A Neutron Diffraction Investigation of High Valent Doped Barium Ferrite With Super-wide Tunable Microwave Absorption

J. Li (✉ lijuna@hit.edu.cn)

Harbin Institute of Technology <https://orcid.org/0000-0002-7645-1997>

Yang Hong

Harbin Institute of Technology

San He

Harbin Institute of Technology

Weike Li

Harbin Institute of Technology

Han Bai

Harbin Institute of Technology

Yuanhua Xia

China Academy of Engineering Physics Institute of Nuclear Physics and Chemistry

Guangai Sun

China Academy of Engineering Physics Institute of Nuclear Physics and Chemistry

Zhongxiang Zhou

Harbin Institute of Technology

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A neutron diffraction investigation of high valent doped barium ferrite with super-wide tunable microwave absorption

Jun LI^{a,b,†,*}, Yang HONG^{c,†}, San HE^{a,b}, Weike LI^{a,b}, Han BAI^{a,b}, Yuanhua XIA^d

Guangai SUN^d and Zhongxiang ZHOU^{a,b,*}

^a School of Physics, Harbin Institute of Technology, Harbin 150001, China

^b Heilongjiang Provincial Key Laboratory of Plasma Physics and Application Technology, Harbin Institute of Technology, Harbin 150001, China

^c School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, China

^d Key Laboratory for Neutron Physics of CAEP, Institute of Nuclear Physics and Chemistry, Mianyang 621999, China

† Jun Li and Yang Hong contributed equally to this work.

* Corresponding author.

E-mail: lijuna@hit.edu.cn, zhouzx@hit.edu.cn

Abstract

The Barium ferrite BaTi_xFe_{12-x}O₁₉ ($x = 0.2, 0.4, 0.6, 0.8$) ceramics doped by Ti⁴⁺ (BFTO- x) were synthesized by a modified sol-gel method. The crystal structure and magnetic structure of the samples were determined by neutron diffraction, and confirm that the BFTO- x ceramics were high quality single phase with sheet micro-structure. With x increasing from 0.2 to 0.8, the M_s decreases gradually but the change of H_c is complex under the synergy of the changed grain size and the magnetic crystal anisotropy field. Relying on the high valence of Ti⁴⁺, double resonance peaks are obtained in the curves of μ'' and the resonance peaks could move towards the low frequency with the increase of x , which facilitate the samples perform an excellent wide-band modulation microwave absorption property. In the $x = 0.2$ sample, the

maximum reflection loss can reach -44.9 dB at the thickness of only 1.8 mm, and the bandwidth could reach to 5.28 GHz at 2 mm when the RL is less than -10 dB. All the BFTO- x ceramics show excellent frequency modulation ability varying from 18 GHz ($x = 0.8$) to 4 GHz ($x = 0.4$), which covers 81% of the investigated frequency in microwave absorption field.

Keywords: barium ferrite; neutron diffraction; microwave absorption.

1 Introduction

The rapid development of electronic information technology and communication industry has increased the requirements of microwave absorption materials to solve the uncovering electromagnetic interference problems [1]. Thus, developing microwave absorption materials of large reflection loss and broad bandwidth is becoming urgent. The inherent properties of microwave absorbing materials, including complex permeability and permittivity, which are significant in enhancing the reflection loss and broadening the effective bandwidth [2].

The electromagnetic absorbing materials can be classified into a resistive type, a dielectric type, and a magnetic medium type according to the loss mechanism [3-5]. The resistive absorbing materials mainly absorb electromagnetic wave by interaction with an electric field, and the absorption efficiency depends on the conductivity and dielectric constant, include carbon black, metal powder, silicon carbide, graphite, and special carbon fiber [6]. For dielectric absorbing materials, the electromagnetic wave is mainly absorbed by the dielectric polarization relaxation loss, the typical representative is barium titanate ferroelectric ceramics [7]. The attenuation of the electromagnetic

wave by the magnetic medium type absorbing materials mainly comes from resonance and hysteresis loss, such as ferrite and carbonyl iron [8]. Among all these materials, the ferrite is an ideal microwave absorbing material for the simple preparation process and the stable performance [9].

M-type barium ferrite ($\text{BaFe}_{12}\text{O}_{19}$), a versatile material, performs excellent electromagnetic properties due to the large magnetic loss at the natural resonance frequency. Pure barium ferrite has large saturation magnetization, high coercivity, magnetic anisotropy constants and the large magnetic loss at the natural resonance frequency, which make barium ferrite have excellent microwave absorption characteristics. To investigate larger reflection loss, broader bandwidth, and even tunable microwave absorbing material, many kinds of research work on barium ferrite doping modification are carried out. The magnetic loss is related to the content of Fe^{3+} in barium ferrite, thus the microwave absorption properties can be adjusted when Fe^{3+} ions are substituted with other trivalent ions or combination of divalent and tetravalent ions. BaM-based cationic substitutions for Fe^{3+} are used to modify the dielectric and magnetic parameters, which play an important role in reflection loss (RL) calculation. The substitutions for Fe^{3+} of BaM-based can be divided into two main approaches: covalent cation substitution such as Ga^{3+} , In^{3+} , and Er^{3+} and heterovalent cationic combination such as $\text{Co}^{2+}\text{-Ti}^{4+}$, $\text{Co}^{2+}\text{-Zr}^{4+}$, $\text{Ni}^{2+}\text{-Ti}^{4+}$, and so on [10-14]. However, recent studies have shown that the introduction of high-valence ions destroys the valence state equilibrium of barium ferrite, resulting in multiple absorption peaks, which can increase the bandwidth of electromagnetic wave absorption of the material

[15,16].

In this work, we synthesized $\text{BaFe}_{12-x}\text{Ti}_x\text{O}_{19}$ (BFTO- x , $x = 0.2, 0.4, 0.6, 0.8$) using only tetravalent Ti^{4+} ions as high valent dopant ions by modified sol-gel method. We systematically analyzed the structure, morphology, magnetic properties and electromagnetic parameters of the sample. By comparing the magnetic structure of the neutron diffraction with the experimental magnetic results, the internal magnetic mechanism of the sample was deeply studied. The modified M-type barium ferrite exhibits better tunability for electromagnetic properties, which have a positive role on the exploration of the novel microwave absorbing materials.

2 Experimental

2.1 Material synthesis

The Ti^{4+} doped M-type barium ferrite ceramics ($\text{BaFe}_{12-x}\text{Ti}_x\text{O}_{19}$, $x = 0.2, 0.4, 0.6, 0.8$) were prepared utilizing the modified sol-gel method that is more effective than conventional solid state method. Barium nitrate ($\text{Ba}(\text{NO}_3)_2$), iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and titanium nitrate ($\text{Ti}(\text{NO}_3)_4$) were weighted in a stoichiometric ratio and dissolved in citric acid solution adequately. The PH value of the solution was adjusted to 8 by adding ammonia water, then the solution was stirred for 2 h and aged for 12 h at room temperature. The mixed solution was placed in 80 °C water bath for 3 h to form a sol, which was then transferred to a dry box at 120 °C for 1 to 2 day until a dry gel was formed. The aerogel was incubated at 210 °C for 3 h to remove organic components from the gel. Calcination was carried out at 1200 °C to get the BFTO- x powder. The powder was pressed into wafers of 13 mm in diameter, and then the wafers

were sintered at 1200 °C for 4 h in air atmosphere to obtain the BFTO- x ceramics.

2.2 Characterizations

The neutron powder diffraction (NPD) experiments were carried out at room temperature using high resolution neutron powder diffractometer (HRND) ($\lambda=1.884$ Å) at China Mianyang Research Reactor (CMRR), and the corresponding Rietveld refinement was achieved by FullProf and SARAh. Morphologies were examined using field emission scanning electron microscopy (SEM, ZEISS Merlin Compact). Magnetic properties were investigated using a vibrating sample magnetometer (VSM, Lake Shore 7404). The electromagnetic properties were studied using air-line method, which were mixed with polyvinyl alcohol (PVA) at a mass ratio of 6:1. The complex permittivity and permeability were measured from 2 to 18 GHz with a vector network analyzer (Keysight Technologies N5234A).

3 Results and discussion

3.1 Effects of titanium substitution on crystal structure and microstructure

The neutron diffraction patterns of BFTO- x ($x = 0.2, 0.4, 0.6, 0.8$) ceramics are shown in Figure 1(a), which contains the complete neutron diffraction pattern before and after refinement using Rietveld method. Since the neutron diffraction patterns include both structural and magnetic information, the process of BFTO- x refinement using FullProf can be divided into two parts: structural and magnetic phase [17]. The detailed results of refinement contained structural and magnetic parameters also appear in the Figure 1(a), and the corresponding refinement factors of each components were also shown in the figure. Compared with the neutron diffraction Bragg positions of pure

barium ferrite, no other impurity peaks were found, indicating that the four components were single phase with space group $P63/mmc$. Moreover, the corresponding magnetic space group of BFTO- x is $R-3m:H$, which was determined by utilizing the Sarah Analysis to calculate the possible magnetic space groups [18]. The result of structural refinement shows that the lattice parameters changes little with the increasing of Ti doping, the corresponding parameters are $x = 0.2(a = b = 5.8946 \text{ \AA}, c = 23.2225 \text{ \AA})$, $x = 0.4(a = b = 5.8940 \text{ \AA}, c = 23.2354 \text{ \AA})$, $x = 0.6(a = b = 5.8942533 \text{ \AA}, c = 23.2402 \text{ \AA})$, and $x = 0.8(a = b = 5.8944 \text{ \AA}, c = 23.2361 \text{ \AA})$. The change may origin from that Ti ion occupies the position of Fe ion in the sublattice, and the atomic radius of Ti^{4+} ion (0.0605 nm), is basically the same with that of Fe^{3+} ion (0.0645 nm). The lattice structure distorted due to the replacement of Ti ions, leading to the cell parameters have changed concomitantly. Another parameter characterizing the crystal and magnetic structure is the Bragg position. The structure Bragg position does not change with the Ti doping, which is correspond with the refinement result of lattice parameters. However, the magnetic Bragg position changes with the increase of Ti doping. New Bragg position generated when $x = 0.6$. This probably because that with the increase of Ti, in order to keep the valence conserve, part of Fe^{3+} ions converted into Fe^{2+} ions, generating new Holland factor. In addition, more analysis about structure are shown in the supporting information Figure S1.

Figure 1(b) shows that the primitive cell of $\text{BaFe}_{12}\text{O}_{19}$ is composed of 10 O^{2-} ions layers, because the radii of Ba^{2+} ion (0.142 nm) and O^{2-} ion (0.140 nm) are not much different, Ba^{2+} ion often occupies the position of O^{2-} ion in the oxygen lattice of the

crystal. Therefore, certain amounts of barium ions are contained in the close-packed structure of oxygen ions. Meanwhile, Fe^{3+} ions exist in the interstices of oxygen ions, forming a stable hexahedral structure. In $\text{BaFe}_{12}\text{O}_{19}$, Fe^{3+} ions are distributed over five different positions, named $12k$, $2a$, $2b$, $4f_1$ and $4f_2$ [19]. Magnetic moment orientations of Fe^{3+} in three positions ($12k$, $2a$, $2b$) spin up while those of $4f_1$ and $4f_2$ positions spin down. In order to obtain the information of exact occupation of Ti, the method of neutron diffraction intensity fitting was utilized to explore the occupation probability of Ti as listed in Table 1. The result of fitting shows that Ti tends to occupy the position $2a$, $2b$, and $12k$, in where Fe is spin-up.

Figure 1. (a) Neutron diffraction and corresponding refinement patterns of BFTO- x ($x = 0.2, 0.4, 0.6, 0.8$) ceramics, and (b) the schematic structure of $\text{BaFe}_{12}\text{O}_{19}$.

Table 1. The occupation probability of BFTO- x ceramics.

	$x = 0.2$	$x = 0.4$	$x = 0.6$	$x = 0.8$
2a(Fe)	0.08292	0.08290	0.08083	0.07965
2a(Ti)	0.00041	0.00043	0.00250	0.00368

2b(Fe)	0.07125	0.05427	0.04083	0.02923
2b(Ti)	0.01208	0.02906	0.04250	0.05410
12k(Fe)	0.49582	0.49830	0.49500	0.49114
12k(Ti)	0.00417	0.00170	0.00500	0.00860

The surface morphologies of BFTO- x ceramics are shown in Figure 2. It can be observed that all components perform typical hexagonal plates, and the grain boundary is distinct. The particle size of BFTO- x ceramics varies with the increase of x , where the grain size of BFTO-0.4 about 1 μm is larger than those of other three components. Compared with the solid state sintering method, the grain size of BFTO ceramics prepared by the sol-gel process is smaller, which has an important effect on coercive force [20].

Figure 2. SEM images of BFTO- x ceramics with $x = 0.2$ (a), $x = 0.4$ (b), $x = 0.6$ (c), $x = 0.8$ (d).

3. 2 Effects of titanium substitution on magnetic properties

The magnetic properties of BFTO- x ($x = 0.2, 0.4, 0.6, 0.8$) ceramics are derived

from magnetic hysteresis loops at room temperature in Figure 3. It can be seen that all samples are approaching saturation as the applied field is increased up to 15 kOe. With x increasing from 0.2 to 0.8, the M_s decreases gradually from 31.87 emu/g to 22.13 emu/g, while the change trend of H_c is complicated. The change trend of M_s and H_c is related to the magnetic moment of Fe^{3+} and the occupied position during doping [21].

The replacement from Ti^{4+} ion to the magnetic Fe^{3+} ion ($5 \mu_B$) would reduce the M_s of barium ferrite ceramics since the Ti^{4+} ion is non-magnetic, and M_s exhibits a downward trend with the increase of Ti^{4+} ion doping [22]. It is known that H_c is mainly affected by anisotropic field (H_a) and grain size. That is, the larger the grain size of ceramics, the smaller the H_c . On the other hand, the H_c is proportional to H_a . According to the formula $H_a = 2K_1/M_s$, H_a is proportional to the magnetic crystal anisotropy constant (K_1), and the inverse proportional relationship with M_s [23]. According to the contribution of different lattice positions to K_1 , the 2b position has the greatest effect on K_1 . Therefore, the more components are doped, the greater the effect on H_c . For the components $x = 0.2, 0.6$ and 0.8 , H_c is declining trend with the increase of the doping. Because the changes of the grain size and M_s are weak, the declining trend of the H_c is contributed to the influence of K_1 . The reason why H_c of BFTO-0.4 ceramic sample sharp declines is relatively complex and can be attributed to two aspects. Firstly, the SEM image of BFTO- x ceramics shows that the grain size of BFTO-0.4 ceramic sample is larger than that of other components, so the H_c of BFTO-0.4 ceramics will be smaller. Secondly, the increase of Ti^{4+} doping and the occupied position would have a greater influence on K_1 , which also causes the obvious change of H_c . However, compared to

BFTO-0.2 ceramic sample, the saturation magnetization change of BFTO-0.4 ceramic sample is smaller than that of BFTO-0.2. Therefore, the effect of M_s on H_c can be neglected, and the change of H_c depends mainly on the grain size and K_1 .

Figure 3. Magnetic hysteresis loops (M - H) of samples at room temperature.

Moreover, refined magnetic structure shows that non-collinear magnetic structure exists in BFTO- x ceramics [17,24]. The magnetic moment of primitive cell varies with the doping content of Ti, which is same with experimental data, and the corresponding results was listed in Table 2. The experimental magnetic moment of primitive cell (M_{pc}) was calculated by the following formula 1:

$$M_{pc} (\mu B) = \frac{M_s (\text{emu/g}) \times 1.0783 \times 10^{20}}{N_A} \times M (\text{BFTO}-x) \quad (1)$$

where M_s (emu/g) is the saturation magnetization, M (BFTO- x) is the molar mass of BFTO- x , and N_A is the Avogadro constant. From the result of magnetic refinement, the theoretical M_{pc} fluctuates with the increase of Ti doping, which is consistent with the trend of experimental result.

Table 2. The magnetic moment of BFTO- x ceramics' primitive cell.

	$x = 0.2$	$x = 0.4$	$x = 0.6$	$x = 0.8$
Experimental (μB)	12.056	11.138	10.819	11.731
Theoretical (μB)	17.167	14.421	11.907	14.231

3. 3 Effects of titanium substitution on electromagnetic and microwave absorption properties

The electromagnetic properties of BFTO- x ceramics were shown in Figure 4, which were measured by the air-line method within the 2~18 GHz. According to the figures, the real part of the dielectric permittivity of $x = 0.4$ component can reach 25, while the real part of the dielectric permittivity of other components is smaller to some extent. For the imaginary part of the dielectric permittivity, there are remarkable dielectric relaxation phenomena in all samples, which can contribute to increasing the reflection loss of the absorbing sample. In Figure 4(d), the apparent resonance phenomenon can be observed. It is necessary to note that the natural resonance frequency of the component $x = 0.2$ is larger than 18 GHz, while the natural resonance frequency of the other three components at a frequency range of 6~14 GHz illustrated in the inset of Figure 4(d) is within the measured frequency range.

Figure 4. Electromagnetic parameters of PVA mixed BFTO- x ceramics: real parts (a) and imaginary parts (b) of the complex permittivity, and real parts (c) and imaginary parts (d) of the complex permeability.

According to the formula $f_r = 1.4gH_a$, the natural resonant frequency is correlated with the magnetic anisotropy field (H_a) and the ceramic sample and the Holland factor (g) [25]. Due to the low anisotropy field of BFTO-0.4 ceramic, the natural resonant frequency of the $x = 0.4$ sample is the lowest and appears near 8 GHz, while double resonance peaks were obtained in $x = 0.6$ and $x = 0.8$ components. The high-valence ionic Ti^{4+} doping, which destroys the valence equilibrium of barium ferrite, will produce a new g factor, and the appearance of double resonance peaks shows that there are two g factors in these samples. With the increase of Ti^{4+} doping, the anisotropy field decreases, and the natural resonance frequency moves to the lower frequency range. Therefore, the appearance of double resonance peak is advantageous to obtain the larger bandwidth. More evidence can be found in Figure S2, which shows the dielectric and magnetic loss of PVA mixed BFTO- x ceramics. The large dielectric and magnetic loss was obtained in $x = 0.2$ sample, which indicates a large reflection loss. The loss curves of $x = 0.6$ and 0.8 have evident fluctuation, and, could get large bandwidth.

The reflection loss (RL) of PVA mixed BFTO- x ceramics can be calculated from the measured electromagnetic parameters [26], as shown in Figure 5. The four components of PVA mixed BFTO- x ceramics have obtained a large reflection loss. The

maximum reflection loss of -44.9 dB that means the absorption of electromagnetic waves can reach 99.99% was obtained in the $x = 0.2$ sample, and the thickness is extreme thin, only 1.8 mm. The absorption of electromagnetic waves can also reach 90% in the other three components. The apparent double absorption peaks appear in Figure 5(c) and (d), which may be origin from the presence of more than one of the Hollander factors in the wave-absorbing material that can benefit for widening the bandwidth of the material. Reflection loss and bandwidth are two important indexes to evaluate the performance of absorbing materials, and high-loss and large-bandwidth materials can be used in a wider range of applications [27].

Figure 5. RL curves of PVA mixed BFTO- x ceramics in the frequency range of 2–18 GHz: $x = 0.2$ (a), $x = 0.4$ (b), $x = 0.6$ (c), and $x = 0.8$ (d).

Figure 6 shows the 3D RL contour plots of BFTO- x ceramics. As can be seen, all samples perform wide bandwidth in the specific frequency and thickness. Although the

absorption of electromagnetic waves by this material is not the best, we can find that with the doping of Ti^{4+} ions, the absorbing properties of M-type barium ferrite have changed significantly. The absorbing characteristics and bandwidth variation in the high frequency band are obvious. This change is mainly due to the transition of trivalent Fe ions to divalent Fe ions, which causes a significant change in the magnetic properties of the material and broadens the absorbing effect at high frequencies [28].

Figure 6. The 3D RL contour plots of BFTO- x ceramics (a) $x = 0.2$, (b) $x = 0.4$, (c) $x = 0.6$, and (d) $x = 0.8$.

Figure 7(a) shows the relationship between bandwidth and reflection loss of BFTO- x samples, and the maximum reflection loss and bandwidth are listed in Table 3. For the $x = 0.2$, the greatest loss can be obtained at the thickness of 1.8 mm, and the

bandwidth can reach to 5.28 GHz at 2 mm when the reflection loss is less than -10 dB, while the bandwidth of other three components is about 3 GHz.

Figure 7. (a) The maximum RL and the corresponding bandwidth over -10 dB of each component, and (b) the attenuation constant of BNZFO- x ceramics.

Table 3. The maximum RL and the corresponding bandwidth over -10 dB of PVA-mixed BNZFO- x ceramics.

Component	Thickness (mm)	Maximum RL (position)	Bandwidth (< -10 dB)
$x = 0.2$	1.8	-44.93 dB (17.28 GHz)	3.28 GHz
$x = 0.4$	1.5	-17.1 dB (11.92 GHz)	3.28 GHz
$x = 0.6$	1.7	-20.3 dB (11.6 GHz)	2.48 GHz
$x = 0.8$	1.7	-19.6 dB (15.92 GHz)	3.76 GHz

In the ion-doped barium ferrite ceramic, the strong absorbing ability originates from the high attenuation constant [29]. The attenuation constant is expressed by equation 2

$$\alpha = \left(\frac{\sqrt{2}\pi f}{c} \right) \sqrt{(\mu''\varepsilon'' - \mu'\varepsilon') + \sqrt{(\mu''\varepsilon'' - \mu'\varepsilon')^2 + (\varepsilon'\mu'' + \varepsilon''\mu')^2}} \quad (2)$$

Herein, f is the microwave frequency and c is the velocity of light. According to the equation, the attenuation constants of the four components of BFTO- x ceramics can

be calculated, as shown in the Figure 8(b). Within the measuring frequency range of 2~18 GHz, four components have a large attenuation constant, wherein the attenuation constant of $x = 0.4$ component is the largest, and is 350. The variation trend of attenuation constants is similar to that of the imaginary part of magnetic permeability, there is a double resonance peak in $x = 0.6$ and 0.8 components. Therefore, the dielectric constant and permeability are the two parameters that determine the microwave absorbing performance, and magnetic and dielectric loss are critical to improve the attenuation of materials to electromagnetic waves.

Besides, frequency modulation is also a standard for measuring the overall performance of absorbing materials. As can be seen from Figure 4-7, the excellent frequency modulation can be obtained in the four components of BFTO- x ceramics. The reflection loss peaks of the $x = 0.2$ component are reduced from near 17 GHz to 6 GHz with varying thickness, and the frequency modulation range covers the 69% of the measuring frequency range, enabling the control of a wide range of absorption frequencies. The frequency regulation ranges of $x = 0.4$, 0.6 and 0.8 components are 4~12 GHz, 5~18 GHz and 6~18 GHz, respectively. The maximum reflection loss peaks of the four components also moved with the Ti^{4+} doping content, varying from 18 GHz ($x = 0.8$) to 4 GHz ($x = 0.4$), which covers 81% of the investigated frequency. In conclusion, all of the four components of BFTO- x ceramics show excellent frequency modulation ability.

4 Conclusion

The hexagonal sheet like $\text{BaTi}_x\text{Fe}_{12-x}\text{O}_{19}$ ($x = 0.2, 0.4, 0.6, 0.8$) ceramics were

synthesized by a modified sol-gel method. Through the refined analysis of neutron diffraction, Ti^{4+} tends to occupy the position 2a, 2b, and 12k of the structure. Saturation magnetization decreases gradually with the increase of Ti^{4+} doping, but the change of the coercive force is complex under the synergy of the changed grain size and the magnetic crystal anisotropy field. The excellent microwave absorption performance - 44.9 dB with board bandwidth in the $x = 0.2$ component can be attributed to the double resonance peak induced by high valent doping of Ti^{4+} . Meanwhile, the reflection loss peak position of the $x = 0.6$ component can be adjusted from 18 GHz to 5 GHz and the remaining components cover a frequency adjusted range of up to 50%, which have a significant potential application value in microwave absorption field.

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Reference

- [1] P. Toneguzzo, G. Viau, O. Acher, *et al.* Monodisperse ferromagnetic particles for microwave applications. *Adv. Mater* 1998, **10**: 1032-1035.
- [2] R. Che, L. Peng, X. Duan, *et al.* Microwave absorption enhancement and complex permittivity and permeability of Fe encapsulated within carbon nanotubes. *Adv. Mater* 2004, **16**: 401-405.
- [3] Y. Ding, L. Zhang, Q. Liao, *et al.* Electromagnetic wave absorption in reduced graphene oxide functionalized with $\text{Fe}_3\text{O}_4/\text{Fe}$ nanorings. *Nano. Res* 2016, **9**: 2018-

2025.

- [4] Y. Li, Y. Zhao, X. Lu, *et al.* Self-healing superhydrophobic polyvinylidene fluoride/Fe₃O₄@polypyrrole fiber with core–sheath structures for superior microwave absorption. *Nano. Res* 2016, **9**: 2034-2045.
- [5] Ye, X., Chen, Z., Ai, S. *et al.* Porous SiC/melamine-derived carbon foam frameworks with excellent electromagnetic wave absorbing capacity. *J. Adv Ceram* 2019, **8**: 479–488.
- [6] S. Chiu, H. Yu, Y. Li, *et al.* High electromagnetic wave absorption performance of silicon carbide nanowires in the gigahertz range. *J. Phys. Chem. C* 2010, **114**: 1947-1952.
- [7] P. Saini, M. Arora, G. Gupta, *et al.* High permittivity polyaniline–barium titanate nanocomposites with excellent electromagnetic interference shielding response. *Nanoscale* 2013, **5**: 4330-4336.
- [8] J. Jia, C. Liu, N. Ma, *et al.* Exchange coupling controlled ferrite with dual magnetic resonance and broad frequency bandwidth in microwave absorption. *Sci. Technol. Adv. Mat* 2013, **14**: 045002.
- [9] R. C. Pullar. Hexagonal ferrites: A review of the synthesis, properties and applications of hexaferrite ceramics. *Prog. Mater. Sci* 2012, **57**: 1191-1334.
- [10] S. V. Trukhanov, A. V. Trukhanov, V. G. Kostishyn, *et al.* Magnetic, dielectric and microwave properties of the BaFe_{12-x}Ga_xO₁₉ ($x \leq 1.2$) solid solutions at room temperature. *J. Magn. Magn. Mater* 2017, **442**: 300-310.
- [11] Xu, J., Lu, Q., Lin, J. *et al.* Enhanced ferro-/piezoelectric properties of tape-casting-

derived Er³⁺-doped Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O₃ optoelectronic thick films. *J. Adv Ceram* 2020, **6**: 693-702

- [12] Kumar, Y., Yadav, K.L., Shah, J. *et al.* Investigation of magnetoelectric effect in lead free K_{0.5}Na_{0.5}NbO₃-BaFe₁₂O₁₉ novel composite system. *J. Adv Ceram* 2019, **8**: 333–344.
- [13] J. Li, S. He, K.Z. Shi, *et al.* Coexistence of broad-bandwidth and strong microwave absorption in Co²⁺-Zr⁴⁺ co-doped barium ferrite ceramics. *Ceram. Int* 2018, **44**: 6953-6958.
- [14] T. Tsutaoka, N. Koga. Magnetic phase transitions in substituted barium ferrites BaFe_{12-x}(Ti_{0.5}Co_{0.5})_xO₁₉ (x=0–5). *J. Magn. Magn. Mater* 2013, **325**: 36-41.
- [15] C. Liu, Y. Zhang, Y. Tang, *et al.* The tunable magnetic and microwave absorption properties of the Nb⁵⁺-Ni²⁺ co-doped M-type barium ferrite. *J. Mater. Chem. C* 2017, **5**: 3461-3472.
- [16] C. Liu, Y. Chen, Y. Yue, *et al.* Formation of BaFe_{12-x}Nb_xO₁₉ and its high electromagnetic wave absorption properties in millimeter wave frequency range. *J. Am. Ceram. Soc* 2017, **100**: 3999-4010.
- [17] J. Rodríguez-Carvajal. Recent advances in magnetic structure determination by neutron powder diffraction. *Physica B* 1993, **192**: 55-69.
- [18] A. S. Wills. A new protocol for the determination of magnetic structures using simulated annealing and representational analysis (SARAh). *Physica B* 2000, **276**: 680-681.
- [19] Y. Shao, F. Huang, X. Xu, *et al.* Multi-susceptible single-phase BaAl_xFe_{12-x}O₁₉

ceramics with both improved magnetic and ferroelectric properties. *Appl. Phys. Lett* 2019, **114**: 242902.

- [20] K. Watanabe, J. Kawabe. Growth and characterization of minute $\text{BaFe}_{12-2x}\text{Ti}_x\text{Co}_x\text{O}_{19}$ crystals from high-temperature solution. *J. Mater. Chem* 1997, **7**:1797-1800.
- [21] D. A. Vinnik, D. A. Zhrebtssov, L. S. Mashkovtseva, *et al.* Ti-substituted $\text{BaFe}_{12}\text{O}_{19}$ single crystal growth and characterization. *Cryst. Growth Des* 2014, **14**: 5834-5839.
- [22] Y. Cheng, X. Ren. Permeability and electromagnetic wave absorption properties of sintered barium hexaferrites with substitution of $\text{Co}^{2+}-\text{Zr}^{4+}$. *J. Mater. Sci. Mater. El* 2016, **27**: 772-775.
- [23] C. Singh, N. S. Bindra, I. S. Hudiara, *et al.* The effect of Co and Zr substitution on dc magnetic properties of Ba–Sr ferrite. *J. Alloys. Compd* 2008, **464**: 429-433.
- [24] H. Zhang, C. Rong, X. Du, *et al.* Investigation on the coercivity and remanence of single-phase nanocrystalline permanent magnets by micromagnetic finite-element method. *J. Magn. Magn. Mater* 2004, **278**: 127-137.
- [25] S. P. Gairola, V. Verma, A. Singh, *et al.* Modified composition of barium ferrite to act as a microwave absorber in X-band frequencies. *Solid. State. Commun* 2010, **150**: 147-151.
- [26] J. R. Liu, M. Itoh, K. Machida. Electromagnetic wave absorption properties of α - $\text{Fe}/\text{Fe}_3\text{B}/\text{Y}_2\text{O}_3$ nanocomposites in gigahertz range. *Appl. Phys. Lett* 2003, **83**: 4017-4019.
- [27] C. M. Watts, X. Liu, W. J. Padilla. Metamaterial electromagnetic wave absorbers.

Adv. Mater. 2012, **24**: OP181-OP181.

- [28] C. Liu, Q. Xu, Y. Tang, *et al.* Zr⁴⁺ doping-controlled permittivity and permeability of BaFe_{12-x}Zr_xO₁₉ and the extraordinary EM absorption power in the millimeter wavelength frequency range. *J. Mater. Chem. C* 2016, **4**: 9532-9543.
- [29] J. Huo, L. Wang, H. Yu. Polymeric nanocomposites for electromagnetic wave absorption. *J. Mater. Sci* 2009, **44**: 3917-3927.

Figures

Figure 1

(a) Neutron diffraction and corresponding refinement patterns of BFTO-x (x = 0.2, 0.4, 0.6, 0.8) ceramics, and (b) the schematic structure of BaFe₁₂O₁₉.

Figure 2

SEM images of BFTO-x ceramics with $x = 0.2$ (a), $x = 0.4$ (b), $x = 0.6$ (c), $x = 0.8$ (d).

Figure 3

Magnetic hysteresis loops (M-H) of samples at room temperature.

Figure 4

Electromagnetic parameters of PVA mixed BFTO-x ceramics: real parts (a) and imaginary parts (b) of the complex permittivity, and real parts (c) and imaginary parts (d) of the complex permeability.

Figure 5

RL curves of PVA mixed BFTO- x ceramics in the frequency range of 2–18 GHz: $x = 0.2$ (a), $x = 0.4$ (b), $x = 0.6$ (c), and $x = 0.8$ (d).

Figure 6

The 3D RL contour plots of BFTO-x ceramics (a) $x = 0.2$, (b) $x = 0.4$, (c) $x = 0.6$, and (d) $x = 0.8$.

Figure 7

(a) The maximum RL and the corresponding bandwidth over -10 dB of each component, and (b) the attenuation constant of BNZFO-x ceramics.

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