Effect of octahedron tilt on structure and magnetic properties of bismuth ferrite

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Rapid Communication

Keywords: bismuth ferrite; magnetism; octahedron tilt.

Posted Date: April 29th, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-24754/v1>

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Version of Record: A version of this preprint was published at Journal of Advanced Ceramics on September 25th, 2020. See the published version at <https://doi.org/10.1007/s40145-020-0398-1>.

Abstract

Multiferroic trivalent ions doped BiFeO₃ ceramics were synthesized using the rapid liquid state method. The trivalent ions (Sm³⁺, Gd³⁺, Y³⁺) doping causes structural distortion without changing the rhombohedral structure. Raman analysis shows that the effect of doping on *E* modes is greater than *A*₁ modes, and FeO₆ octahedron is regulated by ions doping. M-H hysteresis loops show A-site trivalent ions doped samples exhibit improved magnetism compared with pure BiFeO₃ since the suppressed spiral spin structure. Doped samples exhibited natural resonance around 16~17 GHz due to the changes in dielectric loss caused by the tilt of the FeO₆ octahedron.

Introduction

Multiferroic materials are one of the most studied materials in recent years due to their unique properties, which exhibit more than two ferroic orders (such as ferroelectricity, ferromagnetism, ferroelastic etc.). More than two orders can be coupled under certain conditions, exhibiting remarkable physical properties and excellent application potential [1–3]. Multiferroic materials are not only helpful for the applications but also provide a platform for exploring interesting effects like magnetoelectric effect, piezoelectric effect, and so on.

Among various known multiferroic materials, bismuth ferrite (BiFeO₃) is a widely investigated multiferroic material, in which ferroelectricity ($T_C \approx 1100$ K) and ferromagnetism ($T_N \approx 640$ K) coexist at room temperature [4, 5]. The crystallographic structure of BiFeO₃ is rhombohedrally distorted perovskite structure with the space group *R3c*. The unit cell has a lattice parameter of $a = 3.965$ Å and a rhombohedral angle of ~ 89.3 – 89.48° , and the oxygen octahedron is distorted with minimum and maximum O-O distances of 2.710 and 3.015 Å, respectively, and rotated by about 13.8° around the [111] axis [6]. BiFeO₃ is classified as a G-type antiferromagnet below T_N at the magnetic point of view, the combine action of exchange and spin-orbit interactions produce spin canting away from perfect antiferromagnetic ordering. The canted spin structure exhibits a space-modulated spiral structure (SMSS) with a period length of 62 nm, thereby resulting in a helimagnetic structure and a vanishing magnetization in the bulk [7, 8].

The SMSS ordering in BiFeO₃ is stable, and it persists when the temperature varies from 4 K to the Neel temperature [9]. The modification of the spin structure is the key issue for the realization of BiFeO₃-based materials. Many attempts to add ferromagnetic properties to the BiFeO₃ compounds by A or B site substitutions were made. Neutron diffraction studies on Bi_{1-x}La_xFeO₃ show that the SMSS modulation period in BiFeO₃ grows with La [10]. The researchers have found that the leakage current of BFO can be reduced by substituting appropriate element. To improve the electrical and magnetic properties of the BFO, several research groups have attempted to modify with 3+ valence ions of Nd³⁺, Dy³⁺ or Pr³⁺ at the

A-site of BFO [11–13]. The spin-coated Y-doped BiFeO₃ film exhibits low field saturation magnetization by suppressing the spiral spin modulated periodicity due to FeO₆ octahedral distortion [14].

In present work, we study structure, magnetic properties and microwave electromagnetic parameters of BiFeO₃ based ceramics. A-site trivalent ions doping tilted the FeO₆ octahedron in the lattice and changed the space-modulated spiral structure, leading to the improved ferromagnetism of ceramics. Doped samples exhibited enhanced permittivity accompanied natural resonance around 16 ~ 17 GHz, the detailed mechanism has been explained with dielectric loss and defects changed.

Experiment

Polycrystalline BiFeO₃ and Bi_{0.95}M_{0.05}FeO₃ (*M* = Sm, Gd, Y) samples (abbreviated as BFO, BSFO, BGFO and BYFO) were prepared by the rapid liquid state method. Stoichiometric ratios of Bi₂O₃, Fe₂O₃, Sm₂O₃, Gd₂O₃, Y₂O₃ were mixed with agate balls for 24 h using alcohol as the solvent. Each component has an increase of 2.5% Bi₂O₃ on the base of the stoichiometric ratio, taking into account the volatilization characteristic of Bi₂O₃. The powders were pressed into pellets of 8 mm in diameter under 500 MPa rapidly sintered in air at 800 °C for 20 min, and then took a rapid air quenching process.

The phase composition and crystalline structures of the samples were analyzed using X-ray diffraction (XRD, Panalytical X'PERT PRO MPD, with Cu K α radiation). Morphologies were examined using field emission scanning electron microscopy (SEM, ZEISS Merlin Compact). Raman measurement was performed using laser confocal Raman spectrometer (inVia-Reflex, Renishaw). The magnetic properties were investigated by a vibrating sample magnetometer (VSM). The electromagnetic parameters were measured from 2 to 18 GHz with a vector network analyzer (Keysight Technologies N5234A).

Results And Discussion

In order to evaluate the phase formation and crystallinity of the samples, X-ray diffraction study was performed, and the effect of the substitution of doped ions for Bi³⁺ ion on the structure of BiFeO₃ was investigated by Rietveld refinement, which was performed by using the GSAS program. Figure 1 shows the x-ray diffraction (XRD) patterns and the refinement curves of the as-prepared samples. All the exhibited peaks of four samples were well indexed with BiFeO₃ (ICDD-PDF No.71-2494) and have rhombohedral *R*3*c* structure. The corresponding lattice parameters and fitting factors were listed in Table 1, ions introduction played a significant effect on the crystal structure. Since the radius of the doped ions is smaller than that of the bismuth ion (Six coordination ionic radius: rBi³⁺ = 0.103 nm, rSm³⁺ = 0.0958 nm, rGd³⁺ = 0.0938 nm, rY³⁺ = 0.0900 nm), the unit cell volume shrinks after doping. In addition, affected by changes of ion radius in the sublattice, the state of the local electronic cloud changed, so the bond length (Fe-O) and the bond angle (Fe-O-Fe) have changed in the FeO₆ octahedron, and the FeO₆ octahedron distorted.

The angle of rotation of oxygen octahedron is a typical structural parameter of BFO. For cubic perovskite with standard matching ions, this rotation angle is zero. However, in BFO rhombohedral perovskite system, the rotation angle is nonzero for the influence of overlap between the electronic clouds of ions.

Table 1
Refined lattice parameters and structure fitting factors.

Parameters	BFO	BSFO	BGFO	BYFO
a (Å)	5.5795	5.5798	5.5788	5.5794
c (Å)	13.8709	13.8623	13.8609	13.8687
V (Å ³)	373.960	373.767	373.594	373.893
Fe z	0.2222	0.2456	0.2707	0.2316
O x	0.4520	0.4360	0.4440	0.4277
O y	0.0227	0.0003	0.0092	-0.0130
O z	0.9554	0.9807	1.0020	0.9995
Fe-O(1) bond length (Å)	2.071	2.138	2.137	2.122
Fe-O(2) bond length (Å)	1.980	1.905	1.912	1.939
Fe-O-Fe bond angle (°)	165.7	170.3	166.5	166.5
R_{wp}	7.42%	7.63%	6.99%	7.25%
R_p	5.80%	5.87%	5.51%	5.47%
χ^2	2.086	2.997	2.480	2.788

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In the doped system of perovskite structure compounds, the tolerance factor, defined as $\tau = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$, is usually used to depict the stable extent of the structure. r_A , r_B and r_O stand for the ionic radius of A-site, B-site, and O-site in the ABO_3 , respectively [15]. The tolerance factor τ is 0.8404 for the pure BFO, and it is 0.8391, 0.8388, 0.8381 for BSFO, BGFO, and BYFO, respectively. It can be seen that the structure of the four components is relatively stable. The smaller the tolerance factor, the more severely is the bucking between the oxygen octahedron. The smaller A-site ions can not fill the empty space fully leading to the distorted octahedron, shrinking the unit cell space. The octahedral tilt is ~ 11 - 14° along the [111] triple axis and the related Fe-O-Fe band angle is 154 - 156° [16].

Scanning electron microscopy technology was used in pure and doped BFO samples, as shown in Fig. 2. All the samples exhibit distinct morphologies and boundaries, and a certain amount of pores exist in the ceramics. In order to avoid heterogeneous phases during sintering, rapid liquid phase sintering and air quenching were adopted, this has caused a change in the porosity of the ceramics. The grain size of pure BFO was found to be 1 – $3 \mu\text{m}$, with the introduction of doped ions, the average grain sizes of doped ceramics are smaller than that of BFO, which are around 0.5 - $1 \mu\text{m}$. The difference in ionic radii of A-site lead to shrink of unit cell which can hinder crystallite nucleation, and the grain sizes are smaller in the macro perspective.

The crystal structure of BFO is a distorted rhombohedral perovskite at room temperature, which belongs to space group $R3c$. According to group theory, the multiferroic BFO exhibits 13 optical phonon modes, expressed by the equation as (see Equation in the Supplemental Files)

$$\Gamma_{Rhombohedral, R3c} = 4A_1 + 9E$$

where, The A_1 modes polarized along and the doubly degenerate E modes polarized in the x-y plane are both Raman and IR active. The peaks, which represent the Raman modes, are obtained by the Raman spectra and decomposing them into individual components, as shown in Fig. 3. In our polycrystalline ceramics, all the 13 Raman active modes were observed, which matched well with the above structure. Bi atoms participate in low-frequency modes below $A_1(TO1)$, whereas O atoms dominate in modes above $E(TO4)$. Fe atoms are involved mainly in modes between $E(TO2)$ and $E(TO4)$, but also contribute to the development of some higher-wavenumber modes.

We observed all Raman modes of the rhombohedral structure of BiFeO_3 predicted by theory from the spectrum, and labeled them in Fig. 3. Table 2 exhibits the comparison of the Raman modes positions after being deconvoluted of different component samples. By comparing Raman shifts of different modes, it is found that the doping has a certain effect on the E modes, but has little effect on the A_1 modes.

Table 2
Comparison of the Raman modes positions of different component samples.

Raman modes	BFO	BSFO	BGFO	BYFO
$A_1(TO1)$	137	138	140	140
$A_1(TO2)$	170	171	172	173
$A_1(TO3)$	218	224	225	224
$A_1(TO4)$	453	450	450	456
$E(TO1)$	75	76	76	76
$E(TO2)$	121	118	123	121
$E(TO3)$	258	258	266	264
$E(TO4)$	284	279	295	288
$E(TO5)$	340	314	333	338
$E(TO6)$	366	360	370	370
$E(TO7)$	476	477	477	475
$E(TO8)$	523	516	517	522
$E(TO9)$	557	540	571	543

Table 3
Detailed magnetic parameters.

	BFO	BSFO	BGFO	BYFO
M_r (emu/g)	0.009	0.023	0.011	0.019
H_c (Oe)	579	866	331	611

In order to explore the microwave electromagnetic properties of samples, the air-line method was employed to measure the complex permittivity and complex permeability within the 2–18 GHz, as shown in Fig. 5(a) and (b). According to the figures, the real part of permittivity is improved for doped components, and accompanied by a certain resonance at 16 ~ 17 GHz. Among the samples, BGFO shows better dielectric loss. The complex permittivity of all the samples is at a lower level due to ceramics were prepared using rapid liquid state method. The leakage current caused by oxygen vacancy is widely considered to be a major influential factor on the dielectric loss for BFO in the microwave band [20, 21], and we suppose that other defects generated during the preparation process will also have a negligible effect on the dielectric properties of ceramics. The feature of the complex permeability for ceramics exhibits the inherent weak ferromagnetism of samples, which is consistent with previous magnetic analysis.

Conclusion

A series of doped BFO ceramics were successfully synthesized by the rapid liquid state method. The participation of trivalent ions modulated the spatial structure of BFO to a certain extent, tilted the FeO_6 octahedron. The space-modulated spiral structure of BFO was further suppressed due to the minor changes in periodic structure, which is originated from the tilting of oxygen octahedron by the doping of trivalent ions, improved ferromagnetism of doped samples. Moreover, doped samples exhibited enhanced permittivity accompanied natural resonance around 16 ~ 17 GHz, provided a feasible route to further regulate the microwave electromagnetic performance of bismuth ferrite.

Declarations

Acknowledgements

This work was supported by the National Natural Science Foundation of China (51502054), the Postdoctoral Science Foundation of China (2014M551236), the Postdoctoral Science Foundation of Heilongjiang Province (LBH-Z14083).

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Figure 1

Rietveld-refined XRD patterns of BFO, BSFO, BGFO, and BYFO samples.

Figure 2

SEM micrographs of as-prepared ceramics: (a) BFO, (b) BSFO, (c) BGFO and (d) BYFO.

Figure 3

Deconvoluted Raman spectra of all samples.

Figure 4

M-H hysteresis loops for pure and doped BFO ceramics, and the inset depicts partial enlarged curves.

Figure 5

(a) Real and imaginary parts of permittivity and (b) real and imaginary parts of permeability of BFO, BSFO, BGFO, and BYFO, respectively.

Supplementary Files

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