Journal of Magnetism and Magnetic Materials 408 (2016) 147–151

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

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

Structural elucidation and magnetic behavior evaluation of rare earth (La, Nd, Gd, Tb, Dy) doped BaCoNi-X hexagonal nano-sized ferrites

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ARTICLE INFO

Article history:
Received 9 December 2015
Received in revised form
8 February 2016
Accepted 19 February 2016
Available online 22 February 2016

Keywords:
Nanoferrites
Rare-earth metals
XRD
FTIR
Coercivity
Saturation magnetization

ABSTRACT

Rare-earth (RE=La^{3+}, Nd^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}) doped $Ba_2NiCoRE_xFe_{28-x}O_{46}$ (x=0.25) hexagonal ferrites were synthesized for the first time via micro-emulsion route, which is a fast chemistry route for obtaining nano-sized ferrite powders. These nanomaterials were investigated by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), as well as vibrating sample magnetometer (VSM). The XRD analysis exhibited that all the samples crystallized into single X-type hexagonal phase. The crystalline size calculated by Scherrer's formula was found in the range 7–19 nm. The variations in lattice parameters elucidated the incorporation of rare-earth cations in these nanomaterials. FTIR absorption spectra of these X-type ferrites were investigated in the wave number range 500–2400 $cm^{-1.}$ Each spectrum exhibited absorption bands in the low wave number range, thereby confirming the X-type hexagonal structure. The enhancement in the coercivity was observed with the doping of rare-earth cations. The saturation magnetization was lowered owing to the redistribution of rare-earth cations on the octahedral site ($3b_{VI}$). The higher values of coercivity (664–926 Oe) of these nanomaterials suggest their use in longitudinal recording media.

1. Introduction

To deal in electronic devices i.e. radars, mobile phones, wireless devices, refrigerators etc. with a wide range of electromagnetic waves, face a lot of serious problems [1,2]. We are focusing on hexagonal ferrites to solve these problems and in order to make the devices suitable for high range of electromagnetic waves. Nowadays, the magnetic nanocrystal materials are in great focus due to their technological applications and fundamental understanding of nano-magnetism [3]. The hexagonal ferrites are ferrimagnetic materials having high resistivity, permeability and high uni-axial magnetic anisotropy; they are used in various devices such as magnetic recording media, microwave absorber and mm-wave devices [4–7]. These magnetic nano-particles having different unique physical properties such as quantum tunneling of magnetization and super paramagnetism are used as a high density perpendicular recording media, ferrofluids, color imaging, ultrahigh frequency (300 MHz to 3 GHz) devices and magnetic refrigeration [8,9].

The hexagonal ferrites are suitable for microwave absorption due to their excellent stability, high magnetization; low eddy current and high Curie temperature [10–12]. These materials can be used in an inductor and noise reduction devices [13]. The nanomagnetic materials can also be used in the medical field as a drugs carrier inside the body [2]. Due to the high saturation magnetization and low coercivity of X-type hexagonal ferrites, lead on other hexagonal ferrites as a good microwave absorber material [14]. The magnetic properties of X-type ferrites depend on the chemical composition, time, annealing temperature and the preparation method [15]. The crystal structure of X-type ferrites is very complex, which is the superposition of S, R and T blocks [16,17]. X-type ferrites are the composition of M and W type ferrites which are extremely hard [18].

The structural, magnetic and microwave absorption properties of nanomagnetic materials can be improved by the doping of rare-earth metals [19]. The rare-earth metals can affect the

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http://dx.doi.org/10.1016/j.jmmm.2016.02.061
0304-8853/

electromagnetic properties of hexagonal ferrites because the later have certain relaxation properties [14]. Leccabue et al. studied the super exchange interaction between the different rare earth ions and iron ions; the change in magnetic order and magneto crystalline anisotropy of the rare earth doped ferrites [16]. A sol–gel method was used to prepare $Sr_{2-x}Nd_xNi_2Fe_{28-y}Co_yO_{46}$ ($x=0.02$, 0.06, 0.08, 0.10 and $y=0.1$, 0.2, 0.3, 0.4, 0.5) hexagonal ferrites at sintering temperature of 1250 °C for 6 h by Sadiq et al. [14].

The variation in the saturation magnetization was observed with the changing of doping concentrations. This variation was explained on the basis of the distribution of ions in different sites. The increase in the retentivity M_r was observed with the increase of the doping concentration while the decrease in the coercivity H_c was observed with the increase of doping concentration. The overall magnetic properties were improved by doping of Nd^{3+} and Co^{2+}. It was concluded that the prepared materials were good micro-absorbers due to high saturation and low coercivity values. The microwave absorption properties of these X-type hexagonal ferrites were found to increase with the doping of Nd–Co.

Sadiq et al. [10] prepared $Sr_{2-x}Sm_xNi_2Fe_{28-y}Mn_yO_{46}$ with $x=0.02$, 0.04, 0.06, 0.08, 0.010 and $y=0.1$, 0.2, 0.3, 0.4, 0.5, 0.6 X-type hexagonal ferrites by using the sol–gel method. It was observed that the value of the electrical resistivity varied with the doping of Sm–Mn contents due to which the eddy current was reduced. This result showed that the prepared X-type materials were applicable for the microwave devices. Sadiq et al. [2] worked on the magnetic and the microwave absorption properties of Gd–Cd co-doped X-type hexagonal ferrites. The sol–gel method was used to prepare $Sr_{2-x}Gd_xNi_2Fe_{28-y}Cd_yO_{46}$ with ($x=0.00$, 0.02, 0.04, 0.06, 0.08, 0.10 and $y=0.1$, 0.2, 0.3, 0.4, 0.5) X-type hexagonal ferrites. The value of coercivity was found in the range of 484.22–887.47 G. The monotonically decrease in the saturation magnetization and remanance magnetization were observed with the temperature which lead to the hexagonal ferrites. It's also observed that the Gd–Cd doped ferrites had high values of permeability and complex relative permittivity than that of un-doped ferrite. At frequency 11.87 GHz the maximum microwave absorption of 23 dB was observed. The attenuation peak was observed, good agreement to the reflection loss value. Due to the microwave absorption properties these materials were suitable for the super high frequency devices (SHF).

Sadiq et al. [19] discussed the Ce–Zn doped microwave absorbing materials used for X-band. The sol–gel auto-combustion method was used to prepare the polycrystalline samples of $Sr_{2-x}Ce_xNi_2Fe_{28-y}Zn_yO_{46}$ ($x=0.02$, 0.04, 0.06, 0.08, 0.10 and $y=0.1$, 0.2, 0.3, 0.4, 0.5) X-type hexagonal ferrites. The electrical resistivity at room temperature was found to be 10^9 Ω-cm. The value of electrical resistivity confirmed that the prepared materials can be used for the reducing the eddy current losses. The improvements in the magnetic properties i.e. saturation magnetization, remanace magnetization and coercivity were observed with the doping of Ce–Zn in the pure ferrite. Due to the improvements in the magnetic properties and resistivity with the doping of Ce–Zn contents, these materials were found suitable for making of multilayer chip inductors (MLCI). At frequency of 12.858 GHz the maximum reflection loss of 23.4 dB was found with the doping of Ce–Zn content in the pure ferrite. The obtained attenuation constant matched with the reflection loss. It was concluded that due to the microwave absorption properties, these materials were suitable for the super high frequency devices.

Sadiq et al. [20] used the sol–gel auto-combustion method to synthesize $Sr_{1.96}RE_{0.04}Co_2Fe_{27.80}Mn_{0.2}O_{46}$ with (RE=Gd, Nd, La and Sm) X-type hexagonal ferrites. These materials were annealed at 1250 °C for 6 h. The TGA/DSC, XRD, FTIR, SEM, TEM, VSM and dielectric analysis were used to characterize these samples. The single phase X-type ferrite was confirmed from XRD and FTIR analysis. The variations in lattice parameter were observed with the doping of different rare earth metals. The particle size of these samples was found in the range of 54–100 nm by using TEM analysis. The average grain size was found in the range of 0.672–1.01 mm from SEM analysis. From VSM analysis, it was observed that the Gd doped X-type ferrite had higher value of coercivity (526.06 G) then other rare earth doped X-type ferrites which lead to the longitudinal recording media applications. It was also observed that Gd-doped X-type ferrites had maximum reflection loss of 25.5 dB at 11.88 GHz, was a good microwave absorber material then other rare earth doped materials. The shifting of the minimum value of reflection loss towards lower and higher frequency was observed with the doping of rare earth metals which showed that the microwave absorption properties can be changed by the doping of rare earth metals.

The aim of the present work is to synthesize nano-sized X-type hexagonal ferrites ($Ba_2NiCoRE_xFe_{28-x}O_{46}$ ($x=0.25$, RE=La, Nd, Gd, Tb, Dy)) by micro-emulsion method and to investigation the impact of rare earth metal cations on the various properties of these X-type hexagonal ferrites on iron site.

2. Experimental procedure

2.1. Samples preparation

The micro-emulsion method was used to prepare the polycrystalline samples with composition $Ba_2NiCoRE_xFe_{28-x}O_{46}$ ($x=0.25$, RE=La, Nd, Gd, Tb, Dy). The required materials ($Ba(No_3)_2$), $NiCl_2\cdot6\ H_2O$, $(CH_3\cdot COO)_2\cdot Co\cdot4H_2O$, $GdCl_3\cdot6H_2O$, $DyCl_3\cdot6H_2O$, $TbCl_3\cdot6H_2O$, $LaCl_3\cdot7H_2O$, Nd $(No_3)_3\cdot6H_2O$ and $FeCl_3$ were dissolved in deionized water. The obtained salt solutions were mixed and then stirred on magnetic hot plates at 60 °C. The CTAB solution was used as a surfactant in all samples. The ammonia solution was slowly mixed to maintain the pH value up to 11 for all samples. All the mixed samples were then stirred for 5 h by using magnetic hot plates. The stirred samples were then washed with deionized water to remove the precipitates and to reduce the pH value until 7. The microwave oven was used to evaporate the water from the washed samples at 100 °C. All the samples were then annealed at 1250 °C for 6 h. The annealed materials were grinded to convert into powder form. The obtained materials were then characterized by using various techniques.

2.2. Characterization

The crystalline phase formation, crystalline size and lattice parameters were manipulated by using X-ray powder diffractometer with appropriate Cu-K_a radiations having wavelength of ($\lambda=1.5406$ Å). The using of the device having Cu-K_a radiation of $\lambda=1.5406$ Å, show X-ray powder diffraction patterns to determine the crystal structure of the materials [21]. The lattice parameters were calculated by using the cell software [22]. The FTIR Spectrometer was used to record the IR spectra near the infrared region over the range of 500–4500 cm^{-1}. The magnetic properties i.e. saturation magnetization (M_s), remanance magnetization M_r, coercivity H_c and magnetic anisotropic constant were computed by using vibrating sample magnetometer (VSM).

3. Results and discussion

3.1. Structural analysis

Fig. 1 shows the XRD patterns of $Ba_2CoNiRE_xFe_{28}O_{46}$ (RE=La, Nd, Gd, Tb, Dy, $x=0.25$) ferrites annealed at 1250 °C for 6 h. The