In order to enhance the multiferroic properties of BFO-PTO combination, it is reasonable to substitute the Bi³⁺ ion with a rare earth ion that has a small ionic radius and a large magnetic moment. In this study, 0.75Bi_{1-x}Sm_xFeO₃-0.25PbTiO₃ solid solutions with $x = 0.05$ and $x = 0.10$ compositions were synthesized and their ferroelectric, piezoelectric and magnetoelectric properties were investigated.

2. Experimental Details:

A solid state reaction technique was used to synthesize 0.75Bi_{1-x}Sm_xFeO₃-0.25PbTiO₃ solid solution with $x = 0.05$ and $x = 0.10$. Bi₂O₃, Sm₂O₃, Fe₂O₃, PbO, and TiO₂ powders of analytical grade reagents were weighed and thoroughly mixed in an agate mortar for four hours in acetone medium. The finely powdered powder was calcined for two hours at 830°C in a furnace. To prevent subsequent phases, a 5% excess of Bi₂O₃ was added to the initial reactants throughout the synthesis process. After adding a few drops of a polyvinyl alcohol (PVA) binder to each powder composition, the mixtures were ground in the agate mortar for an additional two hours. Blended powders of various compositions were squeezed into circular discs with a pressure of 1.5×10^8 Pascal to prepare pellet specimens of 1 mm thickness and 7 mm in diameter. The specimens were then sintered for two hours at 850°C. The crystal structure and phase development of the samples were examined using an X-ray diffraction at room temperature with CuK radiation at a wavelength of 1.5406 Å on a Bruker D8 Advance X-ray diffractometer. A Ferroelectric loop tracer (aiXACCT Systems GmbH aixPES) was used to analyze the polarization (P) versus electric field (E) loops of shrunk, polishable pellets coated with high conducting silver paste at ambient temperature. The magnetoelectric (ME) coefficient (ME) was determined using highly precise magnetoelectric apparatus consisting of electromagnetic poles with 10 inch diameters and magnetic field homogeneity ranging from 1 to 10⁶. A lock-in amplifier and a power amplifier were used to generate AC magnetic fields. A lock-in amplifier measured the induced voltage across the sample in differential mode to subtract the common-mode induction contribution. The applied frequency's phase was fixed in order to separate the sample's pure induced signal from it. Before to ME measurements, the sample was poled in an electric field for an hour. A 10 Oe AC magnetic field with a frequency of 999 Hz was used in parallel with a variable DC magnetic field ranging from 0 to 5000 Oe to perform dynamic ME coupling measurement.

Results and Discussion:

The ferroelectric behavior of the BiFeO₃ compound is constrained by its larger leakage current. Due to the presence of the Nd³⁺ ion, it has been observed that the leakage current in Nd doped BiFeO₃-PbTiO₃ system is lower than in binary BiFeO₃-PbTiO₃ systems [34]. Ferroelectric hysteresis loops for prepared samples obtained at room temperature for $x = 0.50$ and $x = 0.10$ are displayed in Figure 1. The prepared samples have ferroelectricity due to the coexistence of the rhombohedral phase of BiFeO₃ and the tetragonal phase of PbTiO₃ which is caused by the ferroelectric distortion of the Ti (3d) orbital and the O (2p) orbital of PbTiO₃, as well as the Bi (6s²) lone pair and the O (2p) orbital of the BiFeO₃ crystal. It is seen that saturation polarization and remnant polarization are larger for $x = 0.05$ Sm composition and then decrease with increasing Sm concentration. Table 1 shows the coercive field (E_c), remnant polarization (P_r), and saturation polarization (P_s) for with $x = 0.05$ and $x = 0.10$ compositions. The decrease in remnant polarization may be caused by structural distortions in produced compounds and differences in the ionic radii of the Sm³⁺ and Fe³⁺ ions. In BiFeO₃-PbTiO₃ compounds with Sm doping, Sahu et al. found a comparable decrease in rem polarization values [35].

Furthermore, various studies have shown that oxygen vacancies have an impact on polarization, both theoretically and empirically [36,37]. In particular, PbO evaporation causes the lead and oxygen vacancies to form defect dipoles during the high-temperature sintering process. [38]. These dipoles provide an induced polarization vector that requires more energy to reorient in the field direction. The constant polarization vector also creates a restoring force that favours the domains returning to their initial state, which causes the remnant polarization to diminish. Similar connections between oxygen vacancies and residual polarization were reported in Sr doped BiFeO₃-PbTiO₃ ceramics [39]. The region under the loops represents energy dissipation of the samples. The PE-hysteresis loop exhibits the structural change (rhombohedral-tetragonal). The prepared samples only cover a small region, which may be connected to the ability of the samples to store energy [40]. The similar observations has been observed for Nd doped BiFeO₃-PbTiO₃ solid solutions [41].

Table 1. Saturation polarization (P_s), remnant polarization (P_r), and coercive field (E_c) for 0.75Bi_{1-x}Sm_xFeO₃-0.25PbTiO₃ solid solutions with $x = 0.05$ and $x = 0.10$ compositions.

Composition (x)	P_s ($\mu\text{C}/\text{cm}^2$)	P_r ($\mu\text{C}/\text{cm}^2$)	E_c (kV/cm)
0.05	0.6955	0.4428	5.6144
0.10	0.2737	0.0869	2.9074

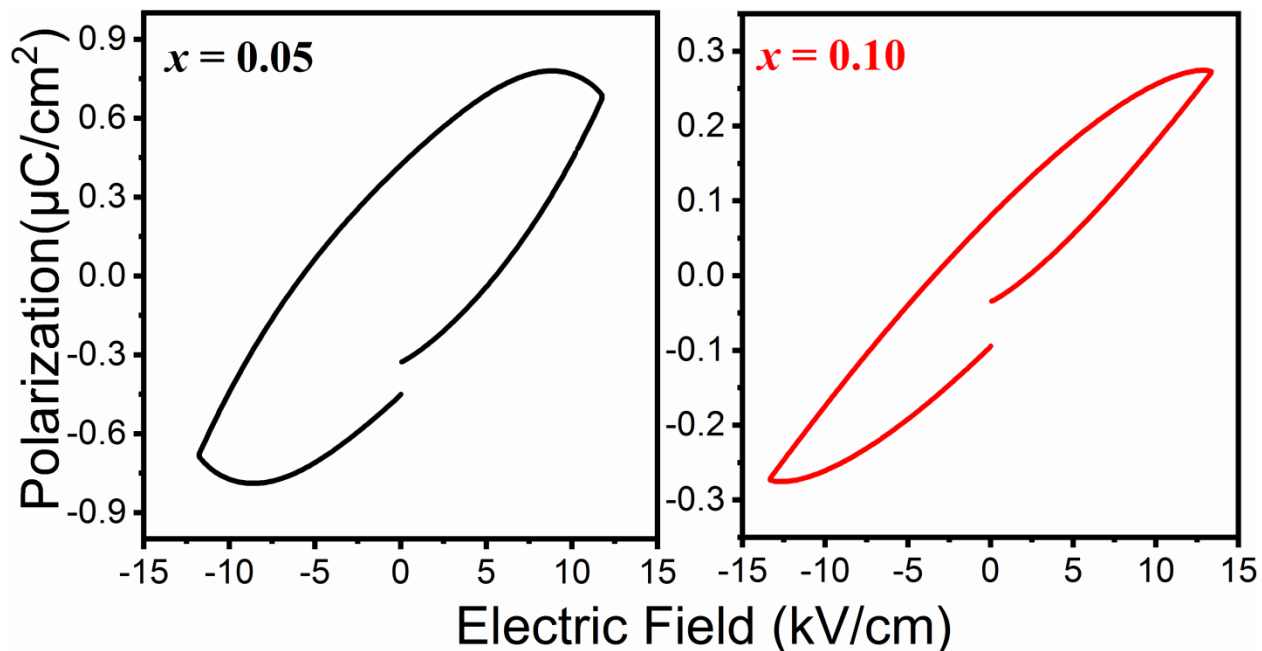


Figure 1. Ferroelectric hysteresis loops (P-E loops) of 0.75Bi_{1-x}Sm_xFeO₃-0.25PbTiO₃ solid solution with $x = 0.05$ and $x = 0.10$ compositions.

The ratio of the maximum strain (S_{max}) to the maximum field (E_{max}) in the cycle was used to determine the converse piezoelectric coefficient (d_{33}^*) [42]. Figure 2 illustrates the variation of the converse piezoelectric constant (d_{33}^*) with composition (x) of 0.75Bi_{1-x}Sm_xFeO₃-0.25PbTiO₃ solid solution at room temperature. The value of d_{33}^* was found to rise as composition x increased. The structural transition with composition close to the morphotropic phase boundary may be connected to the anomalous change in piezoelectric characteristics [43]. In perovskites, the possibility of hybridization between the p-orbital of an oxygen anion and the d-orbital of a transition metal (Fe/Ti) is decreased by increased tetragonal strain (c/a). The maximum value of d_{33}^* was found to be 45.06 pm/V for $x = 0.10$ composition. Long Xue et al. found a similar behavior in the piezoelectric characteristics of BiScO₃-PbTiO₃-based piezoelectric ceramics [44].

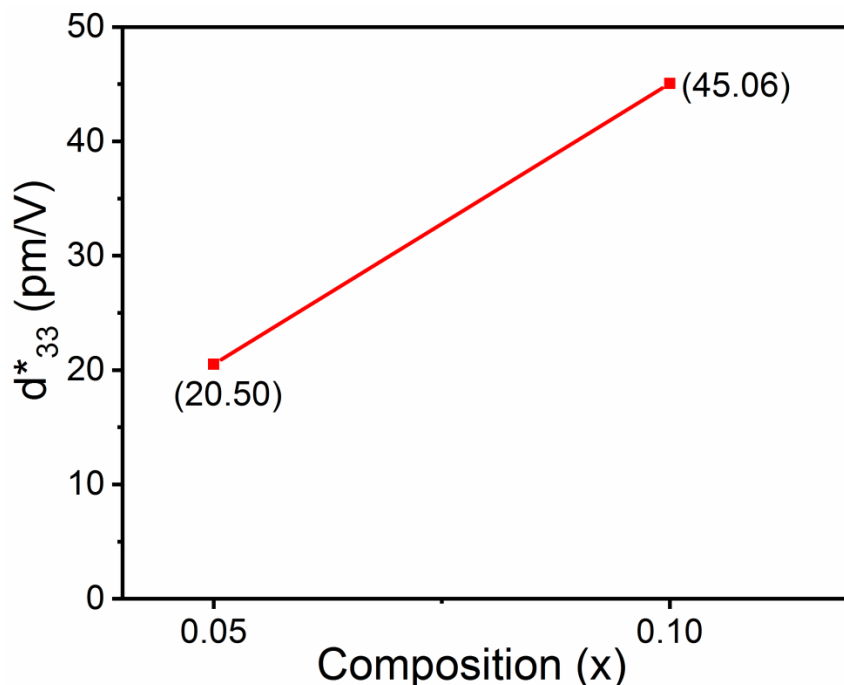


Figure 2. Variation of the converse piezoelectric coefficient (d^*_{33}) with composition (x) for 0.75Bi_{1-x}Sm_xFeO₃-0.25PbTiO₃ solid solution.

The interaction of the electric and magnetic order factors results in the magnetoelectric (ME) effect in multiferroics. ME coupling can be calculated using the ME voltage coefficient related to the applied magnetic field and the observed voltage change. The ME coupling coefficient (α_{ME}) was calculated using the dynamic approach. The linear ME coefficient ' α ' derived from output voltage is as follows:

$$\alpha = \frac{dE}{dH} = \frac{1}{d} \frac{dV}{dH} = \frac{V_{out}}{h_0 d}$$

Where h_0 , V_{out} and d are AC magnetic field, induced output voltage and sample thickness respectively. A fixed DC magnetic field is used to determine the linear coefficient while an AC magnetic field is being simultaneously swept. A parallel 10 Oe AC magnetic field with a 999 Hz frequency and a variable DC magnetic field ranging from 0 to 5000 Oe were applied in order to conduct dynamic ME coupling measurement. The ME coupling coefficient (α_{ME}) is calculated by dividing the output voltage by the sample thickness and the AC magnetic field. Figure 3 displays plots of α_{ME} for 0.75Bi_{1-x}Sm_xFeO₃-0.25PbTiO₃ solid solution at room temperature. α_{ME} steadily increases with increasing magnetic field, reaches a peak, and then gradually drops with increasing magnetic field f . According to Ramana et al., this type of behavior is typically connected with magnetic field dependency of magnetostriction [45]. Due to domain expansion brought on by the applied magnetic field, the value of α_{ME} increases between 1 kOe and 2.5 kOe. Above this field, however, further domain development causes deformation to decrease, which causes the value of α_{ME} to decrease [46]. Table 2 displays the maximum value of α_{ME} for prepared solid solutions. Additionally, it is found that α_{ME} rises with Sm doping, which is

connected to the quenching of the cycloidal spin structure of BiFeO₃. For Nd-doped BiFeO₃ ceramics, Jartych et al. reported a comparable result [47].

Table 2. Maximum value of ME coupling coefficient (α_{ME}) for 0.75Bi_{1-x}Sm_xFeO₃-0.25PbTiO₃ solid solution

Composition (x)	α_{ME} (mV/cmOe)
0.05	1.122
0.10	1.616

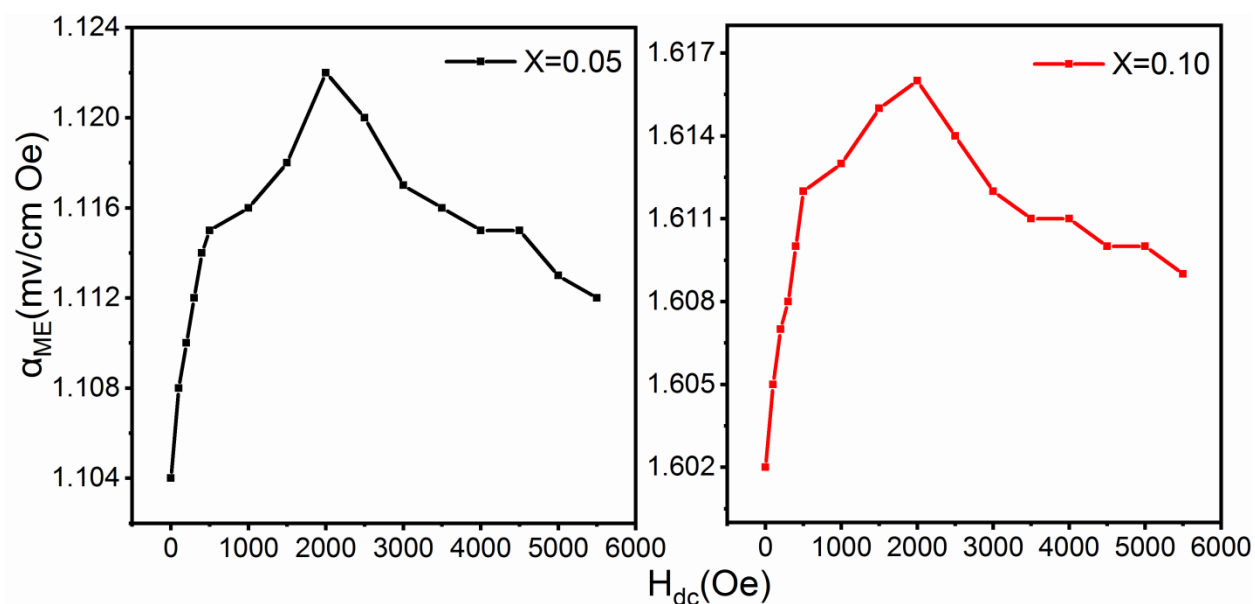


Figure 3. Variation of ME coupling coefficient (α_{ME}) with dc magnetic field (H_{dc}) for 0.75Bi_{1-x}Sm_xFeO₃-0.25PbTiO₃ solid solution

3. Conclusions:

0.75Bi_{1-x}Sm_xFeO₃-0.25PbTiO₃ solid solutions with $x = 0.5$ and $x = 0.10$ compositions were successfully synthesized using the solid-state reaction technique. The pinning effect in ferroelectric loops suggests the energy storage performance of the solid solutions with increasing Sm doping. The prepared samples are capable of producing a modest piezoelectric effect, with a maximum converse piezoelectric coefficient (d^*_{33}) of 45.06pm/V. The magnetoelectric coupling coefficient, which affects the ferroelectric and ferromagnetic behavior of compounds, is improved by an increase in Sm doping. The BiFeO₃ compound's spin cycloid is affected by Sm doping, which can be exploited to enhance multiferroic characteristics and make the substance a desirable contender for future uses.

References

- [1] P. Rovillain et al., Electric-field control of spin waves at room temperature in multiferroic BiFeO_3 . *Nature Mater.* 9 (2010) 975–979.
- [2] H. Béa, M. Gajek, M. Bibes and A. Barthélémy, Spintronics with multiferroics. *J. Phys. Condens. Matter* 20 (2008) 434221-1-11.
- [3] W. Eerenstein, N. D. Mathur and J. F. Scott, Multiferroic and magnetoelectric materials, *Nature*. 442(2006)759-765.
- [4] N.A. Spaldin and M. Fiebig, The renaissance of magnetoelectric multiferroics. *Science*, 309 (2005) 391-392.
- [5] D. Damjanovic, Contributions to the piezoelectric effect in ferroelectric single crystals and ceramics, *J. Am. Ceram. Soc.* 88 (2005) 2663.
- [6] M. Fiebig, Th. Lottermoser, D. Frolich, A.V. Goltsev and R.V. Pisarev, Observation of coupled magnetic and electric domains, *Nature*. 419 (2002) 818-820.
- [7] S.W. Cheong and M. Mostovoy, Multiferroics: a magnetic twist for ferroelectricity, *Nat. Mater.* 6 (2007) 13-20.
- [8] T. Kimura et al., Magnetic Control of Ferroelectric Polarization. *Nature*, 426 (2003) 55–58.
- [9] J. Wang, et al., Epitaxial BiFeO_3 Multiferroic Thin Film Hetero structures. *Science* 299 (2003) 1719–1722.
- [10] M. Fiebig, Revival of the magnetoelectric effect, *J. Phys. D Appl. Phys.* 38 (2005) R123.
- [11] M. K. Singh, R. S. Katiyar, W. Prellier, and J. F. Scott, The Almeida–Thouless line in BiFeO_3 : is bismuth ferrite a mean field spin glass, *J. Phys.: Condens. Matter* 21 (2009) 042202.
- [12] I. A. Kornev and L. Bellaiche, Nature of the ferroelectric phase transition in multi ferroic BiFeO_3 from first principles, *Phys. Rev. B* 79 (2009) 100105 (R).
- [13] R. Haumont et al., Phase stability and structural temperature dependence in powdered multiferroic BiFeO_3 , *Phys. Rev. B* 78 (2008) 134108.
- [14] M. Cebela, D. Zagorac, K. Batalovic, J. Radakovic, B. Stojadinovic, V. Spasojevic and R. Hercigonja, BiFeO_3 Perovskites: A multidisciplinary approach to multiferroics, *Ceram. Int.* 43 (2017) 1256-1264.
- [15] G. Catalan and J. F. Scott, Physics and applications of bismuth ferrite, *Adv. Mater.* 21 (2009) 2463 –2485.
- [16] C. T. Munoz, J. P. Rivera, A. Monnier, and H. Schmid, Measurement of the Quadratic Magnetoelectric Effect on Single Crystalline BiFeO_3 , *Japanese J. of Appl. Phys.* 24 (1985) 1051-1053.
- [17] S. V. Suryanarayana, Magnetoelectric interaction phenomena in materials, *Bull. Mater. Sci.* 17 (1994) 1259-1270.
- [18] S. J. Gong, Q. Jiang, The investigation of the magnetodielectric effect in ferroelectric-ferromagnets, *Phys. Lett. A* 333 (2004) 124–131.

- [19] X.X. Shi, X.Q. Liu and X.M. Chen, Readdressing of magnetoelectric effect in bulk BiFeO₃, *Adv. Funct. Mater.* 27 (2017) 1604037.
- [20] Q. Li, J. Wei, J. Cheng and J. Chen, High temperature dielectric, ferroelectric and piezoelectric properties of Mn-modified BiFeO₃-BaTiO₃ lead-free ceramics, *J. Mater. Sci.* 52 (2017) 229–237.
- [21] L.-F. Zhu et.al., Enhanced piezoelectric properties of Bi(Mg_{1/2}Ti_{1/2})O₃ modified BiFeO₃-BaTiO₃ ceramics near the morphotropic phase boundary, *J. Alloy. Comp.* 664 (2016) 602–608.
- [22] S.R. Das, R.N.P. Choudhary, P. Bhattacharya and R.S. Katiyar, Structural and multiferroic properties of La-modified BiFeO₃ ceramics, *J. Appl. Phys.* 101 (2007) 034104-7.
- [23] K. Chakrabarti et.al. Enhanced magnetic and dielectric properties of Eu and Co co-doped BiFeO₃ nano-particles, *Appl. Phys. Lett.* 101 (2012) 042401-3.
- [24] V.A. Khomchenko et.al., Crystal structure and multiferroic properties of Gd-substituted BiFeO₃, *Appl. Phys. Lett.* 93 (2008) 262905-3.
- [25] C. Correias, T. Hungria and A. Castro, Mechano-synthesis of the whole xBiFeO₃-(1-x)PbTiO₃ multiferroic system: structural characterization and study of phase transitions, *J. Mater. Chem.* 21 (2011) 3125–3132.
- [26] T. P. Comyn et.al., High temperature neutron diffraction studies of 0.9BiFeO₃-0.1PbTiO₃, *J. Appl. Phys.* 105 (9) (2009), 094108.
- [27] E. Gilardi et.al., Effect of dopant-host ionic radii mismatch on acceptor-doped barium zirconate microstructure and proton conductivity, *J. Phys. Chem. C* 121 (2017) 9739–9747.
- [28] A. Singh, A. Gupta and R. Chatterjee, Enhanced magnetoelectric coefficient (α) in the modified BiFeO₃-PbTiO₃ system with large La substitution, *Appl. Phys. Lett.* 93 (2008) 022902.
- [29] J. Cheng, Z. Meng and L.E. Cross, High-field and high-*T_c* piezoelectric ceramics based on Bi(GaFeO₃-PbTiO₃) crystalline solutions, *J. Appl. Phys.* 98 (2005) 084102-1-084102-5.
- [30] G. Shi, J. Chen, L. Zhao, S. Yu, J. Cheng, L. Hong, G. Li, Electromechanical properties of La and Mn co-modified 0.6BiFeO₃-0.4PbTiO₃ ceramics for high power applications, *Curr. Appl. Phys.* 11 (2011) S251–S254.
- [31] M. Shariq, D. Kaur and V.C. Chandel, Structural, magnetic and optical properties of multiferroic (BiFeO₃)_{1-x}(BaTiO₃)_x solid solutions. *Chin. J. Phys.* 55 (2017) 2192–2198.
- [32] S.K. Pradhan et.al., Structural and electrical properties of lead reduced lanthanum modified BiFeO₃-PbTiO₃ solid solution. *J. Mater. Sci. Mater. Electron.* 28 (2017) 1186–1198.
- [33] Z. Yao et.al., Structure and electrical properties of ternary BiFeO₃-BaTiO₃-PbTiO₃ high-temperature piezo ceramics, *J. Adv. Cream.* 1 (2012) 227-231.
- [34] S. Kumar et al., Correlation between multiferroic properties and processing parameters in NdFeO₃-PbTiO₃ solid solutions, *J. Alloys. Compd.* 764 (2018) 824–833.
- [35] T. Sahu, and B. Behera, Investigation on structural, dielectric and ferroelectric

- properties of samarium-substituted BiFeO₃-PbTiO₃ composites, *J. Adv. Dielectr.* 7 (2017) 1750001.
- [36] B.L. Cheng, T.W. Button and M. Gabbay, Oxygen vacancy relaxation and domain wall hysteresis motion in cobalt-doped barium titanate ceramics, *J. Am. Ceram. Soc.* 88 (2005) 907–911.
- [37] W.L. Warren, K. Vanheusden, D. Dimos, G.E. Pike and B.A. Tuttle, Oxygen vacancy motion in perovskite oxides, *J. Am. Ceram. Soc.* 79 (1996) 536–538.
- [38] A. Chandrasekaran, D. Damjanovic, N. Setter and N. Marzari, Defect ordering and defect-domain-wall interactions in PbTiO₃: a first-principles study, *Phys. Rev. B.* 88 (2013), 214116.
- [39] N. Kumar, B. Narayan, A. K. Singh and S. Kumar, Enhanced magneto-capacitance in Sr 2p modified BiFeO₃-PbTiO₃ solid solutions, *Mater.Chem.Phys.*252 (2020) 123313.
- [40] M. Xu et al., Enhanced energy storage performance of (1-x)(BCT-BMT)-xBFO lead-free relaxor ferroelectric ceramics in a broad temperature range, *J. Alloys Compd.* 789 (2019) 303–312.
- [41] M. Baloni et al., Structural modification and evaluation of dielectric, magnetic and ferroelectric properties of Nd- modified BiFeO₃ – PbTiO₃ multiferroic ceramics, *Ferroelectric* 589 (2022) 161-176.
- [42] J. Hao, W. Bai, W. Li, B. Shen and J. Zhai, Phase transitions, relaxor behavior, and large strain response in LiNbO₃-modified Bi_{0.5}(Na_{0.80}K_{0.20})_{0.5}TiO₃ lead-free piezo ceramics, *J. Appl. Phys.*114 (2013) 044103.
- [43] S. Singh and N. S. Panwar, Piezoelectric properties of Na_{1-x}K_xNbO₃, near x =0.500 morphotropic phase region, *Ferroelectrics* 558 (2020) 240–245.
- [44] L. Xue et al., Electrical properties of Sb₂O₃-modified BiScO₃-PbTiO₃-based piezo electric ceramics, *RSC Adv.*10 (2020), 13460-13469.
- [45] E. V. Ramana, F. Figueiras, M. P. F. Graça and M. A. Valente, Observation of Magnetoelectric coupling and local piezoresponse in modified (Na_{0.5}Bi_{0.5}) TiO₃-BaTiO₃-CoFe₂O₄ lead-free composites, *Dalton Trans.* 43 (2014) 9934-9943.
- [46] A. J. Gualdi, F. L. Zabotto, D. Garcia, A. Bhalla, R. Guo, P. C. de Camargo, and A. J. A. de Oliveira, Understanding the dynamic magnetization process for the magneto-electric effect in multiferroic composites, *J. Appl. Phys.*119 (2016) 124110.
- [47] E. Jartych, T. Pikula, K. Kowal, J. Dzik, P. Guzdek and D. Czekaj, Magnetoelectric Effect in Ceramics Based on Bismuth Ferrite, *Nanoscale Res. Lett.* 11 (2016) 234.