Journal of Magnetism and Magnetic Materials

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5.1	2.993
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ISSN: 0304-8853

Journal of Magnetism and Magnetic Materials 456 (2018) 288–291

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Research articles

Significant reduction of saturation magnetization and microwave-reflection loss in barium-natural ferrite via Nd^{3+} substitution

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ARTICLE INFO

Article history:
Received 28 October 2017
Received in revised form 4 February 2018
Accepted 16 February 2018
Available online 16 February 2018

Keywords:
Neodymium
Barium-natural ferrite
Structure
Magnetic properties
Microwave
Reflection loss

ABSTRACT

To minimize the signal degradation, many electronic devices require efficient microwave absorbers with very low reflection-losses within the X-band. We prepared a series of trivalent neodymium-ion (Nd^{3+}) substituted barium-natural ferrite using a modified solid-state reaction method. The effect of the Nd^{3+}-ion content on the structure, surface morphology, magnetic properties, and microwave reflection loss was studied. The composites were characterized using X-ray diffraction, a vibrating sample magnetometer, scanning electron microscopy, and a vector network analyzer. The XRD patterns of the sample without Nd^{3+} reveal the presence of $BaFe_{12}O_{19}$ (hexagonal) and $BaFe_2O_4$ (rhombohedral) phases. Furthermore, a new hexagonal crystal phase of $Ba_6Nd_2Fe_4O_{15}$ appeared after substituting Nd^{3+}. The average size of the prepared barium-natural ferrite particles was estimated to be between 0.4 and 0.8 μm. Both saturation magnetization and microwave reflection losses of these barium-ferrites were significantly reduced by increasing the Nd^{3+} content.

1. Introduction

The reduction of damage due to electromagnetic interference and signal degradation in microwave-based electric devices is a critical issue. Researchers around the world have studied advanced magnetic materials that may be suitable as electromagnetic-wave absorbers, especially for the microwave range [1–8]. Such materials can attenuate and dissipate unwanted electromagnetic wave energy into heat through magnetic and dielectric losses [8,9]. Barium hexaferrite, thanks to its high uniaxial magnetic anisotropy, is a promising microwave absorber [2–4,10,11]. It is also desirable to maximize the ability of these ferrite materials to absorb microwaves in the GHz frequency range.

Previous studies revealed that by substituting divalent or trivalent ions into ferrite systems, it is possible to alter natural resonance-frequencies, permeability, permittivity, saturation magnetization, and the magnetic-field anisotropy [12]. These modifications can improve the effects of electromagnetic interference. The excellent relaxation properties of doped rare-earth ions were also used to modify the magnetic properties and microwave absorption in barium hexaferrite [2,12–16]. In addition, rare-earth ion doped barium hexaferrite with a low coercive field and tiny saturation magnetization can be used to increase microwave absorption [6,16,17]. Inspired by these discoveries, we attempted to reduce both the coercive field and saturation magnetization of barium-natural ferrite, and further enhance the absorption of microwaves.

In this work, the Fe^{3+} ions of a barium hexaferrite system were substituted by Nd^{3+} ions (of variable content) to produce a new barium-natural ferrite (BNF) with improved microwave absorption and magnetic behavior. We chose trivalent Nd^{3+} ions as substituents because of their hexagonal crystal structure and common relaxation properties. The samples were prepared using a modified solid-state reaction and then characterized. We evaluated the Nd^{3+} ions assisted modifications concerning structure, surface morphology, magnetic properties, and microwave reflection loss within the x-band. The results were analyzed, compared, and discussed.

2. Experimental

Four BNFs were prepared using a modified solid-state reaction, where the sol-gel technique was combined with a conventional solid-state reaction. Commercially available analytical grade powder of $Ba(NO_3)_2$ (from Merck, 99% purity), Nd_2O_3 (from Sigma Aldrich, 99%), and natural Fe_3O_4 were used as starting materials to prepare the composites. Nitric acid, HNO_3, was added to natural Fe_3O_4 as well as Nd_2O_3 to obtain $Fe(NO_3)_3$ and $Nd(NO_3)_3$, respectively. A liquid precursor, $(1-x)$ $Ba(NO_3)_2$: x $Nd(NO_3)_3$: 12 Fe

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https://doi.org/10.1016/j.jmmm.2018.02.050
0304-8853/

$(NO_3)_3$, with $0 \le x \le 0.3$ mol, was thoroughly stirred with a magnetic stirrer. Polyethylene glycol was added, during stirring, until a sol formed. The sol was mixed with ethanol and stirred (for 90 min) until a gel formed. The gel was calcined at 350 °C to obtain BNF powder. The powder was compacted and sintered at 1100 °C to produce BNF pellets. The pellets were designated as BNF0, BNF1, BNF2, and BNF3 according to their Nd^{3+} ion content (x) of 0, 0.1, 0.2, and 0.3 mol, respectively. For additional characterizations, some pellets were crushed into fine powder and encapsulated between a pair of transparent plastic sheets (2.5 cm × 1.5 cm) with a thickness of 1 mm [16].

Like in other studies [16,18], a scanning electron microscope (SEM, JSM-6390A) was used to analyze both the surface morphology and microstructure of the synthesized BNFs. The crystalline phases of the BNFs were recorded using an X-ray diffractometer (XRD, Philips PW1710) equipped with $Cu - K\alpha$ radiation (λ = 1.541874 Å). The magnetic properties of the BNFs were measured using a vibrating sample magnetometer (VSM, Oxford 1.2H). The microwave reflection loss (R_L) of the BNFs was evaluated for a frequency range of 8–12 GHz using a vector network analyzer (VNA, Advantest R3770). We used the Transmission/Reflection Line (TRL) method to determine the scattering (S) parameters. It consisted of reflection coefficients (S_{11}, and S_{22}) and transmission coefficients (S_{12} and S_{21}). An encapsulated sample (Material Under Test or MUT) was placed on a waveguide in the coaxial position. Measurements were conducted on two complex ports of scattering parameters via a VNA device to obtain the frequency dependent values of reflection loss (R_L). The measured values of S_{22} and S_{12} were not used because they matched identically with the values of S_{11} and S_{21}, respectively. The values of R_L were evaluated using the expression:

$$R_L = 20 \log |S_{11}| \tag{1}$$

with $S_{11} = S_{11(real)} + jS_{11(imaginer)}$. All characterizations were performed at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of the as-prepared BNFs with and without Nd^{3+} substitution. The XRD pattern of the sample without Nd^{3+} replacement (BNF0) shows several sharp peaks, which can be attributed to the major and minor crystalline phases of $BaFe_{12}O_{19}$ and $BaFe_2O_4$, respectively. The sharp peak at 34.478° is ascribed to the hexagonal crystal structure of $BaFe_{12}O_{19}$, which matches the ICDD number 01-078-0133. The intense peak at 33.458° is attributed to the orthorhombic crystal structure of $BaFe_2O_4$ that is consistent with the ICDD numbers 01-070-2468 and 01-077-2337. The $BaFe_2O_4$ phase suggests a gradual conversion to the $BaFe_{12}O_{19}$ phase. The XRD pattern of BNF1 (with 0.1 mol of $Nd(NO_3)_3$) indicates the emergence of two new phases, including $Ba_6Nd_2Fe_4O_{15}$ and α-Fe_2O_3, together with the dominant pre-existing phases in BNF0. The sharp XRD peak centered at 38.353° is attributed to the hexagonal crystal structure of $Ba_6Nd_2Fe_4O_{15}$ (ICDD number 01-079-2141) with the lattice parameters $a = b$ = 11.815 Å and c = 7.078 Å. The peaks at 24.35°, 33.34°, 35.83°, 49.63°, 54.27°, 62.63°, and 64.22° were allocated to the rhombohedral crystal structure of α-Fe_2O_3 with the lattice parameters $a = b = c$ = 5.424 Å and the ICDD number 01-073-2234. The appearance of the α-Fe_2O_3 phase is due to an incomplete chemical reaction caused by an insufficient amount of Nd^{3+} ions in the composition. Adding more $Nd(NO_3)_3$, for samples BNF2 and BNF3, led to more XRD peaks, which correspond to the hexagonal crystal structure of $Ba_6Nd_2Fe_4O_{15}$ where the peaks of α-Fe_2O_3 phase disappeared utterly. However, the crystal structure of $Ba_6Nd_2Fe_4O_{15}$ is similar to that of $BaFe_{12}O_{19}$ with a crystalline grain size between 29.20 and 54.98 nm.

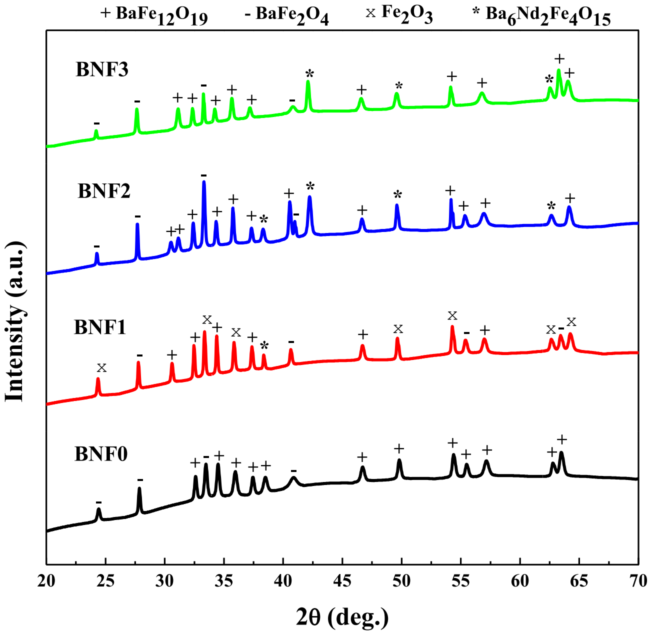

Fig. 1. XRD patterns of all four as-synthesized BNFs.

Fig. 2 presents the SEM images of the hexagonal BNFs, where the surface morphology consists of rough and porous microstructures. The overall morphology and particle size distribution in the BNFs are affected by the substitution of Nd^{3+} ions. For higher Nd^{3+} contents, the microstructure is more elongated, interconnected, and increasingly porous. The mean size of the BNF particles is about 0.4–0.8 μm. The particles appear separated due to the presence of polyethylene glycol. Sintering at 1100 °C could have caused sudden hardening of the composite and the trapping of polyethylene glycol between the BNF particles instead of its evaporation. The observed enhanced roughness and porosity facilitate both the modification of the magnetic properties and increased microwave-reflection loss.

Fig. 3 illustrates the room-temperature magnetic hysteresis loops for all four BNFs. All BNFs show almost similar magnetic properties with a remanent magnetization (M_r) of about 2.5 emu/g and a low coercive field (H_c) of approximately 400 Oe. The saturation magnetization (M_s) decreases significantly after the incorporation of Nd^{3+} ions. This significant reduction of M_s is ascribed to the substitution of Fe^{3+} ions by Nd^{3+} ions at the octahedral site lead to a change in the zero fields ferromagnetic resonance frequency f and magnetic losses μ'' [2,12,19]. In addition, the fraction of a soft magnetic-phase ($Ba_6Nd_2Fe_4O_{15}$) in the ferrite increases the values for M_s for the proposed ferrites saturates at $H_A \approx 20{,}000$ Oe and decreases for higher Nd^{3+} content. BNF3 reveals the lowest M_s ($\approx$9.0 emu/g). It means that the applied magnetic field can quickly move the magnetic domain boundaries in BNF3 to be a single domain, which aligns with the direction of the field.

Fig. 4 depicts the microwave-frequency-dependent reflection-loss (R_L) of all synthesized barium-natural ferrites. Values of reflection loss characterized the ability of the barium hexaferrite to absorb microwaves. BNF0 and BNF1 show similar reflection loss patterns with two weak absorption bands and an average R_L of about -10 dB. BNF2 and BNF3, on the other hand, display two prominent absorption bands around 8.5 and 10.0 GHz, which are accompanied by a significant shift for a higher Nd^{3+} ions content. In other words, substituting Nd^{3+} ions into the lattice could substantially improve the microwave absorption capacity of the BNFs, and R_L was noticeably reduced for 0.2 and 0.3 mol of Nd^{3+}. BNF3 shows the lowest microwave-reflection loss (−45 dB at 8.5 GHz,

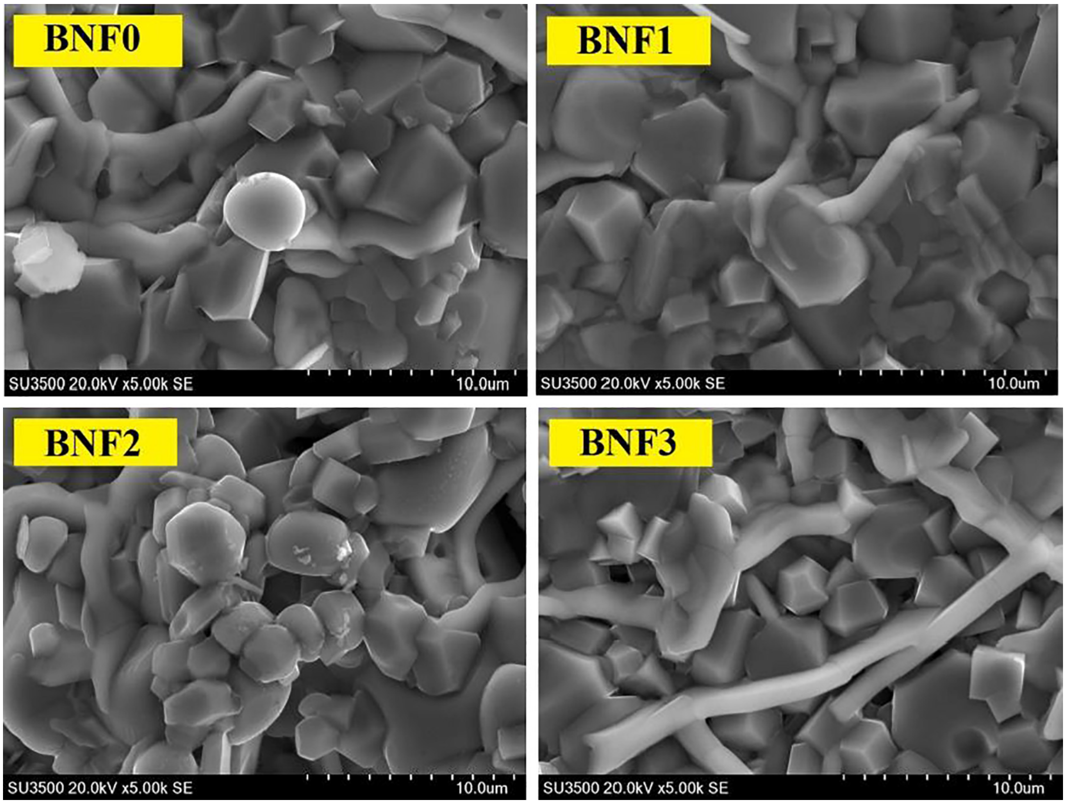

Fig. 2. SEM micrographs of the as-synthesized BNFs.

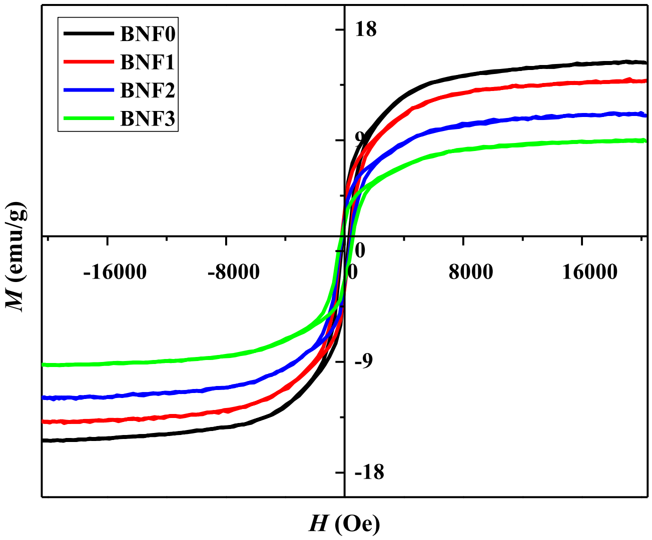

Fig. 3. Magnetic hysteresis loops of the as-synthesized BNFs.

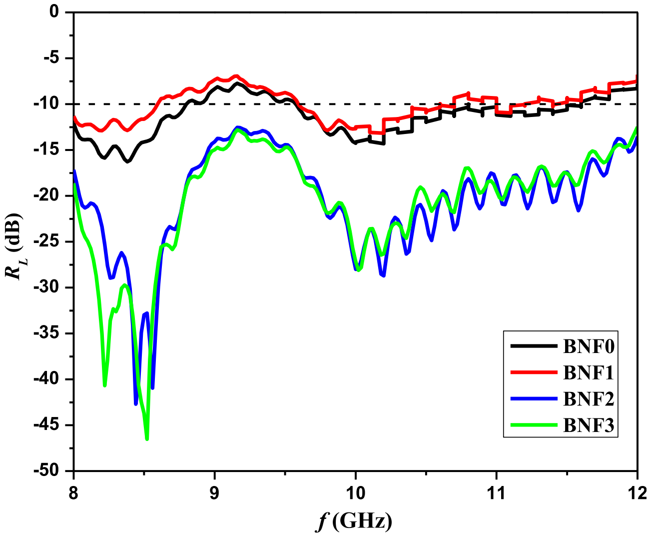

Fig. 4. Microwave-frequency-dependent reflection-loss of the as-synthesized BNFs.

with a bandwidth of 2.5 GHz). Both BNF2 and BNF3 demonstrate a weak microwave-reflection loss between 10 and 12 GHz. Interestingly, BNF which has a higher $Ba_6Nd_2Fe_4O_{15}$ phase content and lowest M_s, absorbs microwaves more efficiently within the x-band. The presence of a small oscillation in the high-frequency region is attributed to the penetration of ethylene glycol into the micropores.

4. Conclusion

New Nd^{3+}-substituted BNFs were synthesized using a modified solid-state reaction method, and their microwave absorption efficacy in the x-band was determined. The effect of the Nd^{3+} content on structure, surface morphology, magnetic properties, and microwave absorption of these BNFs was studied. The incorporation of Nd^{3+} into the BNF matrix was found to alter the crystalline phases of the ferrites. SEM images reveal a rough and predominantly amorphous morphology of the ferrites, with ethylene glycol trapped between microstructures. The observed substantial reduction of both saturation magnetization and microwave reflection loss of the proposed BNFs upon increasing the Nd^{3+} content is attributed to the presence of mainly a crystalline phase of $Ba_6Nd_2Fe_4O_{15}$. It was demonstrated that the microwave-absorption of the ferrite could be tuned by controlling the number of Nd^{3+}, which serve as a substituent for the Fe^{3+} at the octahedral site in the BNF lattice. The new ferrite is promising for the development of efficient microwave absorbing materials, which are needed in electronic devices that benefit from reduced electromagnetic interference.

Acknowledgments

Authors appreciate the financial support from Universitas Jenderal Soedirman, KEMENRISTEKDIKTI Indonesia through HIKOM 2017 (4962/UN23.14/PN/2017), and MOE/GUP/RU Vot. 18H68/17H19 (UTM, Malaysia).

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