Lead-free Rare Earth-modified BiFeO₃ Ceramics: Phase Structure and Electrical Properties

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Abstract: Here we investigated the phase evolutions as well as the relationships between phase structure and electrical properties of BFO ceramics by doping rare earth elements (i.e., Eu, Pr, Sm, La, Dy) with different concentrations. It was found that the phase structure of the ceramics was strongly dependent on the types and concentrations of rare earth elements: rhombohedral phase for Eu, Pr and La with $x \leq 0.10$, Dy with $x \leq 0.15$, Sm with $x \leq 0.075$; orthorhombic for Eu with $0.15 < x \leq 0.30$, and Sm and Dy with $0.20 < x \leq 0.30$; triclinic phase for Pr with $0.20 < x \leq 0.30$, and La with $0.10 < x \leq 0.20$; monoclinic for La with $0.20 < x \leq 0.30$; rhombohedral-orthorhombic for Eu with $0.10 < x \leq 0.15$, Pr with $0.10 < x \leq 0.20$, and Dy with $0.15 < x \leq 0.20$. Interestingly, the ceramics with rhombohedral phase always exhibited better piezoelectric and ferroelectric properties with respect to the ones with multiphase coexistence or other phases. In addition, both high piezoelectric constant ($d_{33} > 40$ pC/N) and low dielectric loss ($\tan \delta \leq 0.01$) can be achieved in the ceramics with rare earth elements (Eu, Pr, Sm, La).

Key Words: BiFeO₃ ceramics; Rare earth; Phase structure; Electrical properties.

Equal Contribution

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1. Introduction

Investigations on multiferroic materials have become one of the hottest topics in material science due to the coexistence of two or more than two ferroics [1-25]. It is well known that the ceramics have been one of the most promising choices in the development of various technological applications [1-25]. For example, both $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) and bismuth layer structured ceramics can be widely used in some electronic devices because of some unique advantages. However, low Curie temperature (T_C) may seriously hinder the high-temperature applications of PZT ceramics, and low piezoelectric constant (d_{33}) also affects the practical applications of bismuth layer structured ceramics [8-15]. BiFeO_3 (BFO) may become another choice as one kind of high-temperature piezoelectric ceramics because of its high T_C (830 °C), Neel temperature ($T_N \sim 370$ °C), and the existence of ferroelectrics and magnetism at room temperature [16-20]. After the strained BFO thin films exhibited a large ferroelectricity [20], the investigations on BFO thin films became a hot topic. However, few breakthroughs were realized in BFO bulks due to the seriously leakage current coming from the high concentrations of Fe^{2+} and oxygen vacancies [21,22], which makes it difficult to warrant the realization of enhanced electrical properties.

Up to now, some methods were used to overcome high leakage current of BFO ceramics. Among these methods, liquid-phase sintering technique can effectively suppress the leakage current of BFO ceramics, realizing the enhancement of their electrical properties [23]. BiFeO_3 bulks belong to rhombohedral ($R3c$) structure [24-30], while it is extremely difficult to synthesize the single-phase BFO ceramics because of the serious loss of Bi_2O_3 during sintering process [24]. Therefore, some impurity

phases (e.g., $\text{Bi}_{25}\text{FeO}_{40}$ and $\text{Bi}_2\text{Fe}_4\text{O}_9$) were often detected in BFO ceramics, which may be harmful to their electrical properties [25]. In order to suppress the formation of impure phases and improve electrical properties of BFO ceramics, some effective methods were attempted. Especially, site engineering is one of the most important ways to reform the structure and improve electrical properties of BFO ceramics, such as ion substitutions (Nd^{3+} , La^{3+} , Sm^{3+} , Eu^{3+} , Y^{3+} , Pr^{3+} , etc.) for Bi^{3+} sites [27-31] and other ion substitutions (Sc^{3+} , Ni^{3+} , etc.) for Fe^{3+} sites [32,33]. More importantly, the addition of rare earth elements can change the phase structure of BFO ceramics, and then their electrical properties can be effectively improved [26-33]. However, some tough issues cannot be well solved till now, such as phase evolutions with the concentration and types of rare earth elements, and the relationship between phase structure and electrical properties. As a result, we hope to establish the relationships between phase structure and electrical properties of BFO ceramics by investigating phase evolutions with the concentration and types of rare earth elements.

In this work, we fabricated $\text{Bi}_{1-x}\text{A}_x\text{FeO}_3$ ($\text{A}=\text{Eu, Pr, Sm, La, Dy}$, $0.05 \leq x \leq 0.30$) ceramics in order to realize these above objectives. Different phase structures can be induced by changing the types and concentration of doped rare earth elements. In addition, electrical properties of BFO ceramics are also strongly dependent on both phase structure and doped elements types. For example, enhanced piezoelectricity ($d_{33} > 40$ pC/N) and low dielectric loss can be obtained in the ceramics modified by some rare earth elements (Eu, Pr, Sm, La) with a low concentration (Table 1), while there is poor d_{33} (< 40 pC/N) and high $\tan \delta$ for the addition of Dy^{3+} . The related physical mechanisms were also addressed.

2. Experiments

Ceramics with a formula $\text{Bi}_{1-x}\text{A}_x\text{FeO}_3$ {abbreviation: BA_xFO } were synthesized by the

conventional solid-state sintering method with raw materials {e. g. Bi_2O_3 (99%), Fe_2O_3 (99%), Eu_2O_3 (99.99%), Pr_6O_{11} (99.9%), Sm_2O_3 (99.9%), Dy_2O_3 (99.9%), and La_2O_3 (99.9%)}. These initial powders were ball milled for 24 h with alcohol after weighted with an electronic balance. These dried powders were pressed into the disks with diameter of 10 mm and thickness of 1 mm under a pressure of 10 MPa. The green pellets were sintered at 885 °C for A= Sm, Eu, Pr, 860 °C for A= Dy and 870 °C for A=La with a dwell time of 5 min after the removal of the water under 300 °C for 12 h. The samples were poled at 100 °C under applied electric fields of 4~7 kV/mm in a bath of silicone oil after the silver electrodes was fired on both surfaces of the ceramics and sintered at 550 °C for 10 min.

The crystal structure of the ceramics was characterized with X-ray diffraction (XRD) patterns with the machine of a Cu k_α radiation in the θ - 2θ scan mode (Bruker D8 Advanced XRD, Bruker AXS Inc., Madison, WI, Cu K_α). Their microstructure of cross section and elements mapping were measured by a field-emission scanning electron microscope (FE-SEM) (JSM-7500, Japan). A piezo- d_{33} meter (ZJ-3 A, China) was used to measure the d_{33} . Relative permittivity (ϵ_r) and dielectric loss ($\tan \delta$) of the samples were measured by the LCR analyzer (Tonghui 2816A, China and HP 4980, Agilent, U.S.A.).

3. Results and discussions

In this work, the phase structures of rare earth-doped BiFeO_3 ceramics were analyzed by XRD patterns. Figures 1(a)-(e) show the XRD patterns of $\text{Bi}_{1-x}\text{A}_x\text{FeO}_3$ ceramics with different elements and contents, measured at $2\theta=20^\circ$ - 70° and room temperature. It can be noted that typical perovskite structure can be formed in the ceramics. Specifically, pure phases appeared in the composition range of $x \leq 0.15$ for A=Eu, $x \leq 0.30$ for A=Pr, $x \leq 0.125$ for A=Sm and $x \geq 0.10$ for A=La. However, some secondary

phases could be observed for $0.20 \leq x \leq 0.30$ with $A=\text{Eu}$, $0.20 \leq x \leq 0.25$ with $A=\text{Sm}$, $x=0.05$ with $A=\text{La}$ and all the contents for $A=\text{Dy}$.

To further confirm the phase structure of the ceramics, the Rietveld refinement of XRD patterns was carried out. Here, we gave a sample ($A=\text{Eu}$ and $x=0.05$) to identify the phase structure, as shown in Fig. 2. One can acquire the crystal lattices for $a=5.574 \text{ \AA}$ and $b=13.843 \text{ \AA}$ with the $\text{sig}=1.11$ and $R_{\text{wp}}(\%)=11.41$ as its XRD pattern was refined with rhombohedral $R3c$ space group. It was also found that the patterns can well match $R3c$ crystal lattice, confirming the involvement of rhombohedral phase. In addition, the lattice parameters also matched the previously reported one [11, 33]. Interestingly, the XRD peak shapes gradually change with the increase of x (Fig. 1). Furthermore, a simple phase diagram can be established according to both our work and some previously reported ones [28, 31-34], as shown in Fig. 3. One can see from Fig. 3 that there is the composition dependence of phase structure of BA_xFO ceramics. In addition, the types and contents of rare earth elements strongly affected phase structure of BFO ceramics. For example, for the ceramics with $A=\text{Eu}$, rhombohedral phase for $x \leq 0.10$, rhombohedral-orthorhombic coexistence phases for $0.10 < x \leq 0.15$, and orthorhombic phase for $0.15 < x \leq 0.30$; For the ceramics with $A=\text{Pr}$, rhombohedral phase for $x \leq 0.10$, rhombohedral-orthorhombic coexistence phases for $0.10 < x \leq 0.20$ and triclinic phase for $0.20 < x \leq 0.30$; For the ceramics with $A=\text{Sm}$, rhombohedral phase for $x \leq 0.075$, orthorhombic-triclinic phases for $0.075 < x \leq 0.20$ and orthorhombic phase for $0.20 < x \leq 0.30$; For the ceramics with $A=\text{Dy}$, rhombohedral phase for $x \leq 0.15$, orthorhombic

phase for $0.20 < x \leq 0.30$ and rhombohedral-orthorhombic coexistence phases for $0.15 < x < 0.20$; For the ceramics with A=La, rhombohedral phase for $x \leq 0.10$, triclinic phase for $0.10 < x \leq 0.20$ and monoclinic phase for $0.20 < x \leq 0.30$. In addition, the types of rare earth elements strongly affected the phase structure of BFO ceramics [33-47]. As a result, one can know that the phase structure of BFO ceramics was dependent on the contents and the types of rare earth elements.

Figure 4 shows the FE-SEM images of cross section in BA_xFO ceramics with different x values. According to Fig. 4, some conclusions may be drawn: for A=Sm and Pr, their grains are unevenly distributed, and their grain sizes almost remain changed for $x \leq 0.15$ and then decrease for $x=0.20$. However, their grain sizes can decrease by doping La or Dy. In addition, by contrasting the images of the ceramics with $x=0.05$, it was found that their grain sizes are strongly dependent on the element types, that is, larger grains can be found in the ceramics doped by Pr and Sm, while there are smaller grains for the ones with Eu, La, and Dy. As a result, the addition of Eu or Pr with appropriate concentrations can be helpful to promote the grain growths of BFO ceramics, and low contents ($x \leq 0.10$) of rare earth elements except for Sm can effectively decrease the formation of porosity, as demonstrated in the previous reports [26,27,29]. It is well known that the pores may originate from both Bi_2O_3 volatilization and oxygen vacancies during synthesis under a high temperature, where higher sintering temperatures always led to the formation of more pores in BFO ceramics [29, 31, 33]. However, different phenomenon occurred for the addition of A=Pr, Sm, La, Dy, and some tiny grains always attached to surface of the grown gains and then their number increases with increasing the contents. In previous articles, the tiny ones should come

from the formation of liquid phases during sintering process, which may affect their electrical properties [35].

Figure 5 displays the composition dependence of piezoelectrical coefficient (d_{33}) in the ceramics. As shown in Fig. 5(a), their d_{33} values show an increasing tendency and then decrease when the contents of Eu increase, and reduce to a low value near to zero for $x=0.30$, getting a maximum value (~ 46 pC/N) for $x=0.10$. According to Figs. 5(b) and (c), there is a similar change tendency, that is, the maximum one (~ 42 -45 pC/N) is shown in Pr-doped ceramics with $x=0.10$ and the Sm-modified ceramics with $x=0.075$. However, one can find that d_{33} of La-doped ceramics can remain around 40 pC/N for $0.05 \leq x \leq 0.20$ with triclinic phase and then gradually decreases for $0.20 < x \leq 0.30$ [Fig. 5(d)]. d_{33} of Dy-doped ceramics decreases from 30 pC/N to 15 pC/N with increasing x values [Fig. 5(e)]. As a result, higher d_{33} can be attained in the ceramics with R phase (Eu, Pr, Sm and Dy) and La-modified ceramics with triclinic phase. In addition, maximum d_{33} of the ceramics with different rare earth elements were obtained in Fig. 5(f) and Table 1. According to this data, one can find that the ceramics doped with Eu, Pr, Sm and La can effectively promote d_{33} (≥ 40 pC/N) while the lower values appear in the ones with Dy.

Except for piezoelectricity, composition-induced dielectric properties of this work were also investigated. Figure 6 shows the composition dependence of dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) of the ceramics, measured at room temperature and 100 kHz. As shown in Fig. 6 (a), one can see that their ϵ_r gradually increased with increasing x , and their $\tan \delta$ decreased and kept a low value when doped by Eu. In addition, there were similar changes in dielectric properties of Sm or La -modified ceramics, as shown in Figs. 6 (c) and (d). Their ϵ_r fluctuated in the range of 50~75, while there was a low $\tan$

δ (<0.01) [Fig. 6 (b)]. As shown in Fig. 6 (e), ε_r firstly increased and then decreased with increasing x , a high $\tan \delta$ (>0.025) can be attained. As a result, the addition of Eu or Sm can effectively enhance ε_r and remain a low $\tan \delta$ value, which is consistent with the previously reported results [28]. Corresponding to piezoelectricity, ε_r and $\tan \delta$ of the ceramics with maximum d_{33} were revealed in Fig. 6 (f). La- or Dy-doped ceramics can facilitate higher ε_r but larger $\tan \delta$ and lower d_{33} while contrasting with Eu, Pr and Sm modified ones illustrating that the dielectricity of BFO ceramics were affected by not only the concentration but also the types of rare earth elements.

In the past, it is difficult to characterize the P - E loops of BFO ceramics due to the high leakage current. Figure 7 shows the P - E hysteresis loops of the ceramics with different compositions, measured at 100 °C. As shown in Figs. 7(a)~(e), all the ceramics exhibited good P - E loops, and their loop shapes were strongly dependent on the compositions and the corresponding contents. For example, the saturated P - E curves can be obtained for A=Eu with $x \leq 0.10$, A=Pr with $x < 0.10$, A=Sm with $x \leq 0.125$, A=La with $x \leq 0.05$, and A=Dy with $x \leq 0.05$. However, there is a slim P - E loop in the ceramics with a high content of additives, especially for the addition of Eu and Dy [Figs. 8(a) and (e)]. As a result, optimum ferroelectric properties can be attained by modifying the contents and the types of rare earth elements, as shown in table 2. Previously, it was reported that this phenomenon may be due to the phase transitions, that is, rhombohedral phase can effectively promote the ferroelectricity of BFO, and triclinic and orthorhombic phases or multiphase coexistence cannot enhance its ferroelectricity [34, 36]. However, there is asymmetric P - E loop for all the ceramics, which was dependent on the composition. The corresponding E_c^+ , E_c^- , and E_{int} values of the ceramics were revealed (Table 2) according to Fig. 7 and the formula $E_{int} = (E_c^+ - E_c^-)/2$. One can see From Table 2 that E_{int} was always affected by compositions and the

corresponding contents, that is, high E_{int} occurs when doped by Pr or La, while relatively low E_{int} were obtained in the ceramics modified by Eu, Sm or Dy. It is well known that some defects can be formed in the BFO ceramics when sintered by the solid-state sintering method, which may lead to asymmetric phenomenon because of pinning effect and internal bias field [36]. Because of the pinning effect of domain walls by defect dipoles or defect clusters, the poling and depoling processes become much more difficult than those of the ones without pinning effect [36]. In addition, the frequency dependence of P - E curves of the ceramics with Sm ($x=0.075$) was obtained, as shown in Fig. 7(f). Ferroelectricity slightly degraded as the measurement frequencies increased from 1 Hz to 10 Hz because the time of domain rotation decreased and then its sufficiency also declined with increasing frequencies [36]. As a result, good ferroelectricity can be achieved in BA_xFO ceramics by optimizing the doped element types and concentrations.

It is significant to characterize stability of piezoelectricity of a ceramic under different temperatures. In this work, effects of annealing temperatures on normalized d_{33} were obtained, as shown in Fig. 8. Their d_{33} values were tested at room temperature after annealing in the muffle under various temperatures for 30 min. As shown in Fig. 8(a), one can see that their d_{33} held high values for A=Eu with $x=0.05$ when the annealing temperature (T_a) is below 500 °C, while the ones gradually with $x \geq 0.075$ decreased with the increase of T_a and reach almost zero at $T_a \sim 800$ °C. However, normalized d_{33} shows a slight fluctuation at $T_a \leq 600$ °C with $x \leq 0.25$ and $T_a \leq 400$ °C with $x=0.30$, and then reduces quickly to zero when T_a approaches to T_C for A=Pr [Fig. 8(b)]. As shown in Fig. 8(c), d_{33} of Sm-doped ceramics keeps a high value and then decreases quickly for $x \leq 0.10$ and gradually reduces for $x \geq 0.15$ as T_a increased from room temperature to 800

°C. It is also noted that all the ceramics with La show a similar change tendency of d_{33} , that is, d_{33} slowly decreases firstly and then quickly reduces to zero for $T_a > 650$ °C [Fig. 8(d)]. Finally, their d_{33} values of the ceramics modified with Dy gradually reduce as T_a increases and then become zero for $T_a \sim 700$ °C [Fig. 8(e)]. Moreover, all normalized maximum d_{33} showed a little fluctuation first and then decreased to zero quickly expect for Eu, as shown in Fig. 8(f). Above all, one can learn that the BFO ceramics with optimized Pr or La contents can achieve good stability of piezoelectric activity, and however the addition of Eu, Sm or Dy possessed worse ones. Importantly, the decreased d_{33} may be due to the disordered polarization vectors under a high T_a because the stability of domain walls becomes weaker and weaker with the increase of T_a , which was reported in previous literatures [37].

4. Conclusion

In this work, high-temperature BiFeO₃ ceramics modified by some rare earth elements (Eu, Pr, Sm, La, Dy) were successfully prepared by the rapid thermal quenching technique, and effects of their contents on their phase structure, microstructure and electrical properties were systematically investigated. The phase structure shows a strong composition dependence. High d_{33} values (> 40 pC/N) and low dielectric loss (≤ 0.01) can be realized in the ceramics with rare earth elements except for Dy³⁺. In addition, strong ferroelectricity can be obtained in the ceramics with a low concentration of Eu, Pr, Sm or La, and excellent stability of piezoelectricity with different annealing temperature can be possessed in the ceramics with the addition of Pr or La. We believe that this investigation can further promote the development of BiFeO₃ ceramics as one kind of high-temperature piezoelectric materials.

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References

- [1] M. Fiebig, T. Lottermoser, D. Frohlich, A. V. Goltsev, R. V. Pisarev, Observation of coupled magnetic and electric domains, *Nature*. 419 (2002) 818-820.
- [2] W. Eerenstein, N. D. Mathur, J. F. Scott, Multiferroic and magnetoelectric materials, *Nature*. 442 (2009) 759-765.
- [3] J. M. Moreau, C. Michel, R. Gerson, W. J. James, Ferroelectric BiFeO₃ X-ray and neutron study, *J. Phys. Chem. Solid*. 32 (1971) 1315-1320.
- [4] G. Catalan, J. f. Sott, Physics and applications of bismuth ferrite, *Adv. Mater*. 21(2004) 2463-2485.
- [5] T. Zhao, A. Scholl, F. Zavaliche, K. Lee, M. Barry, A. Doran, M. P. Cruz, Y. H. Chu, C. Ederer, N. A. Spaldin, R. R. Das, D. M. Kim, S. H. Baek, C. B. Eom, R. Ramesh, Electrical control of antiferromagnetic domains in multiferroic BiFeO₃ films at room temperature, *Nat. Mater*. 5 (2006) 823-826.
- [6] A. S. Tatarenko, G. Srinivasan, M. I. Bichurin, Magnetoelectric microwave phase shifter, *Appl. Phys. Lett*. 88(2006) 18307.
- [7] A. Hussain, X. J. Xu, G. L. Yuan, Y. P. Wang, Y. Yang, J. Yin, J. M. Liu, Z. G. Liu, The development of BiFeO₃-based ceramics, *Chin. Sci. Bull*. 59 (2014) 5161-5169.
- [8] J. Rodel, W. Jo, K. Seifert, E. M. Anton, T. Granrow, D. Damjanovic, Perspective on

- the Development of Lead-free Piezoceramics , *J. Am. Ceram. Soc.* 89 (2009) 1153-1177.
- [9] J. G. Wu, D. Q. Xiao, J. G. Zhu, Potassium—Sodium Niobate Lead-free Piezoelectric Materials: Past, Present, and Future of Phase Boundary, *Chem. Rev.* 115 (2015) 2559-2595.
- [10] E. Hollenstein, M. Davis, D. Damjanovic, N. Setter, Piezoelectric properties of Li- and Ta-modified $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ ceramics, *Appl. Phys. Lett.* 87 (2005) 182905.
- [11] X. Q. Zhang, Y. Sui, X. J. Wang, Y. Wang, Z. Wang, Effect of Eu substitution on the crystal structure and multiferroic properties of BiFeO_3 , *J. Alloys, Compd.* 507 (2010) 157-161.
- [12] T. Takeuchi, T. Tani, Y. Saito, Formation of $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ - $\text{Pb}(\text{Zn}, \text{Nb})\text{O}_3$ System Piezoelectric Thick Films in Low-Temperature Firing Process, *Jpn. J. Appl. Phys.* 38 (1999) 5553–5556.
- [13] Z. H. Peng, Q. Chen, J. G. Wu, X. H. Zhu, D. Q. Xiao, J. G. Zhu, Dielectric and piezoelectric properties of Sb^{5+} doped $(\text{NaBi})_{0.38}(\text{LiCe})_{0.05}[\text{ }_{0.14}\text{Bi}_2\text{Nb}_2\text{O}_9]$ ceramics, *J. Alloys Compd.* 509 (2011) 8483–8486.
- [14] H. Irie, M. Miyayama, T. Kudo, Structure dependence of ferroelectric properties of bismuth layer-structured ferroelectric single crystals, *J. Appl. Phys.* 90 (2001) 4089–4094.
- [15] X. Lv, Z. Y. Li, J. G. Wu, J. W. Xi, M. Gong, D. Q. Xiao, J. G. Zhu, Enhanced piezoelectric properties in potassium-sodium niobate-based ternary ceramics, *Mater. Des.* 108 (2016) 609-614.
- [16] P. Fu, Z. J. Xu, R. Q. Chu, W. Li, G. Z. Zang, J. G. Hao, Piezoelectric, ferroelectric and dielectric properties of La_2O_3 -doped $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06}\text{TiO}_3$ lead-free ceramics, *Mater. Des.* 31 (2010) 796-801.

- [17] P. Uniyal, K. L. Yadav, Study of dielectric, magnetic and ferroelectric properties in $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$, *Mater. Lett.* 62 (2008) 2858-2861.
- [18] C. H. Yang, D. Kan, I. Takeuchi, V. Nagarajan, J. Seidel, Doping BiFeO_3 : approaches and enhanced functionality, *Phys. Chem. Chem. Phys.* 12 (2012) 15953-15962.
- [19] V. A. Khomchenko, D. A. Kiselev, E. K. SeleZneva, J. M. Vieira, A. M. L. Lopes, Y. G. Pogorelov, J. P. Araujo, A. L. Kholkin, Weak ferromagnetism in diamagnetically-doped $\text{Bi}_{1-x}\text{A}_x\text{FeO}_3$ (A=Ca, Sr, Pn, Ba) multiferroics, *Mater. Lett.* 62 (2008) 1927-1929.
- [20] J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig, R. Ramesh, Epitaxial BiFeO_3 Multiferroic Thin Film Heterostructures, *Science*. 299 (2003) 1719–1722.
- [21] J. G. Wu, J. Wang, D. Q. Xiao, J. G. Zhu, Migration Kinetics of Oxygen Vacancies in Mn-Modified BiFeO_3 Thin Films, *ACS Appl. Mater. Interfaces*. 3 (2011) 2504–2511.
- [22] Y. P. Wang, L. Zhou, M. F. Zhang, X. Y. Chen, J. M. Liu, Z. G. Liu, Room-temperature Saturated Ferroelectric Polarization in BiFeO_3 Ceramics Synthesized by Rapid Liquid Phase Sintering, *Appl. Phys. Lett.* 84 (2004) 1731-1733.
- [23] T. Rojac, A. Bencan, G. Drazic, M. Kosec, D. Damjanovic, Piezoelectric Nonlinearity and Frequency Dispersion of the Direct Piezoelectric Response of BiFeO_3 Ceramics, *J. Appl. Phys.* 112 (2012) 064114.
- [24] T. Rojac, A. Bencan, B. Malic, G. Tutuncu, J. L. Jones, J. E. Daniels, D. Damjanovic, D. J. Green, BiFeO_3 ceramics: Processing, Electrical, and Electromathanical Properties, *J. Am. Ceram. Soc.* 97 (2014) 1993-2011.
- [25] S. T. Zhang, Y. Zhang, M. H. Lu, C. L. Du, Y. F. Chen, Z. G. Liu, Y. Y. Zhu, N. B.

- Ming, X. Q. Pan, Substitution-Induced Phase Transition and Enhanced Multiferroic Properties of $\text{Bi}_{(1-x)}\text{La}_x\text{FeO}_3$ Ceramics, *J. Appl. Phys.* 100 (2006) 014106.
- [26] I. O. Troyanchuk, D. V. Karpinsky, M. V. Bushinsky, O. S. Mantytskaya, N. V. Tereshko, V. N. Shut, D. D. Viehland, Phase Transitions, Magnetic and Piezoelectric Properties of Rare Earth-Substituted BiFeO_3 Ceramics, *J. Am. Ceram. Soc.* 94 (2011) 4502–4506.
- [27] D. Varshney, A. Kumar, K. Verma, Effect of A Site and B Site Doping on Structural, Thermal, and Dielectric Properties of BiFeO_3 Ceramics, *J. Alloys Compd.* 509 (2011) 8421–8426.
- [28] F. Xue, L. Liang, Y. Gu, I. Takeuchi, S. V. Kalinin, L. Q. Chen, Composition- and Pressure- Induced Ferroelectric to Antiferroelectric Phase Transitions in Sm-Doped BiFeO_3 System, *Appl. Phys. Lett.* 106 (2015) 012903.
- [29] S. Kumari, N. Ortega, A. Kumar, S. P. Pavunny, J. W. Hubbard, C. Rinaldi, G. Srinivasan, J. F. Sott, R. S. Katiyar, Dielectric anomalies due to grain boundary conduction in chemically substituted BiFeO_3 , *J. Appl. Phys.* 117 (2015) 114102.
- [30] H. Y. Qi, Y. J. Qi, M. Xiao, Leakage mechanisms in rare-earth (La, Nd) doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ferroelectric ceramics, *J. Mater. Sci: Mater Electron.* 25 (2014) 1325-1330.
- [31] P. C. Sati, M. Kumar, S. Chhoker, M. Jewariya, Influence of Eu substitution on structural, magnetic, optical and dielectric properties of BiFeO_3 multiferroic ceramics, *Ceram. Int.* 41 (2015) 2389-2398.
- [32] P. Sharma, D. Varshney, S. Satapathy, P. K. Gupta, Effect of Pr substitution on structural and electrical properties of BiFeO_3 ceramics, *Mater. Chem. Phys.* 143 (2014) 629-636.
- [33] I. O. Troyanchuk, D. V. Karpinsky, M. V. Bushinsky, V. A. Khomchenko, G. N. Kakazei, J. P. Araujo, M. Tovar, V. Sikolenko, V. Efimov, A. L. Kholkin, Isothermal

structure transitions, magnetization and large piezoelectric response in $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ perovskites, *Phys. Rev. B.* 83 (2011) 054109.

[34] C. Sun, Y. P. Wang, Y. Yang, Multiferroic properties of $\text{Bi}_{1-x}\text{Dy}_x\text{FeO}_3$ ($x=0-0.2$) at various temperature, *Mater. Lett.* 72 (2012) 160-163.

[35] H. Y. Dai, T. Li, Z. P. Chen, D. W. Liu, R. Z. Xue, C. Z. Zhou, H. Z. Liu, N. K. Huang, Studies on the structure, electrical and magnetic properties of Ce-doped BiFeO_3 ceramics, *J. Alloy. Compd.* 672 (2016) 182-189.

[36] L. Jin, F. Li, S. J. Zhang, decoding the Fingerprint of Ferroelectric Loops: Comprehension of the Material Properties and Structures, *J. Am. Ceram. Soc.* 1 (2014) 1-27.

[37] Q. Zhou, C. G. Zhou, H. B. Yang, G. H. Chen, W. Z. Li, H. Wang, Dielectric, Ferroelectric, and Piezoelectric Properties of $\text{Bi}(\text{Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3$ -Modified BiFeO_3 - BaTiO_3 Ceramics with High Curie Temperature, *J. Am. Ceram. Soc.* 95 (2012) 3889-3893.

Table 1: Electrical properties of the ceramics with maximum d_{33} when doped by different elements.

Composition	d_{33} (pC/N)	ϵ_r	$\tan \delta$
$\text{Bi}_{0.90}\text{Eu}_{0.10}\text{FeO}_3$	46	57.4	0.007
$\text{Bi}_{0.90}\text{Pr}_{0.10}\text{FeO}_3$	42	55.4	0.008
$\text{Bi}_{0.925}\text{Sm}_{0.075}\text{FeO}_3$	45	51.0	0.009
$\text{Bi}_{0.90}\text{La}_{0.10}\text{FeO}_3$	41	70.3	0.019
$\text{Bi}_{0.95}\text{Dy}_{0.05}\text{FeO}_3$	31	68.4	0.030

Table 2: P_r , E_c and E_{int} values of the ceramics

Elements	Contents	P_r ($\mu\text{C}/\text{cm}^2$)	E_c^+ (kV/cm)	E_c^- (kV/cm)	E_{int} (kV/cm)
Eu	0.05	15.6	93.4	66.08	13.66
	0.1	11.3	91.4	58.1	16.65
Pr	0.05	14.5	84.4	42.2	21.1
	0.1	7.8	88.3	38.27	25.015
Sm	0.075	18.8	85.5	65	10.25
	0.125	19.9	84.5	52.8	15.85
La	0.05	15.3	109.5	53	28.25
	0.1	7.7	108.5	42.8	32.85

	0.25	6.7	105.5	59	23.25
Dy	0.05	12.1	88.8	55	16.9

Figure captions

Figure 1: XRD patterns of the ceramics: (a) $\text{Bi}_{1-x}\text{Eu}_x\text{FeO}_3$ with $x=0.05-0.30$; (b) $\text{Bi}_{1-x}\text{Pr}_x\text{FeO}_3$ with $x=0.05-0.30$; (c) $\text{Bi}_{1-x}\text{Sm}_x\text{FeO}_3$ with $x=0.05-0.25$; (d) $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ with $x=0.05-0.30$; (e) $\text{Bi}_{1-x}\text{Dy}_x\text{FeO}_3$ with $x=0.05-0.25$, measured at $2\theta=20-70^\circ$ and room temperature.

Figure 2: Rietveld refinement XRD patterns of BA_xFO ceramics for $\text{A}=\text{Eu}$ with $x=0.05$.

Figure 3: Phase diagrams of $\text{Bi}_{1-x}\text{A}_x\text{FeO}_3$ ceramics at room temperature.

Figure 4: EF-SEM images of cross section of the ceramics: $x=0.05-0.20$ for Eu; $x=0.05-0.20$ for Pr; $x=0.05-0.20$ for Sm; $x=0.05-0.30$ for La; $x=0.05-0.25$ for Dy.

Figure 5: d_{33} of (a) $\text{Bi}_{1-x}\text{Eu}_x\text{FeO}_3$ with $x=0.05-0.30$; (b) $\text{Bi}_{1-x}\text{Pr}_x\text{FeO}_3$ with $x=0.05-0.30$; (c) $\text{Bi}_{1-x}\text{Sm}_x\text{FeO}_3$ with $x=0.05-0.25$; (d) $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ with $x=0.05-0.30$; (e) $\text{Bi}_{1-x}\text{Dy}_x\text{FeO}_3$ with $x=0.05-0.25$.

Figure 6: Composition dependence of ε_r and $\tan \delta$ in the ceramics with different additives: (a) Eu^{3+} , (b) Pr^{3+} , (c) Sm^{3+} , (d) La^{3+} , and (e) Dy^{3+} .

Figure 7: P - E curves of the ceramics: (a) Eu^{3+} , (b) Pr^{3+} , (c) Sm^{3+} , (d) La^{3+} , (e) Dy^{3+} . (f) are P - E curves of the ceramics with $\text{A}=\text{Sm}$ ($x=0.075$) for different frequencies.

Figure 8: Normolized d_{33} vs temperature in the ceramics with (a) Eu^{3+} , (b) Pr^{3+} , (c) Sm^{3+} , (d) La^{3+} , and (e) Dy^{3+} , measured at room temperature to 800°C .

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Phase structure

Electrical property