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

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
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 Bi24A12O39). 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 ~ 640 K), highest ferroelectric Curie temperature (T_C ~ 1103 K) [4], and large saturated polarization value (P_s ~ 100 μC/cm2) [5]. The high saturated polarization value comes from the stereochemical activity of Bi 6s^2 lone pair electrons hybridizing with the empty 6p^0 orbitals of Bi^{3+} and 2p^6 elections of O^{2-} 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} ~ 2.1 J/cm^3). 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 Fe^{3+}/Fe^{2+}, 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 Bi_{25}FeO_{39} and Bi_{2}Fe_{4}O_{9} 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 BiFeO$_3$ ceramic with larger remnant polarization (0.892 $\mu$C/cm$^2$) and decreased leakage current density (6.58×10$^{-8}$ A/cm$^2$) via the spark plasma sintering method under an oxidizing atmosphere. Perez-Maqueda et al. [14] synthesized the high-density nanostructured BiFeO$_3$ ceramic with a nanometric grain size of ~20 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 La$_2$O$_3$-coated BaTiO$_3$ ceramics and found that the BaTiO$_3$@La$_2$O$_3$ sample had outstanding temperature-stable dielectric properties. Liu et al. [16] prepared Al$_2$O$_3$-coated BaTiO$_3$ ceramics and found that the BaTiO$_3$@Al$_2$O$_3$ sample had fine grains and improve energy storage properties. Aluminum has been confirmed helpful in refining the grain size of BaTiO$_3$ 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 BiFeO$_3$ ceramics and its electric properties research [17].

In this work, Al$_2$O$_3$-coated BiFeO$_3$ particles were prepared via the Stöber coating method. We fabrication fine-grained (1-x)BiFeO$_3$@xAl$_2$O$_3$ ceramics with different coating content, and the microstructure, dielectric and ferroelectric properties, and leakage current density of all (1-x)BiFeO$_3$@xAl$_2$O$_3$ samples were investigated.

**Experimental Details**

(1-x)BiFeO$_3$@xAl$_2$O$_3$ 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 Bi$_2$O$_3$ ($\geq$99%, Sinopharm Group Co., Ltd.), Fe$_2$O$_3$ ($\geq$99%, Sinopharm Group Co., Ltd.), Al(NO$_3$)$_3$·9H$_2$O ($\geq$99%, Sinopharm Group Co., Ltd.) were used as starting materials. The BiFeO$_3$ powder was synthesized via the solid-state reaction method as described in Ref [18]. Firstly, the BiFeO$_3$ powder was added in 50 ml alcohol, then ultrasonicated, and stirred for 1 h to break up the BiFeO$_3$ agglomeration. The Al(NO$_3$)$_3$·9H$_2$O was dissolved in 30 ml alcohol, then the Al(NO$_3$)$_3$·9H$_2$O solution was added into BiFeO$_3$ 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 BiFeO$_3$ 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 Bi$_2$O$_3$, 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)BiFeO$_3$@xAl$_2$O$_3$ 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$\alpha$ radiation ($\lambda=1.5405$ Å, 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 ($\varepsilon_r$) 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-®, 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-$x$)BiFeO$_3$@$x$Al$_2$O$_3$ particles. The grain surface morphology of (1-$x$)BiFeO$_3$@$x$Al$_2$O$_3$ particles was changed with the increase of the Al$_2$O$_3$ coating content. The pure BiFeO$_3$ particles (Fig. 2a) had a smooth surface. With the increase of the Al$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$, because Al$_2$O$_3$ was uniformly coated on the sample and the highest content was only 2.57 wt%. In short, the Al$_2$O$_3$ coated BiFeO$_3$ particles were prepared.

The XRD patterns of all the (1-$x$)BiFeO$_3$@$x$Al$_2$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 Bi$_{25}$FeO$_{39}$ and Bi$_2$Fe$_4$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$_2$O$_3$ coating content, the secondary phases (Bi$_2$Fe$_4$O$_9$ and Bi$_{24}$Al$_2$O$_{39}$) became more pronounced. Bi$_{24}$Al$_2$O$_{39}$ may be produced by the reaction of Al$_2$O$_3$ and BiFeO$_3$ during the sintering process as formula (2). During the sintering process, Al$_2$O$_3$ 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-$x$)BiFeO$_3$@$x$Al$_2$O$_3$ ceramics, owing to the generation of secondary phases.

\begin{align*}
(1) \quad & 49\text{BiFeO}_3 \rightarrow 12\text{Bi}_2\text{Fe}_4\text{O}_9 + \text{Bi}_{25}\text{FeO}_{39} \\
(2) \quad & 48\text{BiFeO}_3 + \text{Al}_2\text{O}_3 \rightarrow \text{Bi}_{24}\text{Al}_2\text{O}_{39} + 12\text{Bi}_2\text{Fe}_4\text{O}_9
\end{align*}
The cross-sectional SEM images of all the (1-x)BiFeO$_3$@xAl$_2$O$_3$ sintered ceramics are shown in Fig. 4. The microstructure was changed after the coating of the Al$_2$O$_3$. 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$_2$O$_3$ 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$_2$O$_3$ was 2.5 mol%. The A5 and A7.5 samples exhibited more fine grains, which may be the Al$_2$O$_3$ 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$_2$O$_3$ could improve the sintering property of BiFeO$_3$ ceramics.

Figure 5 shows the XPS spectra of all the (1-x)BiFeO$_3$@xAl$_2$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 shows two peaks near 156.73 eV and 162.04 eV, respectively, which related to the Bi-O bonds. With the increase of the Al$_2$O$_3$ coating content, the binding energy of Bi-O bonds in (1-x)BiFeO$_3$@xAl$_2$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)BiFeO$_3$@xAl$_2$O$_3$ samples [20]. Besides, Fig. 5c shows the fitted Fe 2p$_{3/2}$ narrow-scan spectra of all samples. The Fe 2p XPS spectra exhibited two peaks near 707.84 eV for Fe 2p$_{3/2}$ and 722.35 eV for 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)BiFeO$_3$@xAl$_2$O$_3$ ceramics was decreased gradually with the increase of the Al$_2$O$_3$ 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)BiFeO$_3$@xAl$_2$O$_3$ ceramics was decreased gradually with the increase of the Al$_2$O$_3$ coating content. The oxygen vacancy (V$_O^{**}$) 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].

\[
(3) \quad 2\text{Bi}_\text{Bi} + 3\text{O}_\text{O} \rightarrow \text{Bi}_2\text{O}_3 + 2\text{V}_\text{Bi}^{''''} + 3\text{V}_\text{O}^{**}
\]

\[
(4) \quad 4\text{Fe}_\text{Fe} + 2\text{O}_\text{O} \rightarrow 4\text{Fe}_\text{Fe}' + \text{O}_2 \uparrow + 2\text{V}_\text{O}^{**}
\]

Therefore, it was easy to conclude that the Al$_2$O$_3$ 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-
Figure 6 depicts the frequency dependence of dielectric constant ($\varepsilon_r$) and loss tangent (tan $\sigma$) of all the (1-$x$)BiFeO$_3@x$Al$_2$O$_3$ 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 Al$_2$O$_3$ 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 Al$_2$O$_3$ coating content at all frequency regions because the dielectric constant values of Al$_2$O$_3$ ($\varepsilon_r=9$) [27] was less than that of pure BiFeO$_3$($\varepsilon_r=96$) [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 BiFeO$_3$ sample because of the Al$_2$O$_3$ coated sample had denser structure, smaller grains size, and fewer oxygen vacancies. These were beneficial for the dielectric properties of (1-$x$)BiFeO$_3@x$Al$_2$O$_3$ samples.

The characteristics of leakage current density versus applied electric field (J - E) of all the (1-$x$)BiFeO$_3@x$Al$_2$O$_3$ samples are shown in Fig. 7. All the samples were measured from $-10$ to $10$ kV/cm. With the increase of the Al$_2$O$_3$ coating content, the leakage current densities of (1-$x$)BiFeO$_3@x$Al$_2$O$_3$ 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 $5.70^{-6} \times 10^{-6}$, $4.61 \times 10^{-6}$, $1.66 \times 10^{-7}$, and $4.44 \times 10^{-8}$ A/cm$^2$, respectively. In comparison with the pure BiFeO$_3$ 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 Al$_2$O$_3$ 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-$x$)BiFeO$_3@x$Al$_2$O$_3$ 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 Al$_2$O$_3$ coating content, the remnant polarization value ($P_r$) of (1-$x$)BiFeO$_3@x$Al$_2$O$_3$ 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 $\mu$C/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 Al$_2$O$_3$ 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 Al$_2$O$_3$ coating will generate too many secondary phases (Bi$_2$Fe$_4$O$_9$ and Bi$_{24}$A$_1$$_2$O$_{39}$). These secondary phases will loss of ferroelectric properties above $-29$ °C (Bi$_2$Fe$_4$O$_9$) [30]. All the (1-$x$)BiFeO$_3@x$Al$_2$O$_3$ samples were hard to measure the exact value of the P-E loops, because the electric coercive ($E_c$) of BiFeO$_3$ 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 BiFeO$_3$ system [32, 33].

**Conclusions**

In summary, (1-x)BiFeO$_3$@xAl$_2$O$_3$ particles with x = 0, 2.5, 5, and 7.5 mol% were prepared via the Stöber coating method using Al(NO$_3$)$_3$·9H$_2$O. SEM images revealed that the A5 and A7.5 samples had a great Al$_2$O$_3$ coating effect. After sintering into ceramics, the excessive Al$_2$O$_3$ coating sample generated many secondary phases (Bi$_2$Fe$_4$O$_9$ and Bi$_{24}$A1$_2$O$_{39}$). With the increase of the Al$_2$O$_3$ coating content, the relative density increased from 87% for pure BiFeO$_3$ ceramic to 96% for A7.5 ceramic, the dielectric constant and loss tangent were decreased. Compared with the pure BiFeO$_3$ sample, the A5 and A7.5 had increasing Bi-O strength, the less reduction of Fe$^{3+}$, and less oxygen vacancy. A5 samples had the highest $P_r$ value (1.53 $\mu$C/cm$^2$). Besides, the leakage current density decreased gradually with the increase of the Al$_2$O$_3$ 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 NiFe$_2$O$_4$ 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 BiFeO$_3$. 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 BiFeO$_3$ 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 Bi\((Zn_{2/3}Nb_{1/3})O_3\)-doped BiFeO\(_3\)-bBaTiO\(_3\) 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\(_2\)O\(_3\)-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\(_2\)O\(_3\) 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 BiFe\(_1-x\)M\(_x\)O\(_3\) (M = Al\(^{3+}\), 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 Bi\(_2\)Fe\(_4\)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 La\(_{0.1}\)B\(_{10.9}\)Fe\(_{1-x}\)Co\(_x\)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 BiFeO$_3$ 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 BiFeO$_3$ ceramics. J Alloys Compd 672:182–189

27. Birey H (1977) Thickness dependence of the dielectric constant and resistance of Al$_2$O$_3$ films. J Appl Phys 48:5209–5212

28. Chandel S, Thakur P, Thakur S-S et al (2018) Effect of non-magnetic Al$^{3+}$ doping on structural, optical, electrical, dielectric and magnetic properties of BiFeO$_3$ 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 Bi$_2$Fe$_4$O$_9$ 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 BiFeO$_3$ Ceramics. Appl Phys Lett 86:1–7

31. Wang J, Neaton J-B, Zheng H et al (2003) Epitaxial BiFeO$_3$ 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 Phy 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 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)BiFeO₃@xAl₂O₃ ceramics.
Figure 3

RT XRD patterns of the (1-x)BiFeO3@xAl2O3 ceramics.
Figure 4

SEM images of the (1-x)BiFeO3@xAl2O3 ceramics: (a) A0, (b) A2.5, (c) A5, (d) A7.5.
Figure 4

SEM images of the (1-x)BiFeO3@xAl2O3 ceramics: (a) A0, (b) A2.5, (c) A5, (d) A7.5.
Figure 5

XPS spectra of the (1-x)BiFeO₃@xAl₂O₃ ceramics: (a) XPS survey spectrum, (b) Bi 4f, (b) Fe 2p, (d) O1s.
Figure 5

XPS spectra of the (1-x)BiFeO3@xAl2O3 ceramics: (a) XPS survey spectrum, (b) Bi 4f, (b) Fe 2p, (d) O1s.
Figure 6

Frequency dependence of dielectric parameters of the (1-x)BiFeO3@xAl2O3 ceramics: (a) $\varepsilon_r$, (b) $\tan\delta$. 
Figure 6

Frequency dependence of dielectric parameters of the (1-x)BiFeO3@xAl2O3 ceramics: (a) $\varepsilon_r$, (b) $\tan\delta$. 
Figure 7

The leakage current density of the (1-x)BiFeO3@xAl2O3 ceramics.
Figure 7

The leakage current density of the (1-x)BiFeO3@xAl2O3 ceramics.
Figure 8

Polarization hysteresis loops of the (1-x)BiFeO3@xAl2O3 ceramics: (a) P-E loops, (b) Pr and EC of (1-x)BiFeO3@xAl2O3 ceramics.