Journal of Magnetism and Magnetic Materials 426 (2017) 483–486

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

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

Structural and magnetic properties of La^{3+} substituted barium–natural nanoferrites as microwave absorber in X-band

W. Widanarto[a,*], F. Amirudin[a], S.K. Ghoshal[b], M. Effendi[a], W.T. Cahyanto[a]

[a] Department of Physics, FMIPA, Universitas Jenderal Soedirman, Jl. dr. Soeparno 61 Purwokerto 53123, Indonesia
[b] Department of Physics, AMORG, Faculty of Science, Universiti Teknologi Malaysia, Johor Bahru, Skudai 81310, Malaysia

ARTICLE INFO

Keywords:
Lanthanum
Barium-natural nanoferrites
Reflection loss
Magnetic properties
Microwave absorption

ABSTRACT

Selection of proper microwave absorbers in the X-band is vital to prevent the interference issues that often damage devices and cause signal degradation. In this spirit, we prepared three La^{3+} substituted barium-natural nanoferrites (BNFs) samples with chemical composition of BaO:(x)La_2O_3:(6-x)Fe_2O_3 (x=0, 0.1, 0.2 in mol) via solid-state reaction route. Synthesized samples were characterized via SEM, XRD, VSM, and VNA measurements to determine the La^{3+} ions concentration dependent variation in the structural, magnetic and microwave absorption properties. Transmission/reflection line (TRL) method was used to evaluate the samples reflection loss. La^{3+} free samples sintered at 1100 °C revealed hexagonal $BaFe_{12}O_{19}$ and rhombohedral Fe_2O_3 phases. SEM images displayed the growth of new particle with the average size of 0.2 – 0.8 μm as filler in BNFs. Furthermore, an incorporation of La^{3+} into the BNF system manifested the emergence of new $BaLa_2Fe_2O_7$ tetragonal crystal phase. The average crystallite size of BNF was found to decrease with increasing La^{3+} ion concentrations. Conversely, substitution of La^{3+} in the BNF caused insignificant changes in the magnetic properties, the real part of the relative permittivity and the natural resonance frequency. Meanwhile, a reasonable shift in the microwave frequency absorption and enhancement in the reflection loss was evidenced due to the inclusion of La^{3+}. BNF sample containing 0.2 mol La_2O_3 exhibited a saturation magnetization and magnetic field anisotropy of 19.02 and 0.36 T, respectively, where the maximum reflection loss is discerned to be −26.61 dB at 10.87 GHz with 1.25 GHz bandwidth. This new class of ferrites may be prospective for microwave absorber in the X-band.

1. Introduction

In the recent past, wireless communication and electronic devices based on microwaves frequency achieved enormous growth. However, the appearance of threatening electromagnetic interference (EMI) effects posed new challenges and hindered the development. This hitch involving EMI is surmounted via the use of new EM wave absorber based on magnetic materials [1–5], which dissipated the undesired signals into thermal radiations [6]. Thus, the demand for such magnetic materials having strong absorption, wide absorption bandwidth, good thermal stability, low production cost, high corrosion resistance, and physical stability are ever-increasing. In this regard, ferrites with the hexagonal structure (hexaferrite) are considered to be the alternative materials for GHz frequency applications [7,8].

It is well-known that the absorption in the magnetic composites is mediated by mechanisms of domain wall movement, incoherent rotational magnetization and spin resonance [4]. Barium hexaferrite crystals with giant magnetic anisotropy field are demonstrated to be greatly potential material for EM wave absorber [2,3,9,10]. The notable advantages of barium hexaferrite such as cost-effectiveness, high coercivity field (H_c), strong remanent (M_r) and saturation magnetization(M_s) make them attractive for such usage [11]. However, the substitution Fe^{3+} ions in the crystal lattice are required in order to improve their absorption and magnetic field anisotropy (H_A) properties. This modification is pre-requisite to shifting the natural resonance frequency (f_r), permeability and altering the anisotropy magnetic field strength [1,7,12]. It is acknowledged that the substitution of Fe^{3+} together with rare earth ions is useful in enhancing the magnetic properties of the barium hexaferrite. Earlier, the classic relaxation properties of rare earth ions are often exploited to improve the magnetic properties of the hexagonal ferrite [2,13]. However, the microwave absorption properties of magnetic materials that are also affected by their relative permeability and permittivity are seldom explored [5].

In this view, we determine the influence of La^{3+} ions substitution on the structure, magnetic and microwave absorption properties of BNFs

* Corresponding author.
E-mail address: wahyu.widanarto@unsoed.ac.id (W. Widanarto).

http://dx.doi.org/10.1016/j.jmmm.2016.11.124
Received 12 August 2016; Received in revised form 18 November 2016; Accepted 26 November 2016
Available online 29 November 2016

prepared via solid-state reaction method. Synthesized samples are thoroughly characterized using various techniques. The La^{3+} impurities stimulated modifications in the structural and magnetic properties of such BNFs are evaluated. Besides, the microwave absorption properties, relative permittivity, and permeability of BNFs are examined in the X-band (8–12 GHz).

2. Materials and methods

Series of La^{3+} substituted BNFs of the form BaO:(x)La_2O_3:(6-x) Fe_2O_3 (x=0, 0.1, 0.2 in mol) were synthesized via the solid-state reaction process. Commercial analytical grade powders of $BaCO_3$ (99.99% purity, Sigma Aldrich) and La_2O_3 (99.5+, Merck) were used as raw materials. Following our earlier reported method [11,12], the ferrite pellets were acquired. Afterward, some pellets were crushed into fine powder and encapsulated between a pair of transparent plastics with the dimension of 2.5×1.5 cm^2 and thickness of 1 mm for further characterizations. Finally, the samples were labeled as LBF1 (x=0 mol), LBF2 (x=0.1 mol), and LBF3 (x=0.2 mol).

The Scanning electron microscopy (SEM–JSM-6390A) and X-ray diffractometer (XRD–Rigaku Miniflex 600) with Cu–Kα radiation (λ=1.541874 Å) were used to determine microstructure and phase of the as-synthesized ferrite pellets, respectively. Magnetic properties of the ferrites were measured using the vibrating sample magnetometer (Oxford VSM 1.2 H). The microwave (MW) absorption properties of the ferrites were recorded using vector network analyzer (VNA–Advantest R3770) in the frequency range of 7–13 GHz [12]. The MW absorption measurement based on Transmission/Reflection Line (TRL) method was conducted in order to yield scattering parameters (S-parameters), which consist of S_{11}, S_{12}, S_{21}, and S_{22}. Measured value of S_{11} is reflection coefficient (Γ). Meanwhile, measured value of S_{21} is transmission coefficient (T). The measured values of S_{22} and S_{12} are not used because they are same with measured values of S_{11} and S_{21}, respectively. Relative permittivity ε_r and permeability μ_r were determined from the S-parameters by the following relation:

$$\varepsilon_r = \sqrt{\frac{c_2}{c_1}}, \quad \mu_r = \sqrt{c_2 c_1} \tag{1}$$

and

$$c_1 = \frac{\mu_r}{\varepsilon_r} = \left(\frac{1+\Gamma}{1-\Gamma}\right)^2, \; c_2 = \mu_r \varepsilon_r = -\left(\frac{c}{\omega d} \ln \frac{1}{T}\right)^2 \tag{2}$$

with c is speed of the light and d is the thickness of the sample, meanwhile Γ and ω denote reflection coefficient and angular frequency, respectively.

3. Results and discussion

Fig. 1 depicts the XRD patterns of the as-synthesized BNF samples without and with La^{3+} substitution. The XRD peaks of sample LBF1 (without La^{3+} substitution) is dominated by $BaFe_{12}O_{19}$ (hexagonal crystal system) together with a minor phase of Fe_2O_3 (rhombohedral crystal system). The estimated lattice parameters of $BaFe_{12}O_{19}$ phase are a =5.928 Å and c =23.407 Å with a unit cell volume of 712.35 $Å^3$. Meanwhile, the estimated cell parameters of Fe_2O_3 phase are a =5.02 Å and c =17.72 Å with unit cell volume of 299.49 $Å^3$. Incorporation of 0.1 mol La_2O_3 into the BNF system (sample LBF2) was observed to produce a new phase of $BaLa_2Fe_2O_7$ (tetragonal crystal symmetry) plus dominant BNF phase. Further addition of La^{3+} by an amount of 0.2 mol (sample LBF3) caused the complete disappearance of peaks related to Fe_2O_3 lattice. Furthermore, the evidenced shift in the diffraction peak position of the hexagonal structure due to the substitution of La^{3+} in the BNF phase was attributed to the change in lattice parameters of the parent phase. This alteration in the lattice parameters caused the phase transformation of the hexagonal

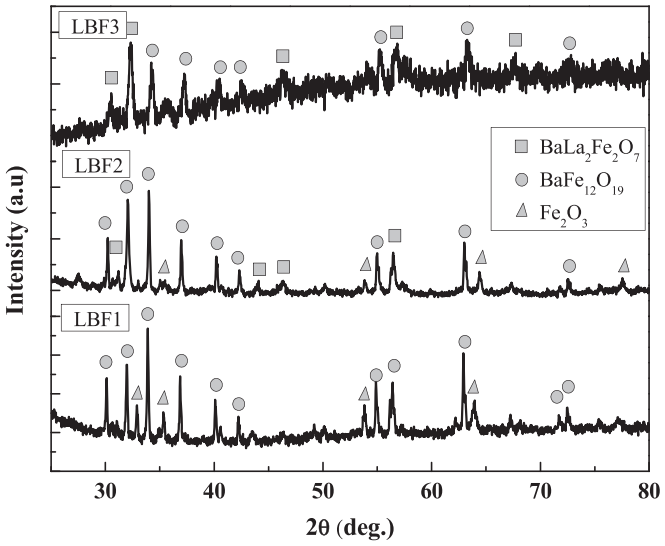

Fig. 1. XRD patterns of the as-synthesized BNFs samples without and with La^{3+} substitution.

$BaFe_{12}O_{19}$ crystal to the tetragonal $BaLa_2Fe_2O_7$ crystal (cell parameters of a =3.93 Å, c =20.85 Å and cell volume of 322.73 $Å^3$). The average crystallite size of all samples determined using Debye–Scherrer equation [14,15] was found to be in the range of 5.13 – 64.01 nm. Besides, LBF3 sample revealed smallest crystallite size (5.13 – 17.30 nm).

Fig. 2 shows the SEM images of the hexagonal BNFs samples, where the effects of La^{3+} substitution are clearly evidenced in LBF2 and LBF3 samples. The nucleation of new particles as filler in BNFs with the average size of 0.2 – 0.8 μm is observed. The obtained difference in the particle size between XRD and SEM measurement is primarily attributed to the existence of molecular structure disorder and lattice strain [16].

Fig. 3 illustrates the room temperature magnetic hysteresis loops of all the samples. All Samples exhibited almost similar magnetic properties with M_r =12.36 emu/g, H_c =0.088 T. Meanwhile, the saturation magnetization M_s is not achieved even though the external magnetic field is increased up to 1 T (maximum). This is because the samples suspected to contain antimagnetic materials. M_s value of 19.53 emu/g was determined by interception of M as function of H. However, the value of M_s for LBF3 sample was found to be lower (19.02 emu/g), which saturated at H_A =0.36 T with increasing external magnetic fields. Incorporation of La^{3+} in the BNF structures that caused a slight shift in the magnetic parameters was ascribed to the substitution of Fe^{3+} ions in the octahedral site by La^{3+} ions, thereby reduced the unpair Fe^{3+} spins.

Fig. 4 shows the frequency-dependent relative permittivity ($\varepsilon = \varepsilon' + \varepsilon''$) for all samples that were measured in the X-band. The real part of the permittivity (ε') spectra showed four prominent peaks centered at 7.5, 8.4, 9.6 and 10.7 GHz, indicating the lack of energy in the material from an external electric field [17]. Meanwhile, the imaginary part of the permittivity (ε'') spectra so called the loss factor exhibited the electrical energy dissipation ability of the synthesized materials. Furthermore, the emergence of the peaks in the ε'spectra is followed by the disappearance of the peaks in the ε'' spectra. Amongst all three samples, LBF3 displayed the best energy storage performance at 10.7 GHz. Conversely, all samples were found to absorb a tiny amount of energy at 9.6 and 12.1 GHz. The absorbed energy is consumed for the magnetic domain wall motion.

The frequency dependent complex relative permeability ($\mu = \mu' + \mu''$) for all the samples is depicted in Fig. 5. The real part of the permeability (μ') spectra exhibited five prominent peaks centered at 7.5, 8.4, 9.5, 10.7 and 12.3 GHz, demonstrating the ability of the