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Effect of rare earth (Lanthanum) substitution on Copper ferrite Nanoparticles

S. Deepapriya [1], P. Annie Vinosha [1], John.D.Rodney [1], S.Krishnan [2], J. Ermine Jose [3], S. Jerome Das [1,]*

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Abstract

In this study, we have focused on the influence of lanthanum doped and undoped copper ferrite nano crystal on the structural and magnetic properties, which were prepared using a facile co-precipitation technique. The effect of lanthanum doped and undoped $CuFe_2O_4$ nanocrystal was studied by XRD, FTIR, TEM and VSM. The doping of rare earth element influences the change in the structural characteristics of the samples (density and porosity). In Fourier Transform Infrared spectrum, two absorption bands were observed at ∼400 and ∼500 cm^{-1} which represents the tetrahedral and octahedral sites. By Transmission Electron Microscopy, the particle size was found to be varying from that of crystallite size calculated from XRD and the morphology of the synthesized samples were observed. The results reveal that on doping lanthanum in $CuFe_2O_4$tend to increase in coercive field, saturation magnetization and retentivity was observed, these results can be partially explained by the weaker nature of the La^{3+}–Fe^{3+} interaction compared to Fe^{3+}–Fe^{3+} interaction.

Keywords: co-precipitation, Lanthanum, XRD, FTIR, TEM, VSM

1 Introduction

Nanostructured materials reveal sporadic physical and chemical properties, significantly diverse from those of conventional bulk materials, due to their enormous small size or large specific surface area. So, their preparation and characterization have engrossed growing attention in the past decade[1]. Copper ferrite ($CuFe_2O_4$) is a well-known spinel magnetic material and has been intensively studied because of the fundamental understanding as well as their applicability in various areas such as magnetic refrigeration, catalysts, gas sensors and medical diagnostics [2]. Addition of rare earth ions to undoped copper ferrite enhances vast functional applications. Copper ferrites possess notable inquisitiveness physical properties, high coercivity, saturation magnetization and high Curie temperature among inverse spinel ferrites[3]. Inverse spinel ferrite transmits discrete properties due to its cubic closed pack structure with divalent and trivalent cations linked in two sub-lattices namely tetrahedral (A) and octahedral (B). Several procedures have been used to synthesis nanocrystalline inverse spinel ferrites such as sol–gel, co-precipitation, hydrothermal, combustion, mechano-chemical, microemulsion method, etc[4]. Different synthesis routes are used to govern the composition and microstructure of soft ferrite particles for various applications. In this study, a facile co-precipitation method have been chosen to understand the magnetic properties of inverse spinel ferrites for Lanthanum doped copper ferrite and undoped copper ferrite, were this a cost effective and simple method to control the particle size distribution by controlling the relative rates of nucleation and growth in the synthesis technique[5].

2 Experimental techniques

2.1 Synthesis

Lanthanum doped copper ferrite and undoped copper ferrite nanoparticles ($CuFe_2O_4$& $CuLaFe_2O_4$) were prepared by co-precipitation technique. $Fe(NO_3)_3.9H_2O$, $La(NO_3)_3.3H_2O$ and $Cu(NO_3)_2.6H_2O$ were bought from commercial sources as analytical reagents and used without further purification in appropriate proportions as starting materials. The reactant solutions were dissolved in distilled water and stirred using a magnetic stirrer to obtain a homogenous mixture. A mineralizer NaOH was added in order to maintain constant pH of 10 throughout the synthesis process. The liquid precipitate was stirred and heated at 80 ^oC for 1 hour. The obtained precipitate was then cooled to room temperature. To divest from excess impurities and nitrate ions, the precipitate was centrifuged twice with distilled water and once in ethanol solution. The precipitate was then annealed at 75 ^oC for 10 hours and grounded to powder. The dried nanoparticles were then calcined at 500 ^oC for 3 hours to obtain the final nanoparticles.

2.2 Characterization

The microstructural characterization and chemical composition of the samples were analysed by X-ray diffraction pattern (XRD) using a BRUKER X-ray powder

* Corresponding author: e-mail jeromedas.s@gmail.com,
[1]Department of Physics, Loyola College, Chennai- 600 034, India
[2]Department of Physics, Ramakrishna Mission Vivekananda College, Chennai-600 004, India
[3]Loyola - ICAM College of Engineering and Technology, Loyola Campus, Chennai-600 034, India

diffractometer with CuKα radiation (λ = 1.5418 Å). The surface morphology and particle size distribution of all samples were analysed by JEOL Transmission Electron Microscope (TEM) (model JEM 2100). The functional groups were identified by Fourier transform infrared spectra (FT-IR) using Perkin-Elmer Spectrum System in the range of 400–4000 cm^{-1}.The Optical properties were analysed by Diffused reflectance spectra using UV-Visible spectrometer (Perkin-Elmer Lambda, model 1050). The magnetic behaviour of the samples was investigated by vibrating sample magnetometer (VSM) Lakeshore VSM 7407 at 300 K with the maximum applied field of 10 kOe.

3 Results and Discussion

3.1 X-ray Diffraction

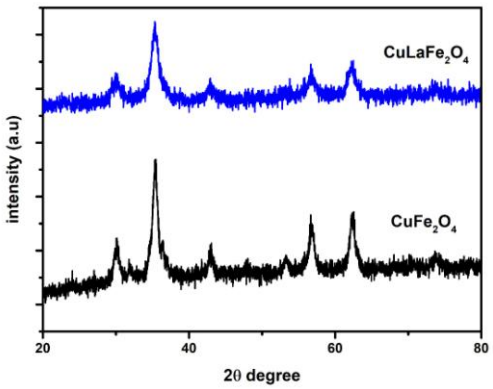

Figure 1X-ray Diffraction of $CuLaFe_2O_4$ and $CuFe_2O_4$

The phase compositions of the lanthanum doped and undoped copper ferrite nanoparticles was studied by using the XRD pattern with CuKα radiations are shown in Fig. 1. The diffraction peaks correspond to the crystal indexes of (220), (311), (222), (400), (422), (511) and (440) planes of the spinel ferrite with a cubic symmetry[6], shows the formation of lanthanum doped and undoped copper ferrite. (JCPDS card no 34 - 0425). A slight shift in the peak value has been observed as the La^{3+}substituted in copper ferrites. The shift in the peak angle indicates the cation occupies lattice sites and this relates with the Bragg's law[7]. Addition of La^{3+} ions signifies an effective increase in the value of lattice parameter, crystallite size and surface to volume ratio, indicates peak broadening decreases the density in Copper ferrite nanoparticles[8]. The increase in the crystallite size is studied by the doping of rare earth ions. The crystallite size was calculated using Scherrer formula,

$$D = \frac{k\lambda}{\beta \cos\theta} \qquad (1)$$

The substitution of La^{3+} ions with larger ionic radii, increases the lattice constant and cell volume compared to Fe^{3+}ions. This might be due to the diffusion of ions in grain boundaries devising an insulating narrow layer throughout the grains, with reduction of spin lattices [9]. The average crystallite size (D) of each as-synthesized sample was found in the range between 11 to 14 nm. Table 1 shows the average crystallite size of lanthanum doped copper ferrite increases compared to that of undoped copper ferrite. The lattice parameters are calculated using,

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \qquad (2)$$

where'd' is the inter-planar distance, 'a' is the lattice constant and 'h', 'k', 'l' are the miller indices.

Table 1 Crystallite size and lattice parameters of as-synthesised materials

Sample	Crystallite size (nm)	Lattice parameter	Crystal symmetry
$CuFe_2O_4$	11	8.126	cubic
$CuLaFe_2O_4$	14	8.356	cubic

3.2 TEM

The surface morphology of lanthanum doped and undoped copper ferrite nanocrystals were examined using Transmission electron microscope. The micrographs show that majority of nanoparticles are in spherical shape and are shown in Fig. 2.

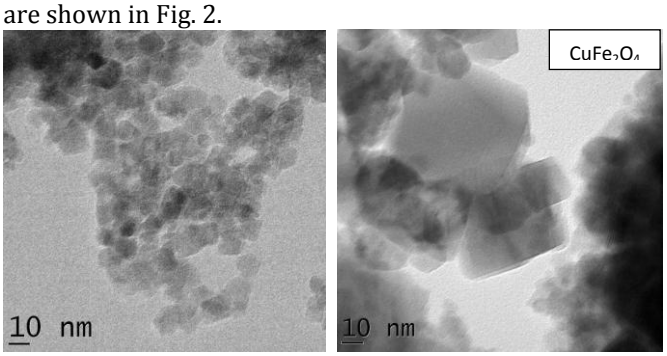

Figure 2 TEM micrograph of as-synthesised material

The nanoparticles exhibit narrowed particle distribution with an average size in relation with crystallite size calculated from XRD. Presence of magnetic property is due to the agglomeration and weak interaction of vander-walls force of as-synthesised material[10]. Copper ferrite possesses spinel structure with requisite consideration, electrical and magnetic properties[11]. Formation of ferrite nanoparticles have been studied, when the nucleation growth is higher than the growth rate.

3.3 FTIR Analysis

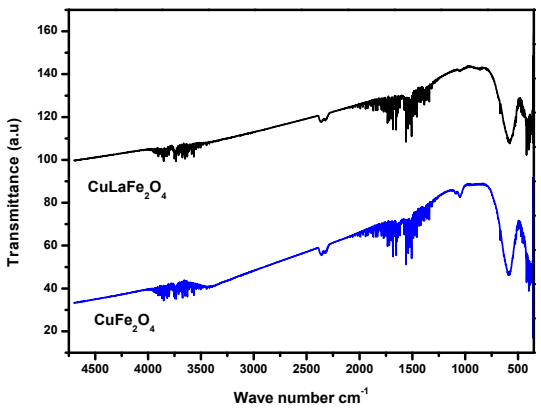

Figure 3 FTIR spectra of as-synthesised materials

The infrared spectra of $CuLaFe_2O_4$ and $CuFe_2O_4$ are shown in Fig. 3. The major bands in FTIR spectra in the range 350 – 800 cm^{-1} are high frequency band υ_1 in the range 563 – 576 cm^{-1} and lower frequency band υ_2 in the range of 435 – 472 cm^{-1}, exhibits common characteristics of inverse spinel structure[12]. As Waldron suggested, the vibration of cubic spinel can be considered in tetrahedral (A) and octahedral site (B), indicating the absorption band v_1 caused by stretching vibrations of metal oxygen bond in tetrahedral site and absorption band v_2 by metal oxygen bond in octahedral site. The difference in Fe^{3+} - O^{2-} distance for the tetrahedral and octahedral sites shows change in band position [13]. The absorption band v_2 shifts to higher frequency range for the lanthanum doped copper ferrite sample. The absorption band v_2 broadens and the intensity decreases, indicating the habitation of La^{3+} on octahedral B site. Broader and less intense band in IR spectra shows that the system is in high disorder state.

3.4 VSM

The hysteresis loop obtained from VSM measurements for lanthanum doped copper ferrite and undoped copper ferrite nanoparticles at room temperature with a magnetic field up to 10 kOe are shown in Fig. 4.

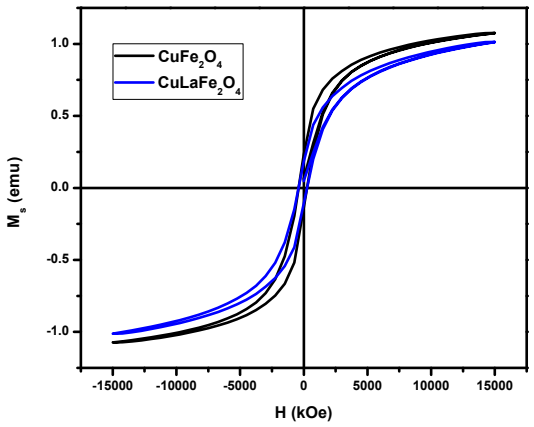

Figure 4 VSM of as-synthesised materials

The low value of M_R/M_S ratios indicate considerable fraction of superparamagnetic particles. Very small particles of ferromagnetic or ferromagnetic nanoparticles exhibit superparamagnetism character[14]. The saturation magnetisation (Ms), coercivity (Hc) and retentivity (Mr) depend on the particle size, as the particle size decrease, the coercive field and saturation magnetisation also decreases[15]. However, the susceptibility and anisotropy have been noted to increase. The values of saturation magnetisation (Ms), coercivity (Hc) and retentivity (Mr) of the as-synthesised $CuFe_2O_4$ and $CuLaFe_2O_4$ are shown in Table 2. Ordering of ionic spin states and the presence of ferromagnetic character is revealed from the hysteresis curve[16]. It has been observed that the saturation magnetization and coercivity increases. This indicates the domain formation.

Table 2 Various parameters obtained from VSM studies

Sample	Saturation magnetization (Ms)	Coercivity (Hc)	Retentivity (Mr)
$CuFe_2O_4$	0.42641	318.29	58.32
$CuLaFe_2O_4$	0.72887	409.14	72.15

4 Conclusions

In this study, we investigated the influence of lanthanum doped and undoped $CuFe_2O_4$ on the structural and magnetic properties obtained via facile co-precipitation technique. The crystallite size was determined around 11 – 14 nm and lattice parameters was calculated using XRD. The impurity phase of crystalline structure has been increased in the lanthanum doped $CuFe_2O_4$ when compared to undoped $CuFe_2O_4$. The TEM micrographs indicate the morphology of as-synthesised nanocrystals with agglomeration, elucidates strong magnetic properties. FTIR verify the presence of functional group and absorption band v_2 shifts to higher frequency range for the lanthanum doped copper ferrite sample. This confirms La^{3+} occupies the octahedral B site. The increase in saturation magnetisation, retentivity and coercivity was observed using VSM studies, substantiates the formation of domains and ferromagnetic nature in ionic states.

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