Fabrication of Al₂O₃-coated BiFeO₃ particles and fine-grained ceramics with improved electric properties

Peijia Bai

Kunming Institute of Precious Metals

Yutong Li

Kunming Institute of Precious Metals

Gang Wang

Kunming Institute of Precious Metals

Jiao Han

Kunming Institute of Precious Metals

Yongxing Wei

Xi'an technological University

Mingwei Li

Kunming Institute of Precious Metals

Duan Mao

Kunming Institute of Precious Metals

Yiming Zeng (✉ zengym0871@126.com)

Kunming Institute of Precious Metals <https://orcid.org/0000-0003-4046-4320>

Research Article

Keywords: BiFeO₃, Al₂O₃-coating, Microstructure, Electric properties

Posted Date: July 6th, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-40088/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Version of Record: A version of this preprint was published at Journal of Materials Science: Materials in Electronics on October 26th, 2020. See the published version at <https://doi.org/10.1007/s10854-020-04685-w>.

Abstract

(1-x)BiFeO₃@xAl₂O₃ ceramics with x = 0, 2.5, 5, and 7.5 mol% were prepared via the Stöber coating method. The effects of Al₂O₃ coating on microstructure, dielectric, and ferroelectric properties had been investigated. At x = 5 and 7.5, the samples had a great Al₂O₃ coating effect. XRD results indicated that excessive Al₂O₃ coating increased the formation of secondary phases (Bi₂Fe₄O₉ and Bi₂₄Al₁₂O₃₉). After the coating of Al₂O₃, the samples had higher relative density and decreased loss tangent. Compared with the pure BiFeO₃ sample, the Al₂O₃-coated samples had improved Bi-O strength, less oxygen vacancy, and the reduction of Fe³⁺ was decreased. The leakage current density decreased gradually. At x = 5, the sample had the highest Pr value (1.53 μC/cm²). These electric properties changes were ascribed to the generation of secondary phases, the fine grains, and the fewer vacancies.

Introduction

The multiferroic materials, which show the coexistence of multiferroic orders (ferroelectric, ferromagnetic, or ferroelasticity), can achieve the mutual control of the electric and magnetic signals. In recent years, multiferroic materials become one of the hottest research topics, and the multiferroic materials have a great application in electric devices such as sensors, spintronics, multi-state memories, and optoelectronic devices [1-3].

Among various multiferroics, BiFeO₃ (BFO) is the most concerning multiferroic materials, owing to its highly G-type anti-ferromagnetic Néel temperature ($T_N \sim 640$ K), highest ferroelectric Curie temperature ($T_C \sim 1103$ K) [4], and large saturated polarization value ($P_S \sim 100$ μC/cm²) [5]. The high saturated polarization value comes from the stereochemical activity of Bi 6s² lone pair electrons hybridizing with the empty 6p⁰ orbitals of Bi³⁺ and 2p⁶ elections of O²⁻ ion [6]. BiFeO₃ contains a G-type of anti-ferromagnetic ordering with a cycloidal modulation of 64 nm along the [110] direction, results in the concentration of macroscopic magnetization [2, 4]. Recently, Wang et al [7] prepared BiFeO₃-based lead-free ceramics with a high recoverable energy density ($W_{rec} \sim 2.1$ J/cm³). Gumiel et al. [8] found the switchable photovoltaic current and both diode effect in BiFeO₃ single crystals, indicating that the BiFeO₃-based materials have widespread potential applications.

However, BiFeO₃ has a series of shortcomings required for device applications, such as large leakage current density, high loss tangent, and weak magneto-electric coupling effects [3, 6]. These defects stem from the volatilization of Bi [9], the valence variation of Fe³⁺/Fe²⁺, and the generation of secondary phases. [10]. Those defects make it difficult to obtain saturated hysteresis polarization loops in the BiFeO₃ sample. It is also hard to synthetic phase-pure BiFeO₃ ceramics with high density because BiFeO₃ is vulnerable to decompose into Bi₂₅FeO₃₉ and Bi₂Fe₄O₉ in the range of 677 – 827 °C [11].

In order to solve those defects, some attempts have been performed. Song et al. [12] prepared BiFeO₃ ceramics via a two-step solid-state sintering method at 830 °C and found that the ceramics contained

secondary phases, and the microstructure was inhomogeneous with a low density, resulting in a decrease of ferroelectric properties. Wang et al. [13] prepared BiFeO₃ ceramic with larger remnant polarization (0.892 $\mu\text{C}/\text{cm}^2$) and decreased leakage current density ($6.58 \times 10^{-8} \text{ A}/\text{cm}^2$) via the spark plasma sintering method under an oxidizing atmosphere. Perez-Maqueda et al. [14] synthesized the high-density nanostructured BiFeO₃ ceramic with a nanometric grain size of $\sim 20 \text{ nm}$ via flash sintering technology. However, these sintering methods were more expensive and more complicated. It is well-known that the Stöber coating is a quite effective way to modify the surface of ceramic particles and to form the core-shell structure. Wang et al. [15] prepared La₂O₃-coated BaTiO₃ ceramics and found that the BaTiO₃@La₂O₃ sample had outstanding temperature-stable dielectric properties. Liu et al. [16] prepared Al₂O₃-coated BaTiO₃ ceramics and found that the BaTiO₃@Al₂O₃ sample had fine grains and improve energy storage properties. Aluminum has been confirmed helpful in refining the grain size of BaTiO₃ ceramics, the fine grains make it possible to decrease leakage current density and improve the electric properties of ceramics. However, there are few studies focus on the fabrication of coating BiFeO₃ ceramics and its electric properties research [17].

In this work, Al₂O₃-coated BiFeO₃ particles were prepared via the Stöber coating method. We fabrication fine-grained (1-*x*)BiFeO₃@*x*Al₂O₃ ceramics with different coating content, and the microstructure, dielectric and ferroelectric properties, and leakage current density of all (1-*x*)BiFeO₃@*x*Al₂O₃ samples were investigated.

Experimental Details

(1-*x*)BiFeO₃@*x*Al₂O₃ samples, where *x* = 0, 2.5, 5, and 7.5 mol% (denoted as A0, A2.5, A5, A7.5, respectively), were prepared via the Stöber coating method. Reagent pure Bi₂O₃ ($\geq 99\%$, Sinopharm Group Co., Ltd.), Fe₂O₃ ($\geq 99\%$, Sinopharm Group Co., Ltd.), Al(NO₃)₃·9H₂O ($\geq 99\%$, Sinopharm Group Co., Ltd.) were used as starting materials. The BiFeO₃ powder was synthesized via the solid-state reaction method as described in Ref [18]. Firstly, the BiFeO₃ powder was added in 50 ml alcohol, then ultrasonicated, and stirred for 1 h to break up the BiFeO₃ agglomeration. The Al(NO₃)₃·9H₂O was dissolved in 30 ml alcohol, then the Al(NO₃)₃·9H₂O solution was added into BiFeO₃ suspension slurries drop by drop. After titration, the suspension was aged for 2 h under stirring. Subsequently, the suspension was dried at 80 °C for 12 h. The dried powder was calcined at 550 °C for 30 min and the complex oxide-coated BiFeO₃ was fabricated. The coated powders were pressed into pellets with 10 mm in diameter and 1-2 mm in thickness using a 4 wt% polyvinyl alcohol binder. In order to reduce the evaporation of Bi₂O₃, the pellets were placed in a sealed corundum crucible and sintered at 780 °C for 2 hours. The schematic illustration of the preparation of (1-*x*)BiFeO₃@*x*Al₂O₃ ceramic as shown in Fig. 1.

The phase-purity of powders and ceramics was analyzed using the Rigaku Smart-Lab X-ray diffraction (RT-XRD, DMX-2200, Rigaku, Tokyo, JP) with Cu-K α radiation ($\lambda = 1.5405 \text{ \AA}$, 40 kV, and 75 mA). Micrographs of all the samples were measured using Field emission scanning electron micrograph

(FESEM, TM-1000, Hitachi, JP). The Archimedes method was used to measure the relative densities of all samples. The X-ray photoelectron spectroscopy (ESCALAB 250Xi, Thermo, USA) was used to investigate the valence state of ions of all samples. For electric properties measurements, Ag-conductive paste was painted on both sides, and fired at 550 °C for 15 min. The dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) were measured using an impedance analyzer (Agilent 4294A, Agilent, USA) in a wide frequency range (10^2 - 10^7 Hz). The polarization hysteresis loops (P-E loops) and leakage current density were measured via the ferroelectric analyzer (Radiant Technologies, premier-III, USA). All the sintered pellets were polished to a thickness of 0.2 mm for the measurements of P-E loops.

Results And Discussion

Figure 2 shows SEM images, EDS patterns, and the XRD patterns of all the $(1-x)\text{BiFeO}_3@x\text{Al}_2\text{O}_3$ particles. The grain surface morphology of $(1-x)\text{BiFeO}_3@x\text{Al}_2\text{O}_3$ particles was changed with the increase of the Al_2O_3 coating content. The pure BiFeO_3 particles (Fig. 2a) had a smooth surface. With the increase of the Al_2O_3 coating content, A5 and A7.5 particles were tightly coated by small grain and had a rough surface. Through EDS analysis, the A0 particle only contained Bi, Fe, and O elements, indicating pure BiFeO_3 . The small grain coated on the A7.5 particle (position 4) had only the Al and O elements, indicating that the Al_2O_3 coated samples were successfully prepared. However, positions 2 and 3 contained Bi, Fe, Al, and O elements, owing to the penetrability of the X-ray, the internal Bi, and Fe elements were also detected. Figure 2f shows the XRD patterns of all particles after calcined at 550 °C, the patterns were well-indexed with the peaks in JCPDS Card No: 74-2016 (space group R3c), revealing that the main phase of all the samples was BiFeO_3 . However, there were no diffraction peaks match with Al_2O_3 , because Al_2O_3 was uniformly coated on the sample and the highest content was only 2.57 wt%. In short, the Al_2O_3 coated BiFeO_3 particles were prepared.

The XRD patterns of all the $(1-x)\text{BiFeO}_3@x\text{Al}_2\text{O}_3$ sintered ceramics are shown in Fig. 3. It can be observed that the pure BiFeO_3 sample contained a little secondary phase, owing to BiFeO_3 is vulnerable to decompose into $\text{Bi}_{25}\text{FeO}_{39}$ and $\text{Bi}_2\text{Fe}_4\text{O}_9$ in the range of 677 – 827 °C. The BiFeO_3 decomposition process can be expressed by formula (1) [11]. With the increase of the Al_2O_3 coating content, the secondary phases ($\text{Bi}_2\text{Fe}_4\text{O}_9$ and $\text{Bi}_{24}\text{Al}_2\text{O}_{39}$) became more pronounced. $\text{Bi}_{24}\text{Al}_2\text{O}_{39}$ may be produced by the reaction of Al_2O_3 and BiFeO_3 during the sintering process as formula (2). During the sintering process, Al_2O_3 coating on the surface reacted with a part of BiFeO_3 to generate secondary phases, which will further improve the coating effect. However, it will also bring some serious changes to the electric properties of the $(1-x)\text{BiFeO}_3@x\text{Al}_2\text{O}_3$ ceramics, owing to the generation of secondary phases.

The cross-sectional SEM images of all the $(1-x)\text{BiFeO}_3@x\text{Al}_2\text{O}_3$ sintered ceramics are shown in Fig. 4. The microstructure was changed after the coating of the Al_2O_3 . The pure BiFeO_3 sample (A0) presented the large grains which had an irregular shape and a large number of porosities between the grains. With the increase of the Al_2O_3 coating content, the A2.5 sample had a mixture of larger and small grains, indicating that the coating effect is poor when the content of Al_2O_3 was 2.5 mol%. The A5 and A7.5 samples exhibited more fine grains, which may be the Al_2O_3 coated on the surface of the BiFeO_3 and the second phase produced by the reaction. Besides, the relative density increased from 87% for pure BiFeO_3 ceramic to 96% for A7.5 ceramic, indicating that the coating of Al_2O_3 could improve the sintering property of BiFeO_3 ceramics.

Figure 5 shows the XPS spectra of all the $(1-x)\text{BiFeO}_3@x\text{Al}_2\text{O}_3$ samples. The spectra were simulated and fitted via the XPS SPEAK 41 analysis software. The C, O, Al, Bi, and Fe elements were observed in Fig. 5a. the C1s peaks located 282.6 eV was used to rectify the binding energy of the XPS spectra[19]. Figure 5b show two peaks near 156.73 eV and 162.04 eV, respectively, which related to the Bi-O bonds. With the increase of the Al_2O_3 coating content, the binding energy of Bi-O bonds in $(1-x)\text{BiFeO}_3@x\text{Al}_2\text{O}_3$ samples gradually increased, indicating that the Bi-O bond strength in the oxygen octahedron was improved, which leads to a more stable perovskite structure for $(1-x)\text{BiFeO}_3@x\text{Al}_2\text{O}_3$ samples [20]. Besides, Fig. 5c shows the fitted $\text{Fe } 2p_{3/2}$ narrow-scan spectra of all samples. The Fe 2p XPS spectra exhibited two peaks near 707.84 eV for $\text{Fe } 2p_{3/2}$ and 722.35 eV for $\text{Fe } 2p_{1/2}$ which corresponded to the Fe-O bonds [21]. A satellite peak was present in the middle of these two peaks (near ~ 717 eV), indicating that the existence of Fe^{3+} oxidation state [22]. On the basis of the ratio of the fitted peak areas, the concentration ratios of Fe^{3+} to Fe^{2+} in A0, A2.5, A5, and A7.5 were 37.20 : 62.80, 46.92 : 53.08, 51.39 : 48.61, and 58.26 : 41.74, respectively, revealing that the reduction of Fe^{3+} in $(1-x)\text{BiFeO}_3@x\text{Al}_2\text{O}_3$ ceramics was decreased gradually with the increase of the Al_2O_3 coating content. Figure 5d shows the fitted O1s narrow- scan XPS spectra of all samples, there were two subpeaks near 527.4 eV and 529.4 eV, indicating two types of oxygen atoms. The former peak (O_F) can be attributed to the main peak of oxygen atoms in BiFeO_3 lattice, and the latter peak (O_L) was related to the presence of oxygen vacancy [23]. Combine with the fitted results, the concentration ratios of O_F to O_L in A0, A2.5, A5, and A7.5 were calculated as 58.83 : 41.17, 62.87 : 37.13, 64.17 : 35.83, and 74.10 : 25.90, respectively, indicating that the concentration of oxygen vacancy in $(1-x)\text{BiFeO}_3@x\text{Al}_2\text{O}_3$ ceramics was decreased gradually with the increase of the Al_2O_3 coating content. The oxygen vacancy ($\text{V}_\text{O}^{\bullet\bullet}$) was stem from the volatilization of Bi and the reducing of Fe^{3+} during the sintering process, as shown in formula (3) and (4) [24].

Therefore, it was easy to conclude that the Al_2O_3 coating was helpful to improve the Bi-O strength and decrease the reduction of Fe^{3+} , which resulted in a decrease of the vacancy concentration of (1-

x)BiFeO₃@xAl₂O₃ sample.

Figure 6 depicts the frequency dependence of dielectric constant (ϵ_r) and loss tangent ($\tan \sigma$) of all the (1-x)BiFeO₃@xAl₂O₃ samples. It was observed in the plots that the value of dielectric constant decreased with the increase in the frequency and then becomes almost constant. The higher dielectric constant at low frequency is a characteristic for all the dielectric materials, the Maxwell-Wegner model can be used to describe this behavior [25, 26]. With the increase of the Al₂O₃ coating content, the dielectric constant value of A5 and A7.5 samples changed little with the increase of the frequency, because these samples had fewer vacancies and higher relative density. The dielectric constant value decreased gradually with the increase of the Al₂O₃ coating content at all frequency regions because the dielectric constant values of Al₂O₃ ($\epsilon_r = 9$) [27] was less than that of pure BiFeO₃ ($\epsilon_r = 96$) [28]. The value of loss tangent decreased with the increase in frequency, and the loss tangent values of A5 and A7.5 samples were less than that of pure BiFeO₃ sample because of the Al₂O₃ coated sample had denser structure, smaller grains size, and fewer oxygen vacancies. These were beneficial for the dielectric properties of (1-x)BiFeO₃@xAl₂O₃ samples

The characteristics of leakage current density versus applied electric field (J - E) of all the (1-x)BiFeO₃@xAl₂O₃ samples are shown in Fig. 7. All the samples were measured from -10–10 kV/cm. With the increase of the Al₂O₃ coating content, the leakage current densities of (1-x)BiFeO₃@xAl₂O₃ samples decreased gradually. At the applied electric field of 10 kV/cm, the leakage current density of A0, A2.5, A5, and A7.5 samples were 5.70×10^{-6} , 4.61×10^{-6} , 1.66×10^{-7} , and 4.44×10^{-8} A/cm², respectively. In comparison with the pure BiFeO₃ sample, the leakage current density of A5 and A7.5 samples was decreased about two orders of magnitude. Because A5 and A7.5 samples had a great Al₂O₃ coating effect resulting in denser microstructure, fine grains, and fewer vacancies. The fine-grains ceramic had a longer grain boundary to delay charge transmission, and the charges were easily accumulated around the small grains to increase the resistance of ceramics [29].

The polarization hysteresis loops (P-E loops) of all the (1-x)BiFeO₃@xAl₂O₃ samples are shown in Fig. 8. The P-E loops were recorded at 50 Hz. All samples presented a saturated polarization hysteresis loop. With the increase of the Al₂O₃ coating content, the remnant polarization value (P_r) of (1-x)BiFeO₃@xAl₂O₃ samples increase at first and then decreased. The remnant polarization value of A0, A2.5, A5, and A7.5 samples were 0.93, 1.37, 1.53, and 0.92 $\mu\text{C}/\text{cm}^2$, respectively, under a maximum alternating-current electric field (E_m) of 100 kV/cm. A5 sample had the highest remnant polarization value, owing to the great Al₂O₃ coating effect, the sample had denser microstructure, improve Bi-O bond strength, and less vacancy. However, the A7.5 sample had lower P_r value than that of A2.5 and A5 samples, owing to the excessive Al₂O₃ coating will generate too many secondary phases (Bi₂Fe₄O₉ and Bi₂₄Al₁₂O₃₉). These secondary phases will loss of ferroelectric properties above -29 °C (Bi₂Fe₄O₉) [30]. All the (1-x)BiFeO₃@xAl₂O₃ samples were hard to measure the exact value of the P-E loops, because the electric coercive (E_c) of BiFeO₃ is more than 200 kV/cm [31], and the electrical penetration occurred before full

switching. Besides, all the P-E loops were not closed, which was also related to the low electric field breakdown, those behaviors were common in the BiFeO₃ system [32, 33].

Conclusions

In summary, (1-*x*)BiFeO₃@*x*Al₂O₃ particles with *x* = 0, 2.5, 5, and 7.5 mol% were prepared via the Stöber coating method using Al(NO₃)₃·9H₂O. SEM images revealed that the A5 and A7.5 samples had a great Al₂O₃ coating effect. After sintering into ceramics, the excessive Al₂O₃ coating sample generated many secondary phases (Bi₂Fe₄O₉ and Bi₂₄Al₁₂O₃₉). With the increase of the Al₂O₃ coating content, the relative density increased from 87% for pure BiFeO₃ ceramic to 96% for A7.5 ceramic, the dielectric constant and loss tangent were decreased. Compared with the pure BiFeO₃ sample, the A5 and A7.5 had increasing Bi-O strength, the less reduction of Fe³⁺, and less oxygen vacancy. A5 samples had the highest *P_r* value (1.53 μC/cm²). Besides, the leakage current density decreased gradually with the increase of the Al₂O₃ coating content.

Declarations

Acknowledgments

This work was supported by the Research Project of the National Key Laboratory of Chinese Academy of Sciences (Grant No. KLIFMD201605) and the Basic Applied Research Foundation of Yunnan Province (Grant No. 2016FD125, 2016FB083),

References

1. Cai K-M, Yang M-Y, Ju H-L et al (2017) Electric field control of deterministic current-induced magnetization switching in a hybrid ferromagnetic/ ferroelectric structure. *Nature Mater* 16:712–716
2. Yang M, Deng Y, Wu Z et al (2019) Spin Logic Devices via Electric Field Controlled Magnetization Reversal by Spin-Orbit Torque. *IEEE Electron Device Lett* 40:1554–1557
3. Zhou H, An Z, Yuan C et al (2019) Light-modulated ferromagnetism of strained NiFe₂O₄ nanocrystals. *Ceram Int* 45:13319–13323
4. Yang S, Zhang F, Xie X et al (2018) Enhanced leakage and ferroelectric properties of Zn-doped BiFeO₃ thin films grown by sol-gel method. *J Alloys Compd* 34:243–249
5. Dho J, Qi X, Kim H, MacManus-Driscoll J-L et al (2010) Large Electric Polarization and Exchange Bias in Multiferroic BiFeO₃. *Adv Mater* 18:1445–1448
6. Dai H, Li T, Chen Z et al. Studies on the structural, electrical, and magnetic properties of Ce-doped BiFeO₃ ceramics. *J. Alloys Compd* 2016, 72:182–189

7. Wang D-W, Fan Z-M, Li W-B et al (2018) High energy storage density and large strain in $\text{Bi}(\text{Zn}_{2/3}\text{Nb}_{1/3})\text{O}_3$ -doped BiFeO_3 - BaTiO_3 ceramics. *Acs Appl Energy Mater* 1:4403–4412
8. Gumiel C, Jardiel T, Bernardo M-S et al (2019) Combination of structural and microstructural effects in the multiferroic response of Nd and Ti co-doped BiFeO_3 bulk ceramics. *Ceram Int* 45:5276–5283
9. Jiang Q-H, Nan C-W, Shen Z-J (2006) Synthesis and properties of multiferroic La-modified BiFeO_3 ceramics. *J Am Ceram Soc* 89:2123–2127
10. Li J, Yan D-Z (2018) Low-temperature synthesis of pure BiFeO_3 phase and variation in its morphology with temperature. *Ceram Int* 44:18271–18278
11. Palai R, Katiyar R-S, Schmid F (2008) T et al. Beta phase and gamma-beta metal-insulator transition in multiferroic BiFeO_3 . *Phys Rev B* 77:014110
12. Song S-H, Zhu Q-S, Weng L-Q (2015) A comparative study of dielectric, ferroelectric, and magnetic properties of BiFeO_3 multiferroic ceramics synthesized by conventional and spark plasma sintering techniques. *J Eur Ceram Soc* 35:131–138
13. Wang T, Song H-S, Ma Q et al (2019) Multiferroic properties of BiFeO_3 ceramics prepared by spark plasma sintering with sol-gel powders under an oxidizing atmosphere. *Ceram Int* 45:2213–2218
14. Perez-Maqueda L-A, Gil-Gonzalez E, Perejon A et al (2017) Flash sintering of highly insulating nanostructured phase-pure BiFeO_3 . *J Am Ceram Soc* 100:3365–3369
15. Wang Y, Cui B, Liu Y et al (2014) Fabrication of submicron La_2O_3 -coated BaTiO_3 particles and fine-grained ceramics with temperature-stable dielectric properties. *Scripta Mat* 90:49–52
16. Liu B, Wang X, Zhao Q et al (2015) Improved energy storage properties of fine-crystalline BaTiO_3 ceramics by coating powders with Al_2O_3 and SiO_2 . *J Am Ceram Soc* 98:2641–2646
17. Cao T-F, Dai J-Q, Zhu J-H et al. Thermal stability, and electrical properties of $\text{BiFe}_{1-x}\text{M}_x\text{O}_3$ ($\text{M} = \text{Al}^{3+}, \text{Ga}^{3+}$) ceramics. *J Mater Sci-Mater Electron* 2019, **30**:3647-54
18. Bai P-J, Zeng Y-M, Han J et al (2019) Influence of Al doping on structural, dielectric, and ferroelectric properties of multiferroic BiFeO_3 ceramics. *Ceram Int* 45:7730–7735
19. Tian Y-M, Yuan S-L, Wang X-L (2009) Size effect on magnetic and ferroelectric properties in $\text{Bi}_2\text{Fe}_4\text{O}_9$ multiferroic ceramics. *J Appl Phys* 106:103912
20. Wang T, Song S-H, Ma Q et al (2019) Multiferroic properties of BiFeO_3 ceramics prepared by spark plasma sintering with sol-gel powders under an oxidizing atmosphere. *Ceram Int* 45:2213–2218
21. Dai Z-H, Akishige Y (2014) BiFeO_3 ceramics synthesized by spark plasma sintering. *Ceram Int* 38:S403–S406
22. Li X-Y, Dai J-Q, Cao T-F et al (2019) Structure and physical properties of (Zn, Ti) co-doped BiFeO_3 ceramics prepared using three different processes. *Ceram Int* 45:5015–5022
23. Wang S-Y, Liu W-F, Gao J et al (2012) Resistive switching and threshold switching behaviors in $\text{La}_{0.1}\text{Bi}_{0.9}\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ ceramics. *J Appl Phys* 3:034110–034115

24. Cai W, Fu C-L, Gao R-L et al (2014) Photovoltaic enhancement based on improvement of ferroelectric property and band gap in Ti-doped bismuth ferrite thin films. *J Alloys Compd* 617:240–246
25. Dai H-Y, Xue R-Z, Chen Z-P et al (2014) Effect of Eu, Ti co-doping on the structural and multiferroic properties of BiFeO₃ ceramics. *Ceram Int* 40:15617–15622
26. Dai H, Li T, Chen Z et al (2016) Studies on the structural, electrical, and magnetic properties of Ce-doped BiFeO₃ ceramics. *J Alloys Compd* 672:182–189
27. Birey H (1977) Thickness dependence of the dielectric constant and resistance of Al₂O₃ films. *J Appl Phys* 48:5209–5212
28. Chandel S, Thakur P, Thakur S-S et al (2018) Effect of non-magnetic Al³⁺ doping on structural, optical, electrical, dielectric and magnetic properties of BiFeO₃ ceramics. *Ceram Int* 44:4711–4718
29. Tian T-M, Yuan S-L, Wang X-L (2009) Size effect on magnetic and ferroelectric properties in Bi₂Fe₄O₉ multiferroic ceramics. *J Appl Phys* 106:123–133
30. Qi X-D, Dho J, Tomov R et al (2005) Effect of Nd Doping on Structural, Electrical, Thermal and Magnetic Properties of Multifunctional BiFeO₃ Ceramics. *Appl Phys Lett* 86:1–7
31. Wang J, Neaton J-B, Zheng H et al (2003) Epitaxial BiFeO₃ multiferroic thin film heterostructures. *Science* 299:1719–1722
32. Cao Y, Rushforth A, Sheng Y et al. Spintronic Synapses: Tuning a Binary Ferromagnet into a Multistate Synapse with Spin-Orbit-Torque-Induced Plasticity. *Adv Funct Mater* 2019, **29**:1808104.1-1808104.8
33. Cheng Z-X, Li A-H, Wang X-L et al (2008) Structure, ferroelectric properties, and magnetic properties of the La-doped bismuth ferrite. *J Appl Phys* 103:123–130

Figures

Figure 1

Schematic illustration of the approach used to prepare the (1-x)BiFeO₃@ xAl₂O₃ ceramics.

Figure 2

SEM images, EDS patterns and XRD patterns of the (1-x)BiFeO₃@xAl₂O₃ calcined particles: (a-d) SEM image of the (1-x)BiFeO₃@ xAl₂O₃ particles, (a) A0, (b) A2.5, (c) A5, (d) A7.5, (e) EDS patterns of different areas, (d) XRD patterns for the (1-x)BiFeO₃@xAl₂O₃ particles.

Figure 3

RT XRD patterns of the $(1-x)\text{BiFeO}_3@x\text{Al}_2\text{O}_3$ ceramics.

Figure 4

SEM images of the $(1-x)\text{BiFeO}_3@x\text{Al}_2\text{O}_3$ ceramics: (a) A0, (b) A2.5, (c) A5, (d) A7.5.

Figure 5

XPS spectra of the $(1-x)\text{BiFeO}_3@x\text{Al}_2\text{O}_3$ ceramics: (a) XPS survey spectrum, (b) Bi 4f, (c) Fe 2p, (d) O 1s.

Figure 6

Frequency dependence of dielectric parameters of the $(1-x)\text{BiFeO}_3@x\text{Al}_2\text{O}_3$ ceramics: (a) ϵ_r , (b) $\tan \delta$.

Figure 7

The leakage current density of the (1-x)BiFeO₃@xAl₂O₃ ceramics.

Figure 8

Polarization hysteresis loops of of the $(1-x)\text{BiFeO}_3@x\text{Al}_2\text{O}_3$ ceramics: (a) P-E loops, (b) Pr and EC of $(1-x)\text{BiFeO}_3@x\text{Al}_2\text{O}_3$ ceramics.