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Effect of iron substitution on structural, magnetic and nonlinear optical properties of zinc chromite nanoparticles

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ABSTRACT

In this paper we report the structural, magnetic, nonlinear optical properties of iron substituted zinc chromite nano crystalline mixed ferrites prepared by sol-gel technique. The XRD patterns revealed the absence of any impurity peak and points to the formation of pure cubic spinel structure in all the compounds. Magnetic analysis using Vibrating Sample Magnetometer showed a change in magnetic behavior from paramagnetism to super paramagnetism as the concentration of Fe^{3+} ion got increased from (x = 0.00 to x = 2.00) Zero Field Cooling (ZFC) and Field Cooling (FC) was used to confirm the super paramagnetic behavior of $ZnFe_2O_4$ nanoparticles. The optical limiting properties are investigated using the open aperture z-scan technique. The optical nonlinearity increased and the material shows better optical limiting characteristics at higher iron doping concentrations. The values of optical limiting parameters of iron substituted zinc chromite nano composite makes it a potential material for the development of nonlinear optical devices with a relatively small limiting threshold. To the best of our knowledge a systematic variation of the optical limiting property with doping concentration has not been reported elsewhere.

1. Introduction

The interesting properties of spinel ferrites depend on the nature of ions and the site distribution of the ions among the tetrahedral and octahedral sites. Significance of spinel ferrites in the nano regime lies in the interesting structural, magnetic and electrical properties which differ from their bulk counter parts [1]. Various methods are used for the preparation of ferrite nanoparticles of which sol-gel technique is a simple and cost effective technique for preparing ferrite nanoparticles [2]. Effect of chromium ion substitution in spinel ferrites have been reported by many researchers. Costal et. al [3] reported effect of chromium ion concentration in Ni-Zn ferrite. The variation of magnetic properties of lithium ferrite with chromium content was reported by Fu et. al [4]. Oles [5] investigated the structural features of $ZnCr_{2-x}Fe_xO_4$ nano powders synthesized by ceramic method. Borhon et. al [6] also have reported the influence of chromium ion on the structural and electrical properties of zinc ferrite.

The main objective of our study was to synthesize the phase pure Nanocrystaline particles with general formula, $ZnCr_{2-x}Fe_xO_4$ (x = 0.00, 0.40, 1.00, 1.40, 2.00), by sol–gel technique and to study their structural, magnetic and nonlinear optical properties. Reports on nonlinear optical properties of ferrites are rare in literature.

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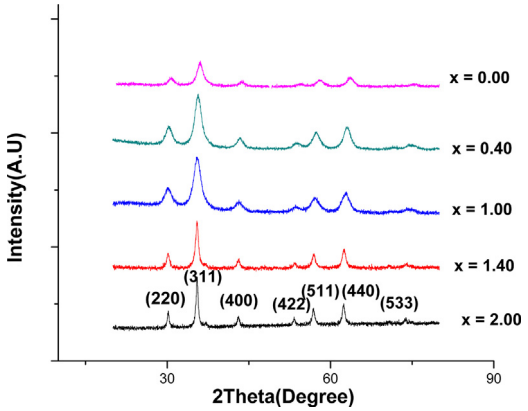

Fig. 1. XRD patterns for all the samples of the series $ZnCr_{2-x}Fe_xO_4$.

Table 1
Variations of crystallite size, lattice constant and X-ray density for $ZnCr_{2-x}Fe_xO_4$ System.

Composition (x)	Lattice Constant (Å)	Crystallite Size (nm)	X-ray Density (ρ_x) (gm/cm^3)
0.00	8.282	6.27 ± 0.05	5.46
0.40	8.336	5.94 ± 0.12	5.41
1.00	8.374	6.13 ± 0.18	5.37
1.40	8.410	12.90 ± 0.17	5.35
2.00	8.433	18.64 ± 0.32	5.34

2. Synthesis of nanoparticles

Iron substituted zinc chromite with general formula $ZnCr_{2-x}Fe_xO_4$ (x = 0.00, 0.40, 1.00, 1.40, 2.00) was synthesized using AR grade zinc nitrate, chromium nitrate, ferric nitrate in ethylene glycol as solvent. The details of the preparation technique are explained in our previous work [7]. The finely grounded powders were sintered at 400 °C for two hours. For optical nonlinear studies the finely grounded nano particles were dispersed in pure ethylene glycol at 1.5 μM/L.

3. Results and discussion

3.1. X-ray diffraction studies

The X-ray analysis of the prepared samples of the series $ZnCr_{2-x}Fe_xO_4$ (x = 0.00, 0.40, 1.00, 1.40, 2.00) revealed that single phased fcc spinel structure without any impurity phase. Fig. 1 represents the XRD patterns of $ZnCr_{2-x}Fe_xO_4$ series.

Average crystallite size of the prepared samples are calculated using the Scherrer formula [8].

$$D = \frac{0.9\lambda}{\beta cos\theta} \tag{1}$$

where λ is the wavelength of the X- ray source, β is the full width at half maximum, θ is the braggs angle for the specific peak.

The lattice constant 'a' is calculated using the equation [9].

$$a_{311} = d_{311}\sqrt{h^2 + k^2 + l^2} \tag{2}$$

The X-ray density (d_x) of the prepared samples is calculated using the equation [10]

$$d_x = \frac{8M}{Na^3} \tag{3}$$

M is the molecular mass of the sample, N the avagadro number and a is the lattice constant. The variation of the crystallite size, lattice constant and X-ray density of the $ZnCr_{2-x}Fe_xO_4$ series is presented in Table 1.

From, the Table 1 it is clear that the lattice constant increased with increase in iron content, which results from the expansion of the unit cell caused by the replacement of Cr^{3+} ions of smaller ionic radius (rCr^{3+} = 0.615Å) by Fe^{3+} ions of higher atomic radius (rFe^{3+} = 0.654Å) [6]. Crystallite size was found to increase with increase in the iron content. The X-ray density was found to decrease with increase in iron content, which is attributed to the expansion of the lattice as a result of the replacement of Cr^{3+} ion by Fe^{3+} ion.