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Influence of lanthanum on the optomagnetic properties of zinc ferrite prepared by combustion method

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ABSTRACT

Pure and lanthanum doped zinc ferrite nanoparticles were synthesized by a combustion method using glycine as fuel. The mechanism of formation of these nanoferrites is discussed briefly. The prepared nanoparticles characterized using powder X-ray diffraction analysis (XRD) revealed the formation of cubic spinel phase with high crystallinity. Average crystallite size, X-ray density and bulk density were found to decrease with an increase in La^{3+} concentration. The chemical elements and states on the surface of these ferrites were determined using X-ray photoelectron spectroscopy (XPS). The detailed core level spectra of the photoelectron peaks of Zn 2p, Fe 2p, La 3d and O 1s were analyzed. The magnetic behavior of these nanoparticles was studied using a vibrating sample magnetometer (VSM) and corresponding changes in the saturation magnetization (*Ms*), coercivity (*Hc*) and remanent magnetization (*Mr*) were analyzed. The optical behavior of these ferrite nanoparticles was characterized by UV–Diffuse reflectance studies (UV–DRS). From the UV–DRS studies, the optical band gap was found to be in the range of 1.87–1.97 eV. The combustion method significantly produces large amount of products within a short time. Therefore, this method is potentially suitable for manufacturing industries for preparing the magnetic nanoparticles.

1. Introduction

Researchers have put in much effort to prepare magnetic materials in the order of nanoscale; mainly ferrite based magnetic materials because of their various attractive physical and chemical properties. Ferrite magnetic materials like $ZnFe_2O_4$ (ZFO) is one of the high temperature stable material and finds important applications in the field of data storage technology (memory devices), spintronics, power electronic devices and transformers due to the rapid development in electronic technology [1–5]. In addition, zinc ferrite has excellent optical properties. Due to its smaller band gap (1.9 eV) it can be used in as photo catalyst and also water splitting for hydrogen energy production [6]. This ZFO material comes under spinel type with cubic structure of the general formula $X^{2+}Y_2^{3+}O_4$ where X and Y refer to the metal ions that occupy in tetrahedral and octahedral sites, respectively. Recently it has been published that rare earth doped zinc ferrite compounds are highly susceptible to magnetization and are employed in applications for magnetic data storage devices. Different synthesis route like multi-step homogeneous non-aqueous solution synthesis method [7], conventional ceramic technique [8], citrate precursor method [9], co-precipitation [10], sol–gel [11], ball milling method [12], wet-milling process [13], mechanochemical reaction [14] etc. have been reported for nanoscale ZFO materials. In particular, one of the wet chemical techniques is the combustion method which enables fast reaction rate, chemical homogeneity and high reactivity. In previous reports combustion method with various types of fuels has been used to prepare the pure and various transition/rare earth doped ZFO. However, no reports have been published on producing lanthanum doped zinc ferrite by the combustion method using glycine as fuel. In the present work, we report the synthesis of ZFO and various concentrations of lanthanum doped zinc ferrite nanoparticles by the combustion method with glycine (NH_2CH_2COOH) as a fuel. Furthermore, the structural, magnetic, optical, surface elements and oxidation states of the prepared samples were also studied using XRD, XPS, VSM and UV–DRS.

2. Experimental

2.1. Synthesis

Pure and lanthanum doped zinc ferrite nanoparticles were synthesized by the combustion method. The starting precursors namely zinc nitrate hexahydrate purified ($Zn(NO)_2 \cdot 6H_2O$, 96%

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purity, Merck), Iron (III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, 98–100% purity, Alfa Aesar), Lanthanum nitrate ($La(NO_3)_2 \cdot 6H_2O$, 99% purity, Alfa Aesar) were employed as oxidizing agent and fuel glycine ($C_2H_5NO_2$, 98.5% purity, Qualigens) acts as a reducing agent which drives the combustion process. All analytical reagents were used without further purification.

Based on the concepts of propellant chemistry, the oxidizing and reducing valences of different elements are as follows: Zn = +2, N = 0, O = −2, Fe = +3, C = 4, H = 1. In the glycine to nitrate reaction, total reducing valence of glycine (NH_2CH_2COOH) is +9 and total oxidizing valence of nitrates is −40. Therefore, fuel (NH_2CH_2COOH)-nitrates composition becomes $2\times(-15)+1\times(-10)+n(+9)=0$, $n=4.44$ mol in the reaction. Hence, fuel-nitrate composition indicates Glycine/NO^{3-} = 1.48 (Glycine-to-nitrate ion ratio). The chemical reaction at equilibrium conditions can be expressed as given below:

$$Zn\ (NO_3)_2 \cdot 6H_2O + (2\text{-}x)\ Fe\ (NO_3)_3 \cdot 9H_2O + x\ La\ (NO_3)_2 \cdot 6H_2O + 4.44\ NH_2CH_2COOH \rightarrow ZnFe_{2-x}La_xO_4 + 5.72N_2\uparrow + 8.88CO_2\uparrow + 11 \cdot 1H_2O\uparrow \quad (1)$$

In this present work, we consider stoichiometric amount of fuel to nitrates composition as 1.48; this results in the formation of pure and lanthanum doped zinc ferrite nanoparticles.

At first, stoichiometric amounts of starting precursors like zinc ferrite ($Zn\ (NO_3)_2 \cdot 6H_2O$), ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) and lanthanum nitrate ($La(NO_3)_2 \cdot 6H_2O$) were dissolved in 20 ml of distilled water at room temperature. 10 ml of nitric acid (HNO_3) was slowly added into the solution and then stirred for 30 min to get a clear aqueous solution. Then glycine ($C_2H_5NO_2$), which acts as fuel was added to the solution in the ratio of 1.48 (glycine-to-nitrates ion ratio). The solution was stirred with heating at 100 °C for 2 h using magnetic stirrer until the water slowly evaporated and becomes a dark brown viscous gel. The obtained dark brown viscous gel was kept on a hot plate at 200 °C for 10 min, when critical temperature is reached the foams and sparks were ignited to form dried brown powders with the evolution of gaseous fumes. After completion of the combustion process, brownish ferrite nanopowders were obtained. The time taken for actual ignition and the end of the reaction during combustion process was less than 20 s. Finally, as-prepared nanoscale zinc ferrites samples were kept out of hot plate and ground using an agate mortar and pestle to form fine powders. The fine powders were stored for characterization.

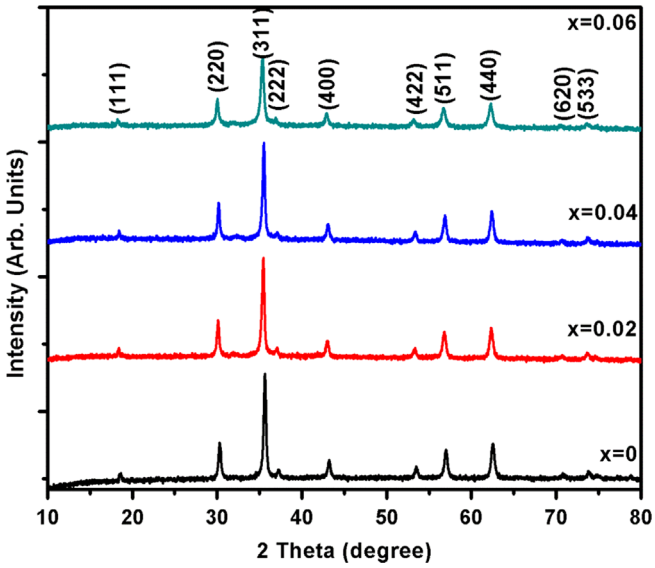

Fig. 1. X-ray diffraction pattern of the as-prepared $ZnFe_{2-x}La_xO_4$ (x=0, 0.02, 0.04, 0.06) nanoparticles by the combustion method using glycine as fuel.

2.2. Characterization

The crystal structure of the as-synthesized powder was identified by X-ray measurements of Bruker D2 Phaser Powder X-ray diffractometer using CuKα radiation (λ=1.5418 Å) in the range of 10° to 80° with step mode of 0.2/min. Information about the oxidation states of these samples was obtained from X-ray photoelectron spectroscopy (XPS) using Kratos Analytical Axis Ultra DLD with Al Kα1 source. The energy of an X-ray photon of 1.486 keV with pass energy of 160 eV was used for the survey spectrum and 40 eV for narrow scans. The spectra were collected using the combination of electrostatic and magnetic lens (hybrid mode) for an analyzed area of (700 × 300 μm). The angle between the normal to the sample surface and the direction of photoelectron collection are perpendicular to each other. Surface charging effects were minimized using a charge balance operating at 3.6 V and 1.8 V maintained as filament bias. For magnetic properties, the magnetic measurements were carried out using the vibrating sample magnetometer (VSM) Lakeshore (7410) at room temperature with an applied magnetic field of 20 kOe. The optical properties of the investigated powder samples were performed by a UV-2102 PCS Spectrophotometer.

3. Results and discussion

3.1. XRD studies

The structural identification was performed using XRD analysis. The powder X-ray diffraction (XRD) patterns of ZFO with different chemical compositions of La^{3+} are shown in Fig. 1. All the diffraction peaks indicate the formation of cubic spinel structure (JCPDS Card no. 82-1042) for all the samples. The broad XRD peak shows that the prepared samples are of nanosize. No additional or impurity phase corresponding to any structure were detected in the XRD pattern. The average crystallite size, X-ray density, lattice constant, surface area, bulk density and porosity obtained from the XRD data are listed in Table 1. The average crystallite size (d) of the ferrite samples with the above mentioned dopant concentration was estimated from the width of the prominent (311) reflection using Scherrer formula [15].

$$d = 0.9\lambda/\beta\ \cos\ \theta \quad (2)$$

Table 1
Structural parameters of $ZnFe_{2-x}La_xO_4$ (x=0, 0.02, 0.04, 0.06) nanoparticles by the combustion method.

x	Average crystallite size (d) (nm)	X-Ray density(d_X) (g/cm^3)	Surface area (S) (m^2/g)	Bulk Density (d_B) (g/cm^3)	Lattice constant (a) (Å)	Porosity (P)	Band gap (Eg) (eV)
0.0	37.6	5.46	29.23	4.42	8.361	0.19	1.87
0.02	36.9	5.45	29.79	2.09	8.374	0.62	1.89
0.04	35.4	5.44	31.12	1.67	8.398	0.69	1.93
0.06	27.4	5.43	40.41	1.31	8.415	0.74	1.97

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