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Structure and electromagnetic behavior of $BaFe_{12-2x}(Ni_{0.8}Ti_{0.7})_xO_{19-0.8x}$ in the 2–12 GHz frequency range

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ABSTRACT

The non-stoichiometric $Ni^{2+}Ti^{4+}$ substituted barium ferrites have been prepared. The structure, complex permeability, complex permittivity and microwave absorption of $BaFe_{12-2x}(Ni_{0.8}Ti_{0.7})_xO_{19-0.8x}$ with $0 \leq x \leq 2.0$ were measured with X-ray diffraction (XRD), Mössbauer spectroscopy and microwave vector network analyzer. The XRD results show that a single-phase M-type barium hexaferrite can be obtained for $x \leq 1.2$. The microwave measurement results show that the non-stoichiometric $Ni^{2+}Ti^{4+}$ substitution has weak effect on the μ' and ε'', but can significantly affect the μ'', ε' and microwave absorption properties of barium ferrites in the frequency range from 2.0 to 12.0 GHz. With increasing substitution, the peak values of the imaginary part of complex permeability increase first, then decrease slimly, with the maximum of 0.4 for $x = 1.2$. The variation of absorption loss has been studied as a function of the frequency and the degree of substitution x. The maximum loss reaches −12.6 dB when the substitution amount of the $Ni^{2+}Ti^{4+}$ ions is 0.8. The peak positions of the maximum loss and imaginary part of complex permeability shift into lower frequency band. The substitution or vacancy content is possibly responsible for this microwave response behavior of the non-stoichiometric $Ni^{2+}Ti^{4+}$ substituted barium ferrites.

1. Introduction

With the rapid development of the wireless and telecom/datacom industries, the electromagnetic wave pollution has become a serious problem. Electromagnetic wave absorbers are becoming quite indispensable to preventing the electromagnetic pollution of the environment. Two kinds of magnetic absorbers, including magnetic metal materials and ferrite materials, have been developed for the megahertz to gigahertz frequency range microwave absorbers. In the development of ferrite-based microwave absorbers, the spinel ferrites have been most widely utilized as microwave absorbing materials. But it is difficult to use at frequency over 2 GHz due to Snoek's limit [1–3]. Compared to spinel ferrites with a cubic crystallographic structure, the hexagonal ferrites with a magnetoplumbite structure, have a higher resonance frequency and a higher microwave permeability, and therefore are more useful in the higher frequency range. Many works have been reported on hexaferrite barium ferrites for use as microwave absorption materials. Currently, the studies focused on modifying the electric magnetic parameters and resonance frequency of ferrites based on doped small amounts of oxides [4–8]. In addition, the substitution of other ions for some Fe^{3+} ions is also an effective method to vary the magnetic properties and electrical properties of ferrites [9–11]. In the hexaferrite family, M-type barium ferrite (MBF) is of great interest for use as microwave absorbers. Its crystal structure can be divided in several blocks according to the stacking from closely packed oxygen ions. The S block contains two oxygen layers forming a spinel structure and R block is a three oxygen layer block, containing the barium ion. It has a collinear five sublattice magnetic structure (12k, $4f_2$, 2a, $4f_1$, 2b), the Fe^{3+} ions are arranged in five different kinds of interstitial sites, three of the Fe^{3+} sites are octahedral (12k, $4f_2$, 2a), one is tetrahedral ($4f_1$), and one is trigonal bipyramidal (2b). After the Fe^{3+} or Ba^{2+} ions are substituted with other trivalent elements or a mixture of tetravalent and divalent elements, the saturation magnetization, coercivity, anisotropy constant and ferromagnetic resonant frequency of MBF can be changed significantly. In previous studies, the MBF samples were usually prepared with stoichiometric composition, i.e. $BaFe_{12}O_{19}$, the substitution of non-magnetic cations may lead to decrease of magnetic properties and especially specific saturation magnetization, for example, the magnetizations reduced by 23%, for $x = 0–0.8$, for the $Co^{2+}Zr^{4+}$ substituted MBF [12]. Recently, some interesting work has been done concerning about the non-stoichiometric barium hexaferrites [13–16]. The study reveals that

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Table 1
Compositions and labels of $BaFe_{12-2x}(Ni_{0.8}Ti_{0.7})_xO_{19-0.8x}$ samples.

	Sample label					
	a	b	c	d	e	f
Composition (x)	0	0.4	0.8	1.2	1.6	2.0
Vacancy in Fe site	0	0.2	0.4	0.6	0.8	1.0
% vacancy in Fe site	0	1.67	3.33	5.0	6.67	8.33

non-stoichiometric M-type hexaferrites may have excellent magnetic properties and the lower thermal expansion coefficients compared to stoichiometric M-type barium hexaferrite. The presence of vacancies possibly facilitates diffusion of ions, affects the splitting of the crystal field states, and thereby might be profitable for the improvement of microwave absorption properties of M-type ferrite-based absorber, however, there is little published information relating the microwave absorption behavior of this material. In this work, we prepared the single phase non-stoichiometric substituted M-type hexaferrites $BaFe_{12-2x}(Ni_{0.8}Ti_{0.7})_xO_{19-0.8x}$ (x varies from 0 to 2.0 in steps of 0.4) employing a modified sugar-nitrate method, and investigated the effects of the $Ni^{2+}Ti^{4+}$ substituted MBF. The crystalline structure, microwave absorption properties, complex permittivity and complex permeability of the $Ni^{2+}Ti^{4+}$ substituted non-stoichiometric barium ferrites were studied from the viewpoint of microwave absorbing.

2. Experimental

The hexaferrites with composition $BaFe_{12-2x}(Ni_{0.8}Ti_{0.7})_xO_{19-0.8x}$ were prepared with a modified sugar-nitrate method [17]. The raw materials utilized in the present paper were barium nitrate, iron nitrate, nickel nitrate, $Ti(OC_4H_9)_4$ and sugar. The precursor solution was evaporated at 80 °C until a gel formed. It was dried at 120 °C and turned into a dry gel. The dry gel was pre-sintered at 450 °C for 5 h, and finally was calcined at 950 °C for 1 h to obtain $BaFe_{12-2x}(Ni_{0.8}Ti_{0.7})_xO_{19-0.8x}$ powders, the nominal compositions, the vacancy in the Fe site and the sample labels are given in Table 1. The purity of phases was checked by X-ray diffraction (XRD) and crystallite sizes were determined from the line broadening of the reflections using the Scherrer formulas. It was performed on a Bruker-AXS D8 advanced diffractometer with Cu Kα radiation in the 2θ range from 20° to 80° with a step width of 0.02°.

The lattice parameters a and c are calculated by the following formula:

$$d = \frac{1}{\sqrt{((4(h^2+hk+k^2))/3a^2)+(l^2/c^2)}} \qquad (1)$$

where d is the crystal face distance and ($h\,k\,l$) is the Miller indices.

The cell volumes (V) of $BaFe_{12-2x}(Ni_{0.8}Ti_{0.7})_xO_{19-0.8x}$ powders were calculated with the formulae $V = \sqrt{3} \times a^2 \times c/2$, where a and c are the unit length of a-axis and c-axis, respectively.

The particle size was determined from the XRD lines broadening together with the Scherrer formula $D = k\lambda/\beta cos\theta$, where λ is the X-ray wavelength, β is the half-peak width, θ is the Bragg angle, and $k = 0.94$ [18].

Mössbauer spectroscopy was used in order to obtain the hyperfine parameters of the powders. Mössbauer investigations were carried out by use of transmission spectrometer arranged in vertical geometry, $^{57}Co(Pd)$ source of gamma radiation and a drive system working in a constant acceleration mode. The velocity scale was calibrated with a pure iron foil.

A network analyzer (Agilent Technologies, E8363A) was employed to determine the values of the complex permittivity ($\varepsilon_r = \varepsilon' - j\varepsilon''$) and permeability ($\mu_r = \mu' - j\mu''$) at the frequency range of 2–12 GHz by using coaxial reflection/transmission technique. For this, the samples were prepared with 80% (weight percentage) ferrite loading in epoxy resin, and toroidal shaped samples of 3.0 mm inner diameter, 7.0 mm outer diameter and 3–4 mm length were prepared. The test samples of toroidal shape were tightly inserted into the standard coaxial line, the measured values of the complex permittivity ($\varepsilon_r = \varepsilon' - j\varepsilon''$) and permeability ($\mu_r = \mu' - j\mu''$) were used to determine microwave absorption [19].

3. Results and discussion

3.1. XRD and Mössbauer spectra of $BaFe_{12-2x}(Ni_{0.8}Ti_{0.7})_xO_{19-0.8x}$

The XRD patterns are shown in Fig. 1(a–f) for samples of $BaFe_{12-2x}(Ni_{0.8}Ti_{0.7})_xO_{19-0.8x}$ powders with $x = 0$–2.0. When $x \leq 1.2$, the samples show a single-phase non-stoichiometric $Ni^{2+}Ti^{4+}$ substituted M-type hexaferrite (JCPDS, No. 84-0757). But when x reaches 1.6, it can be seen that some diffraction peaks of non-magnetic phase such as Fe_2O_3 appears in Fig. 1(e). After x is further increased to 2.0, the final powders contain hexaferrite barium ferrite, a little Fe_2O_3 and $BaFe_2O_4$ shown in Fig. 1(f). It should be noted that the amount of vacancy at the Fe sites is as high as 5.0% in the composition of $x = 1.2$, and yet the crystal structure does not break down nor do any other phases occur, indicating that the Ni^{2+} and Ti^{4+} ions can enter the lattice and do not result in the collapse of the crystal structure of hexaferrite barium ferrite within the substitution range of $x < 1.6$.

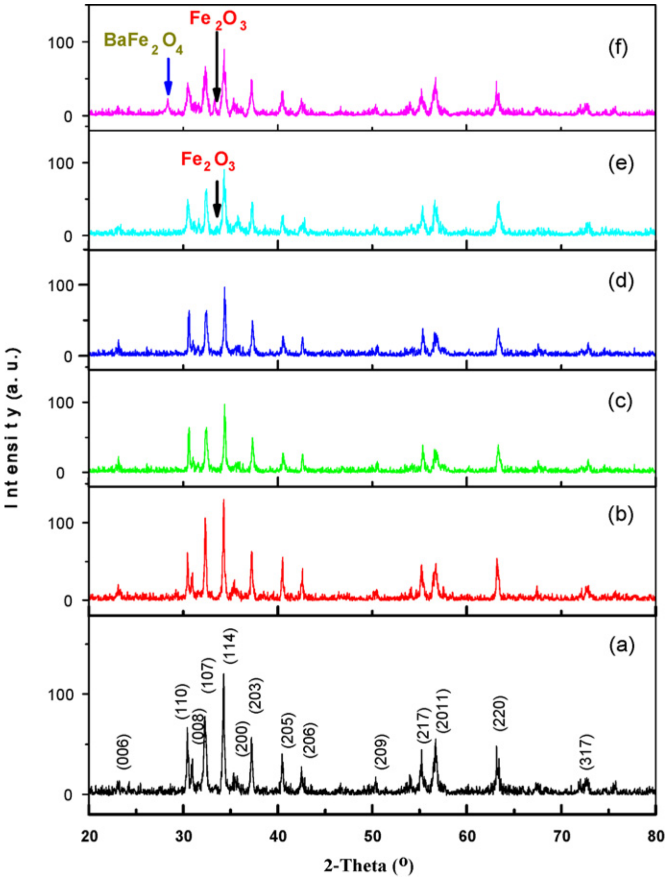

Fig. 1. XRD patterns of $BaFe_{12-2x}(Ni_{0.8}Ti_{0.7})_xO_{19-0.8x}$ powders (a: $x = 0$; b: $x = 0.4$; c: $x = 0.8$; d: $x = 1.2$; e: $x = 1.6$; f: $x = 2.0$).

The structural parameters and the size of particles are tabulated in Table 2. We can see that the “a” parameter increases little, the “c” parameter increases from 23.2386 to 23.3220 Å and the ratio of c/a increases from 3.9463 to 3.9590 with increasing the substitution value of x. The variations of a-axis and c-axis lengths may be explained in terms of the structure of the M-type hexaferrite. As described elsewhere, the magnetoplumbite crystal structure of $BaFe_{12}O_{19}$ (space group $P63/mmc$) consists of a close-packed stacking of oxygen or barium–oxygen layers, and the Fe^{3+} cations are distributed within three kinds of octahedral sites, one tetrahedral site and one bipyramid site. Because in a unit cell, 10 oxygen planes are staked along the c-axis, the Fe^{3+}, Ni^{2+} and Ti^{4+} ions occupy interstitial positions, whereas along the a-axis, there are only two oxygen atoms. Due to the relatively big ionic radii of Ni^{2+} and Ti^{4+} over that of Fe^{3+} ($R_{Ni^{2+}} = 0.069$ nm, $R_{Ti^{4+}} = 0.068$ nm and $R_{Fe^{3+}} = 0.064$ nm) [20], it is also shown that the crystal structure of barium ferrite was expanded after being substituted. This suggests that