Materials Science in Semiconductor Processing 40 (2015) 631–642

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Combustion synthesis of Mg–Er ferrite nanoparticles: Cation distribution and structural, optical, and magnetic properties

R. Tholkappiyan, K. Vishista

Department of Physics, College of Engineering Guindy, Anna University, Chennai 600025, Tamil Nadu, India

ARTICLE INFO

Article history:
Received 12 April 2015
Received in revised form
18 June 2015
Accepted 29 June 2015

Keywords:
Ferrite nanoparticles
Combustion process
X-ray photoelectron spectroscopy
Optical and magnetic properties
Oxidation state

ABSTRACT

Rare earth ion (Er^{3+})-doped magnesium ferrite nanoparticles of basic composition $MgFe_{2-x}Er_xO_4$ ($x=0$, 0.02, 0.04, and 0.06) were synthesized for the first time by a combustion method with use of glycine as fuel. The synthesized nanoparticles were characterized by X-ray diffraction, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy, UV-diffuse reflectance spectroscopy, and vibrating sample magnetometer analysis in order to study the structural, compositional, morphological, and magnetic changes with addition of dopant. The X-ray diffraction pattern revealed a single phase with cubic spinel structure, and from the Scherrer formula and the Williamson–Hall formula, the average grain sizes ranged from 35 to 56 nm and from 31 to 54 nm, respectively. The lattice parameter (a) increases with the increase of the Er^{3+} concentration x in the lattice. The cation distributions among the tetrahedral (A) and octahedral (B) sites of spinel-type Er-doped magnesium ferrites were also investigated. The Fourier transform infrared spectroscopy spectra of synthesized samples illustrate that the higher-frequency bands lying in the range from 550 to 620 cm^{-1} and the lower-frequency bands lying in the range from 410 to 450 cm^{-1} are associated with the asymmetric stretching modes of the AB_2O_4 type of spinel transition metal oxides. Information about the chemical elements and oxidation states of the samples was obtained from high-resolution core-level X-ray photoelectron spectroscopy spectra of Mg 1s, Fe 2p, Er 4d, and O 1s. Further information about the morphology of the nanoparticles was obtained by scanning electron microscopy. From UV-diffuse reflectance spectroscopy studies, the optical band gaps were found to range from 1.81 to 1.96 eV. The magnetic hysteresis curves clearly indicate the soft ferromagnetic nature of the samples. Various magnetic properties such as saturation magnetization, coercivity, and remanent magnetization obtained from M–H loops were observed to increase with Er^{3+} substitution.

1. Introduction

Understanding structural, optical, electrical, magnetic, catalytic, and mechanical behavior in ferrite materials has been an area of intense research for material scientists in the past decade. Ferrite materials in the nano-regime could provide more advantages over bulk ferrites with remarkable changes in the physical properties. The physics of such magnetic materials is strongly modified by several factors, such as an external magnetic field, anisotropy, large surface-to-volume ratio, and temperature. Ferrites are magnetic materials containing iron oxide as a major constituent. On the basis of the crystal structure and magnetic ordering, ferrites can be classified into four different types—namely, spinels, hexaferrites, garnets, and orthoferrites. Spinel ferrites have the general formula $A^{2+}B_2{}^{3+}O_4$, where the A site is occupied by a metal ion with a valence of +2 (e.g., Zn, Cu) and the B site is occupied by the Fe^{3+} ion. Spinels are classified into three types—namely, normal, inverse, and random—on the basis of the distribution of cations in the two principal sites—namely, tetrahedral and octahedral sites. Magnesium ferrites have an inverse spinel structure with chemical formula $A^{2+}Fe_2{}^{3+}O_4$, where A is the metal cation, such as Mg, Co, Zn, Mn, or Ni, which normally occupies the eight tetrahedral sites out of 34 sites in a unit cell, whereas Fe^{3+} cations occupy 16 octahedral sites among 32 sites in a unit cell. Magnesium ferrites are the most versatile of the ferrites and allied compounds, with potential applications in data storage and transmission, spintronics, microwave devices, and sensors [1]. Magnesium ferrites are soft magnetic n-type semiconducting materials which exhibit low saturation magnetization, high resistivity, and reproducible characteristics [2]. In addition, magnesium ferrites have excellent optical properties owing to their small band gap of 2.4 eV, which makes them suitable as a photocatalyst

---

E-mail address: thols2006@gmail.com (R. Tholkappiyan).

http://dx.doi.org/10.1016/j.mssp.2015.06.076
1369-8001/© 2015 Elsevier Ltd. All rights reserved.

[3].

Researchers have proposed several synthesis approaches, such as co-precipitation [4], a microwave hydrothermal method [5], combustion synthesis [6], a sol–gel method [7], a citrate precursor technique [8], a solvothermal method [9], and a microwave-assisted method [10,11]. Each of these methods has its advantages and limitations in synthesizing these nanomaterials. Currently, attention has turned toward a simple, low-temperature solution method for preparing nanoparticles. One of the novel and simple methods for the synthesis of nanomaterial is the combustion method as it is cost-effective, simple, and rapid, which allows effective synthesis of a variety of nanosized materials compared with the conventional routes.

Apart from the synthesis of pure magnesium ferrite nanoparticles, there has been a trend toward doping the pure magnesium ferrite to control the structure, particle size, morphology, surface features, and chemical composition, which in turn has a great influence on the optical and magnetic properties of the host materials. Transition metal and rare earth ions have received extensive attention as dopants owing to their remarkable properties. Recently, Al^{3+}-doped $MgFe_2O_4$ was synthesized by Modi and Joshi [12], Kim et al. [13] prepared $MgFe_{2-x}Al_xO_4$ thin films through a sol–gel method, Sagar et al. [14] synthesized Ge-substituted magnesium ferrite $Mg_{1+x}Ge_xFe_{2-2x}O_4$ ($x=0$–0.4) nanoparticles and studied the cation distribution, Pradeep and Chandrasekaran [15] prepared $M_{0.5}Mg_{0.5}Fe_2O_4$ (M is Ni, Cu, or Zn) nanoparticles by a sol–gel method, Mittal et al. [16] synthesized $Mg_xNi_{1-x}Fe_2O_4$ ($x=0$–1) through a solid-state route and characterized the particles by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), and Hankare et al. [17] obtained magnesium ferrites with Cr substitution via a co-precipitation technique using NaOH at pH 9.5. An average crystallite size ranging from 42.67 to 51.78 nm for Sm–Gd-doped magnesium ferrite was obtained through a sol–gel method by Naidu et al. [18,19].

Rare earth ions such as Er^{3+} have unpaired 4f electrons, and the magnetocrystalline anisotropy in ferrites is related to the 4f–3d coupling between the rare earth and transition metal ions [20]. Thus, the properties of these ferrites can be improved by addition of the appropriate amount of Er^{3+} in place of Fe ions within the inverse spinel lattice.

Because there has been no report on the effect of Er substitution on magnesium ferrite nanoparticles synthesized by the combustion method, we have attempted to investigate how the exact locations of the doping Er^{3+} ions and cationic Er^{3+} defects present in magnesium ferrite affect the optical and magnetic properties by changing the structural regularity in the material. We report the synthesis of pure magnesium ferrite and Er^{3+}-substituted magnesium ferrite with various concentrations of Er as $x=0.02$, 0.04, and 0.06 by a combustion method with use of glycine as fuel. The stoichiometric amounts of fuel and metal nitrates are discussed. The various structural properties were investigated by XRD and Fourier transform infrared (FTIR) spectroscopy. The surface morphology of the samples was characterized by scanning electron microscopy (SEM). The oxidation state and distribution of Er^{3+} present in the prepared compounds were studied by XPS. Furthermore, the optical and magnetic properties of Er-doped magnesium ferrites were investigated by UV-diffuse reflectance spectroscopy (UV-DRS) and vibrating sample magnetometer (VSM) analysis, respectively.

2. Experimental

2.1. Materials and synthesis

Metal nitrates such as purified magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$, 98%, Alfa Aesar), iron(III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, $98-100\%$, Merck), and erbium nitrate ($Er(NO_3)_3 \cdot 5H_2O$, 99.9%, Alfa Aesar) were used as starting materials, and glycine ($C_2H_5NO_2$, 98.5%, Qualigens) was used as fuel. The raw starting materials were of analytical grade without further purification.

A precursor aqueous solution containing a mixture of $Mg(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, and $Er(NO_3)_3 \cdot 5H_2O$ was prepared in 20 ml of distilled water under magnetic stirring for 20 min. Then, 5 ml of concentrated nitric acid (HNO_3) was added to the mixture to produce a clear aqueous solution. The appropriate amount of glycine (fuel) was then added to the above-mentioned system, and the mixture was stirred for 20 min until complete dissolution occurred. We then concentrated the solution by heating it at 8 °C for 2 h in a magnetic stirrer until excess free water had evaporated and it became a dark brown viscous gel, which was transferred to and kept on a hot plate at 20 °C. Continuous heating led to the autoignition of the dried resin. At the beginning of combustion, it starts to foam and produce sparks on the sides of the container/beaker. At the point of spontaneous combustion, it begins to burn, and a dark brownish powder was obtained with the evolution of a large quantity of smoke. The time between the actual ignition and the end of the reaction was less than 20 s. Finally, the as-synthesized products were removed and allowed to cool to room temperature; the resultant products were ground by hand with an agate mortar and pestle to obtain a fine powder. The fine powder was calcined at 400 °C for 4 h to study the phase formation of the product and stored for further measurements. For identification of $MgFe_{2-x}Er_xO_4$ ($x=0$, 0.02, 0.04, and 0.06), the samples were assigned as MF, MF2, MF4, and MF6 respectively.

2.2. Characterization

The crystal structure of the as-synthesized powder was identified by X-ray measurements with a Bruker D2 Phaser powder X-ray diffractometer with use of Cu K_α radiation ($\lambda = 1.5418$ Å) in the range from 10° to 80° with a step of 0.02°/min. Formation of pure phase was also analyzed with a Bruker ALPHA FTIR spectrophotometer with use of Opus 6.5. For the recording of infrared spectra, powder was mixed with KBr and then pressed into a disc of 1-mm thickness. Infrared measurements were conducted at room temperature in the range from 350 to 1400 cm^{-1}. Information about the oxidation states of these samples was obtained from XPS with use of a Kratos Analytical Axis Ultra DLD instrument with an Al $K_{\alpha1}$ source. The energy of an X-ray photon of 1.486 keV with a pass energy of 160 eV was used for the survey spectrum, and 40 eV was used for narrow scans. We collected the spectra using a combination of electrostatic and magnetic lenses (hybrid mode) for an analyzed area of 700×300 μm. Surface charging effects were minimized by means of a charge balance operating at 3.6 V and 1.8 V maintained as the filament bias. The angle between the normal to the sample surface and the direction of photoelectron collection was 90°. CasaXPS was used for peak fitting, and the procedure used for this analysis was consistent for all of the sample conditions. In brief, a Shirley background was used, and the relative area, full width at half maximum (FWHM), Lorentzian–Gaussian (20% Lorentzian, 80% Gaussian) ratios, and peak positions were allowed to vary. The number of peaks for fitting was manually varied, and the fewest number of peaks that gave a reasonable fit was used for the analysis. The optical properties of the powder samples were investigated with a UV-2102 PCS spectrophotometer. For investigation of magnetic properties, the magnetic measurements were conducted with a Lake Shore 7410 VSM at room temperature with an applied magnetic field of 20 kOe.