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Influence of copper ions on structural and non-linear optical properties in manganese ferrite nanomaterials

S. Yuvaraj, N. Manikandan, G. Vinitha*

Division of Physics, School of Advanced Sciences, VIT University, Chennai Campus, Chennai 600127, India

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ABSTRACT

A series of $Mn_{1-x}Cu_xFe_2O_4$ (x = 0, 0.15, 0.30, 0.45, 0.60 and 1) particles were prepared using chemical co-precipitation method with metal nitrates as precursor materials. Samples were synthesized under various annealing temperatures and 800 °C was found to be the optimal temperature for phase formation. Powder XRD analyses confirm the formation of spinel manganese ferrites along with the α-Fe_2O_3 phase which got reduced with increase in copper concentration. Samples were characterized using spectroscopic and microscopic techniques. UV-Diffuse reflectance spectroscopy was employed to calculate the band gap which varied between 1.51 eV and 1.83 eV. HR-SEM images reveal the spherical nature of the particles. Ferromagnetic nature of these materials was confirmed from vibrating sample magnetometer (VSM) measurements. Z-scan technique was employed to measure the non-linear optical properties. The non-linear refraction, non-linear absorption and non-linear susceptibility are found to be of the order of 10^{-8} cm^2/W, 10^{-4} cm/W and 10^{-6} esu respectively. The samples showed a defocusing effect which was utilized to explain the optical limiting behavior at the same wavelength using the continuous-wave laser beam. The results show that these materials have potential for exploitation towards device applications like optical limiting and switching.

1. Introduction

The current trend in research deals with nanomaterials which are widely used for technological applications. In general, metal-oxide nano particles which vary from their bulk particles draw considerable interest due to their unique properties [1]. Since produced by Snock in 1935, nano structured ferrites especially spinel ferrites are examined for their extraordinary features of electrical, optical and structural characteristics [2,3]. The crystal structure of Spinel ferrite is AB_2O_4, where A denotes tetrahedral site and B denotes octahedral site. The unit cell of spinel ferrites comprises of 32 octahedral sites and 64 tetrahedral sites. Lattice consisting of 8 tetrahedral sites filled by divalent metal ions and 16 octahedral sites filled by trivalent iron ions aid in maintaining electrical neutrality in these samples [4].

Manganese ferrites possess impressive properties such as outstanding chemical stability, large saturation magnetization, prominent magneto – crystalline anisotropy and elevated mechanical hardness that makes them unique among all the spinel ferrites [5]. Manganese ferrites are frequently used for microwave and magnetic recording applications owing to their excellent magnetic behavior [6]. These samples were also found to show good electromagnetic absorbent properties leading to their application in wide areas [7]. Consequently, it is reasonable to investigate $MnFe_2O_4$ nanomaterials for various other applications.

Numerous synthesis approaches have been used for the preparation of $MnFe_2O_4$ nanocrystals, such as microwave-assisted ball mill [8], sono chemical [9], hydrothermal [10], sol-gel auto combustion [11], ultrasonic [12], solvothermal [13], thermal decomposition [14] and co-precipitation [15]. Among all the wet chemical methods in use, co-precipitation method is most preferable in view of the fact that it is more cost effective, non-hazardous and involves low level of toxic materials with high productivity of ferrite nanoparticles [15].

Recent research has shown that nanomaterials show better non-linear effects compared to their bulk counterparts [16]. These low dimensional materials with large nonlinear responses can be used in various applications like photocatalysis and optical limiting [17,18]. Magnetic nanomaterials have attracted substantial attention as optical limiters since the optical properties of such opto-electronic devices are controllable by an external stimulus such as magnetic field [19]. Optical nonlinearities in ferrites are relatively

* Corresponding author.
E-mail address: vinitha.g@vit.ac.in (G. Vinitha).

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unexplored compared to metals, semiconductors and organometallic compounds [20]. Modifications in optical nonlinearity caused by the inclusion of different transition metals into a spinel ferrite system would be of considerable interest owing to their applications in the field of optics.

Z-scan is an accurate system to find out the nonlinear optical response of the material. Closed aperture scan provides information about both nonlinear refraction and absorption, while the open aperture yields the values pertaining only to nonlinear absorption of the materials [21]. This nonlinearity observed in materials is due to their intensity-dependent absorption and refraction [22].

In this paper, $Mn_{1-x}Cu_xFe_2O_4$ ferrite powders with x = 0, 0.15, 0.30, 0.45, 0.60 and 1.0 were prepared using chemical co-precipitation route and their nonlinear properties were studied. To the best of knowledge of the authors, it is the initial article which reports the optical nonlinearity of Cu^{2+} substituted Mn ferrites and their device realization.

2. Samples

2.1. Materials

For the chemical co-precipitation route, manganese (II) nitrate monohydrate (Min. 98%, Himedia), copper (II) nitrate tetrahydrate (Min. 98% Himedia) and iron (III) nitrate hexahydrate (Min. 98%, Himedia) were employed as starting materials. Sodium hydroxide was taken as precipitating agent. To make the entire solution, double distilled water was used and all received chemicals were used without any further refinement.

2.2. Synthesis of nanocrystalline $Mn_{1-x}Cu_xFe_2O_4$ ferrite

The proposed nano-sized ferrites were prepared by chemical co-precipitation route, using pure materials: (0.1 M) Manganese (II) nitrate, (0.1 M) Copper (II) nitrate, (0.1 M) Iron (III) nitrate. The ratio between Fe and MnCu was kept at 2:1 respectively. All the starting pure materials were dissolved one by one in double distilled water and mixed together to form aqueous solution. The aqueous solution of 3 M NaOH was slowly poured into the mixed solution under stirring at a temperature of 100 °C. pH was maintained at 11–12 for all the cases to make the entire metal cations precipitated. The mixture was then heated at 120 °C for one and half an hour before cooling down slowly to room temperature. Black precipitates were obtained in this routine. To eliminate impurities, the product was frequently washed by using double distilled water and ethanol. Hot air oven maintained at 100 °C for 24 h was used to dry the samples. Finally the black color powder was obtained which was annealed at 800 °C for 5 Hours. The same method was adopted for all the compositions.

3. Results and discussion

3.1. Phase analysis

XRD structural pattern of the analyzed samples are as represented in Fig. 1. According to the XRD results of synthesized samples, one can state that the combination of α-Fe_2O_3 and $MnFe_2O_4$ phase exists for the concentration x = 0 (Fig. 1(a)). The sample x = 0.15 (Fig. 1(b)) clearly shows the bragg reflection peaks related to the hkl planes of (220), (311), (222), (400), (422), (511) and (440) indicating the structural formation of Mn–Cu spinel ferrites along with the cubic symmetry which is marked as '●' and has been confirmed with JCPDS (Card No: 74-2072). The minor peaks with the symbol which is marked '*' is related to α-Fe_2O_3 (as per JCPDS data 84-0307). As reported in Ref. [23], if metal nitrates are used as

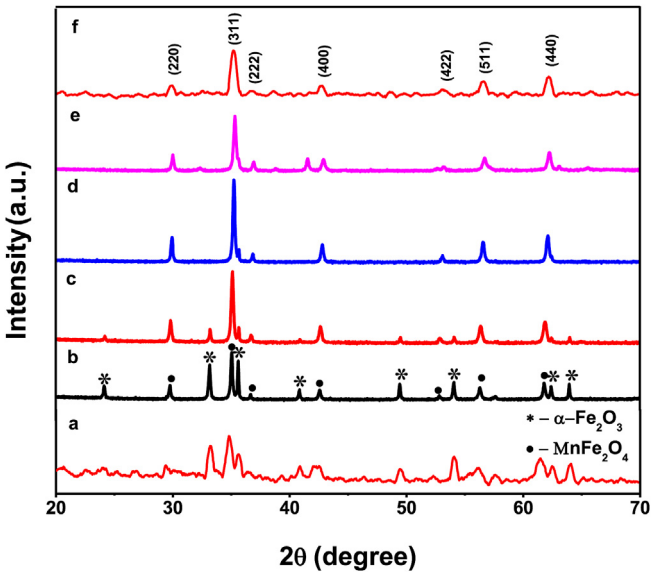

Fig. 1. Phase diagram of (a) $MnFe_2O_4$ (b) $Mn_{0.85}Cu_{0.15}Fe_2O_4$ (c) $Mn_{0.70}Cu_{0.30}Fe_2O_4$ d) $Mn_{0.55}Cu_{0.45}Fe_2O_4$ (e) $Mn_{0.40}Cu_{0.60}Fe_2O_4$ and (f) $CuFe_2O_4$ sample.

raw materials, it needs high annealing temperature of around 1200 °C to form pure phase.

It was noted that when the sample was annealed at more than 500 °C, Cu doped manganese ferrite exhibits few minor impurity peaks which demonstrates the decomposition of the ferrites to α-Fe_2O_3 phase. It was observed that when the annealing temperature is made higher than 900 °C, the secondary minor peaks start to slowly disappear and it may completely disappear when the temperature is elevated beyond 1200 °C [24]. For the composition x = 1.0, which is a copper ferrite, pure phase is obtained.

The degree of crystallinity is determined from the diffracted peak of nano ferrite at the hkl plane (311) which exhibits the highest intensity. The effective crystallite size of $Mn_{1-x}Cu_xFe_2O_4$ samples were evaluated via applying the Debye–Scherrer formula,

$$L = \frac{0.89\lambda}{\beta cos\theta}$$

Where θ is the diffracted angle of the highest intensity peak, β is the full width at half maxima (FWHM) and λ is wavelength of the X-ray. The calculated results exposed that the pure $MnFe_2O_4$ possesses smaller crystallite size (21.72 nm). Addition of copper ions showed variations in particle size ranging from 12 to 51 nm (See Fig. 2). The range of effective crystallite size expresses the fluctuation with raising copper percentage in manganese ferrites. In 2015, similar kind of findings was recorded by Appas et al. for zinc doped manganese ferrites [44].

X- ray diffraction data is used to find out the lattice parameter (a) from the formula,

$$\frac{1}{a^2} = \frac{1}{d^2}\left(h^2 + k^2 + l^2\right)$$

Table 1 presents the estimated amount of lattice constant (a) and crystallite size for all the Cu^{2+} concentrations. Increase of copper ions in $MnFe_2O_4$, gradually reduced the lattice constant from 8.545 Å to 8.420 Å.

The relative ionic radius describes the reason behind the continuously decreasing rate of lattice constant with linear increase in the copper percentage. The divalent manganese ions contain larger ionic radius (0.63 Å) compared to divalent copper ionic