Materials Research Bulletin 101 (2018) 48–55

Contents lists available at ScienceDirect

Materials Research Bulletin

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

Structural elucidation, and morphological and magnetic behavior evaluations, of low-temperature sintered, Ce-doped, nanostructured garnet ferrites

Majid Niaz Akhtar[a,*], Kashif Ali[b], Asim Umer[c], Tahir Ahmad[d], Muhammad Azhar Khan[e]

[a] *Department of Physics, Muhammad Nawaz Sharif University of Engineering and Technology (MNSUET), 60000 Multan, Pakistan*
[b] *Department of Mathematics, Muhammad Nawaz Sharif University of Engineering and Technology (MNSUET), 60000 Multan, Pakistan*
[c] *Department of Chemical Engineering, Muhammad Nawaz Sharif University of Engineering and Technology (MNSUET), 60000 Multan, Pakistan*
[d] *Department of Metallurgy and Materials Engineering CEET, University of the Punjab, Lahore, Pakistan*
[e] *Department of Physics, The Islamia University of Bahawalpur, Bahawalpur 63100, Pakistan*

ARTICLE INFO

Keywords:
Nanostructured garnets X-ray diffraction (XRD)
Fourier transform infrared spectroscopy (FTIR)
Field emission scanning electron microscopy (FESEM)
Magnetic properties
Switching field distribution (SFD)

ABSTRACT

Low-temperature sintered $Ce_xGd_{3.5\text{-}x}Fe_{4.5}O_{12}$ (x = 0.0, 0.4, 0.8, 1.2, 1.6, 2.0 and 2.4) garnet ferrites were synthesized via a sol-gel self-combustion route. Phase, structure, morphology and magnetic investigations were done using FTIR, XRD, FESEM, and VSM, respectively. Single-phase structures of all Ce^{3+} substituted nano-sized garnet ferrites were confirmed through XRD. The crystallite size was decreased with Ce^{3+}incorporation. Relevant structural parameters such as site radii, bond lengths, ionic radii, and shared edges were calculated using XRD. The vibrational spectroscopy stretching band studies were also done using FTIR. The grain size and morphology were also analyzed using FESEM. The magnetic remanance, saturation, and coercivity were found to increase systematically with an increase in Ce^{3+} concentration in these garnets. Switching field distribution curves were also plotted using the first derivative of the demagnetization data from MH loops. The better magnetic properties of these nanogarnets suggest their use for miniaturization of the devices in various applications.

1. Introduction

Microwave magnetic materials have importance due to their applications in industrial and technological fields [1]. Magnetic nanoferrites have importance because of high resistivity, small dielectric parameters, moderate permeability, low electromagnetic and eddy current losses, and better thermal and mechanical properties. Due to these properties, magnetic nanoferrites are considered versatile materials for potential applications in many fields [2,3]. Garnet nanoferrites with unique magneto optical and electromagnetic properties have three lattice sites represented by (b), [c], and {d}, respectively. These lattice sites are (b) octahedral, tetrahedral [c] and dodecahedral sites {d} occupy the $16Fe^{3+}$, $24Fe^{3+}$ and $24R^{3+}$ ions respectively, whereas oxygen ions are equally located at the interstitial sites in the lattice [4–6]. Garnet structure is similar to the spinel structure except for the dodecahedral sites. However, Fe^{3+}, Al^{3+}, In^{3+}, Ga^{3+}, and Si^{4+} cations prefer to go on to the B-site; and they formed the polyhedral with the oxygen ions in the garnet lattice. In the garnet structure, each tetrahedron is inter-connected to four other octahedra, whereas each octahedra is connected with the six tetrahedra. The shared corners are distorted and formed networks of dodecahedrons. The dodecahedral cavities are occupied by the rare-earth metal cations with the tetrahedral sites [7]. Among the A and B sites, Fe^{3+}cations have importance for the variations in the magnetic properties of the garnet structure. This could be attributed to the anti parallel arrangement and strong anisotropy at the A and B sites, accordingly. Moreover, the rare earth cations aligned themselves in opposite direction to the cations at the A and B sites [8]. Gd^{3+} doped nanocrystalline ferrites were prepared using a non-conventional method at a low sintering temperature. They found that the nano powders of these ferrites have low dielectric constant and high saturation magnetization. Furthermore, they investigated that with Gd^{3+} contents, microwave absorption properties were increased [9]. However, gadolinium ferrites were mixed with iron and gadolinium oxides. The atomic ratios of Gd:Fe were important and these played key role in synthesizing gadolinium-iron garnets ($Gd_3Fe_5O_{12}$). Gd is a rare earth metal, and its electrical resistivity is $\sim 10^6$ Ω-cm [10]. Dy^{3+} substituted YIG garnets were synthesized, and their magnetic properties were investigated. The single-phase structure,

---

[*] Corresponding author.
E-mail addresses: majidniazakhtar@gmail.com, majidniazakhtar@mnsuet.edu.pk (M.N. Akhtar).

https://doi.org/10.1016/j.materresbull.2018.01.009
Received 15 June 2017; Received in revised form 28 December 2017; Accepted 9 January 2018

along with enhanced magnetic properties, was reported [11]. $Dy_{3-x}Ni_xFe_5O_{12}$ (with x = 0.0, 0.1, 0.2, 0.3, 0.4, and 0.5) garnet ferrites were synthesized using the ceramic method. XRD studies revealed the single-phase garnet structure. Magnetic measurements such as initial permeability with temperature were evaluated in this study. They found that initial permeability was increased with temperature. However, the critical temperature (T_C) was dropped due to the change of magnetic phase ordering in ferrimagnetic materials [12].

Several researchers have prepared the garnet ferrites through different methods. Numerous methods have been adopted to synthesize garnet nanoferrites—methods such as co-precipitation [13], glass crystallization [14], microwave [15], hydrothermal [16], sol-gel self-combustion [17], mixed conventional metal oxide (MCMO) [18], and sol-gel auto combustion [19]. Ce^{3+} substitution in the YIG garnet structure may enhance the MO Faraday rotation. However, due to the larger ionic radius and consequently lower stability of Ce^{3+} compared to Y^{3+}, it may be difficult to substitute into the garnet structure [20,21]. The substitution of Ce in gadolinium (Gd) based garnet ferrites was done using the sol-gel method. The reported work was to find out the morphological, structural and magnetic properties. However, the single-phase Ce-Gd nanoferrites were achieved at high sintering temperature (950 °C). Magnetic properties of the samples were also measured at room temperature [22].

In this article, magnetic rare earth Ce^{3+} ions have been substituted in Gd based garnets using the sol-gel method. The samples were sintered at low sintering temperature 650 °C. The aim of the present investigation is to prepare single-phase garnet nanomaterials at low sintering temperature. The purpose of the low sintering temperature was to get better structural, morphological, and magnetic properties along with reduced particle size of the nanoferrites. However, the systematic detailed studies on the structural and magnetic parameters of the Ce-substituted garnets have also been appraised.

2. Experimental procedure

2.1. Materials

Gadolinium oxide (Gd_2O_3), cerium oxide (Ce_2O_3), iron nitrate [(Fe $(NO_3)_3{\cdot}9H_2O$)], citric acid ($C_6H_8O_7$) and nitric acid (HNO_3) of analytical grade with 99.99% purity were used for the fabrication of Ce-substituted garnets.

2.2. Preparation of Ce-substituted Garnets

Ce-substituted garnets with nominal composition $Ce_xGd_{3.5-x}Fe_{4.5}O_{12}$ (x = 0.0, 0.4, 0.8, 1.2, 1.6, 2.0 and 2.4) were prepared using the sol-gel self-combustion method. The stoichiometric amounts of iron nitrate [(Fe $(NO_3)_3{\cdot}9H_2O$)] and citric acid ($C_6H_8O_7$) was calculated for the preparation of aqueous solution. Both cerium and gadolinium oxides were dissolved separately in nitric acid (HNO_3) to prepare the cerium nitrate hexahydrate [$Ce(No_3)_3{\cdot}6H_2O$] and gadolinium nitrate hexahydrate [$Gd(NO_3)_3{\cdot}6H_2O$], respectively. The solutions were mixed and stirred using a hot plate magnetic stirrer for 3 days. Ammonia was used to control the value of pH ∼ 7. The pH of the solution is the important factor for the oxidation of the rare earth metal cations. In addition, redox chemistry explains the phenomena of reduction for states in acid and in alkali solutions. Therefore, it is found that Ce^{3+} is oxidized to Ce^{4+} in alkali and Ce^{4+} reduced to Ce^{3+} in acid solutions. Moreover, pH of the Ce-substituted samples assured the valence state of Ce during the preparation of the nanoferrites.

The solutions were evaporated by continuous heating at 70 °C with agitation until the formation of viscous gel. Drying gels burned until the gels were completely burnt to form powder. The samples were dried by heating them in an oven at 110 °C for 1 day. The dried powders were sintered in air furnace at 650 °C for 3 h. Finally, the sintered powders were ground using the mortar and pestle.

2.3. Characterization of Ce-substituted Garnets

The XRD analysis was done from the XRD patterns (recorded using Bruker D8 advance) with CuK_α at 1.5406 Å. The structure, phase, lattice micro strain, crystallite size, and cell volume were determined using XRD patterns. Fourier transform infrared (FTIR) spectroscopy analysis was employed using a Shimadzu IR 8400S spectrometer. FTIR was used to find out the structure and stretching vibrations of the atoms. Field emission scanning electron microscopy (FESEM) was used to investigate the morphologyand shape of, and to measure the grain size of, the garnet nanoferrites using SUPRA-55VP-ZEISS. Magnetic evaluations were performed using vibrating sample magnetometer (VSM) model LakeShore/7404. The applied magnetic field was with in the range of 0–12 KOe. However, the magnetic remanance (M_r), saturation magnetization (M_s) and coercivity (H_c) of the garnets were also evaluated using MH Loops. Switching field distribution (SFD) was also measured by taking the 1st derivative of the demagnetization curves obtained from the MH loops of the Ce-substituted garnets.

3. Results and discussion

3.1. X-Ray diffraction studies

X-ray diffraction patterns of $Ce_xGd_{3.5-x}Fe_{4.5}O_{12}$ with different compositions (x = 0.0, 0.4, 0.8, 1.2, 1.6, 2.0 and 2.4) are presented in Fig. 1.XRD patterns of all the Ce-substituted samples showed single-phase structure with better crystallinity at comparatively low sintering temperature. The samples are indexed using the JCPDS cards 00-023-0237 and 00-087-0900, respectively. No extra peak is observed; and this represents the purity of the different Ce-substituted garnets. The crystallite size, lattice parameter and cell volume of these nanoferrites were also calculated. The crystallite cell and lattice parameter were decreased with an increase of Ce^{3+} contents at low temperature. However, the lattice parameter, crystallite size, cell volume, and other related parameters show variations and random behavior of Ce-incorporated nanocrystalline ferrites [22]. The volume of the unit cell of these nanocrystalline ferrites shows shrinkage. This shrinkage is attributed to the greater bond length and binding energy between the oxygen ions and the metal cations [23].The high-intensity peak [420] shows the single-phase garnet structure. While it can be seen that this high-intensity peaks represent rather less intensity at the maximum Ce^{3+} contents. However, the [400]-intensity peak increased at the maximum Ce^{3+} concentration. Table 1 depicts the crystallite size,

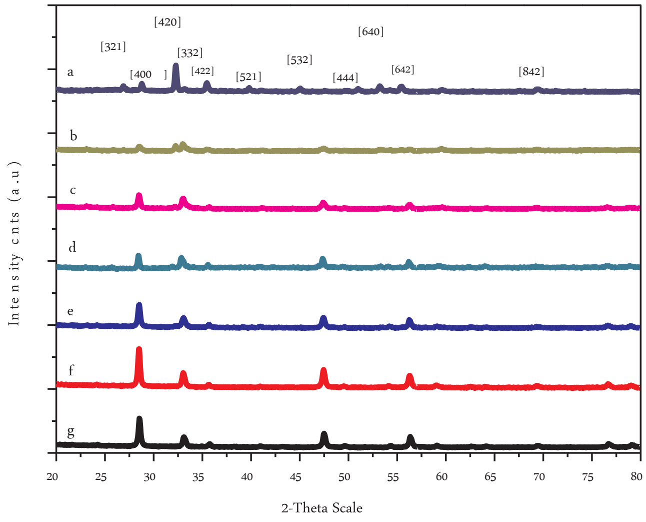

Fig. 1. XRD of CexGd3.5-xFe4.5O12 samples with (a) x = 0, (b) x = 0.4, (c) x = 0.8, (d) x = 1.2, (e) x = 1.6, (f) x = 2.0 and (g) x = 2.4 prepared by sol-gel self combustion method at 650 °C.