

Effect of Al-Cr Co-doping on the Structural Properties of Nickel Ferrite Nanoparticles

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Abstract: Investigations on the structural properties of Al-Cr co-doped nickel ferrite nanoparticles have been carried out in the present work. A simple, inexpensive and yielding high quality fine powder sol-gel auto combustion technique was employed for the synthesis of Al-Cr co-doped nickel ferrite nanoparticles. The prepared nanoparticles were characterized by X-ray diffraction technique (XRD) for structural analysis. XRD pattern reveals the formation of single phase with cubic spinel structure. The crystalline size of pure and Al-Cr co-doped nickel ferrite nanoparticles were calculated using Scherrer's formula and was found to be 55 nm and 38 nm respectively. The other structural parameters such as lattice constant, unit cell volume, hopping lengths and interstitial radii were also calculated and reported here.

Index Terms - Nickel ferrite nanoparticles, Al-Cr co-doping, XRD.

I. INTRODUCTION

The magnetic properties of spinel ferrite nanoparticles have been of great concern in recent years due to the nanosize constituent particles or crystallites. The magnetic properties of the ferrite nanoparticles are found to undergo changes due to superparamagnetism, surface screen effects and also with their cation distribution which depend on synthesis method. Much attention has been devoted on investigations of nanosized spinel ferrite particles because of their potential applications in several areas of microwave devices, recording media, magneto fluids, catalysis, magneto refrigeration systems and gas sensors [1-2]. Magnetic nanoparticles of spinel ferrite are found to be thermally and chemically stable, that's why they deserved their applicability in special kind of applications.

Among the various spinel ferrites, the inverse spinel is particularly interesting because of its high magneto-crystalline anisotropy, high saturation magnetization, high electrical resistivity, low eddy current and dielectric losses and unique magnetic structure. NiFe_2O_4 is a cubic ferrimagnetic oxide which has an inverse spinel structure where Ni^{2+} ions occupy octahedral B-sites and Fe^{3+} ions occupy both tetrahedral A-sites and octahedral B-sites. Normally, inverse spinel structure is found in bulk nickel ferrite. Nickel ferrite when prepared in nanosize form, the small particle size promotes a mixed spinel structure. It shows ferrimagnetism that originates from magnetic moment of anti parallel spins between Fe^{3+} ions at tetrahedral sites and Ni^{2+} ions at octahedral sites. The nickel ferrite in the ultra-fine form exhibit non collinear spin structure and magnetic moment at low temperature is appreciably lower than the value for the bulk material.

Nickel ferrite has received much attention because it is widely used in spintronics, microwave absorption, catalysis, gas sensors, and lithium ion batteries and even in biomedicine [3]. Recently, nickel ferrite nanoparticles with various particle sizes, surface areas, and morphologies have been prepared by many wet chemical methods such as sol-gel, co-precipitation, microemulsion, hydrothermal, microwave, etc [4].

Among the developed methods, sol-gel auto combustion method have special attention for the preparation of nickel ferrite nanoparticles because of many advantages like rapid heating, shorter time, fast reaction, easy reproducibility, particle size and shape control, high yield, high purity, efficient energy transformation and volume heating [5]. Considering the importance of nickel ferrite in many technological applications, the present work reports the effect of co-doping of trivalent ions i.e. Al-Cr on structural properties of nickel ferrite nanoparticles..

II. EXPERIMENTAL METHOD

Materials

Nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), Aluminium nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), Chromium nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and citric acid were used as a raw materials for sol-gel auto combustion synthesis of Al-Cr co-doped nickel ferrite nanoparticle. All the reagents used for the synthesis were of analytical grade (AR) and used as received without further purification.

Preparation

Al-Cr co-doped nickel ferrite nanoparticle were synthesized by sol-gel auto combustion method using citric acid as a fuel. The stoichiometric proportions of metal nitrates to fuel (citric acid) ratio as 1:3 were taken into separate glass beakers. The mixed solution was stirred for 20 - 25 minutes to dissolve completely into distilled water. After complete dissolution they were mixed together. Ammonia was added drop-wise into the solution to adjust pH value at 7 and stabilize the nitrate-citric acid solution. Then the neutralized solution was constantly magnetically stirred and heated at 90°C - 100°C for 6 h on a hot plate. On the formation of sol-gel, very viscous gel the temperature was further raised up to 110°C so that the auto combustion of the dried gel started and finally powder was obtained.

Characterizations

The prepared nanoparticle of Al-Cr co-doped nickel ferrite was characterized by X-Ray diffraction (XRD) technique. The room temperature XRD pattern was recorded in the range of 20° and 80° with the appropriate wavelength. Using XRD data, various structural parameters such a crystallite size, lattice constant, unit cell volume, hopping lengths and interstitial radii were calculated.

III. RESULTS AND DISCUSSION

X-Ray diffraction studies

The X-ray diffraction (XRD) pattern of $\text{NiAl}_x\text{Cr}_x\text{Fe}_{2-2x}\text{O}_4$ ($x = 0.0$ and 0.1) were recorded at room temperature using X-ray diffractometer (Philips) in the 2θ range of 20° to 80°. **Fig. 1** depicts XRD patterns of both the samples under investigations. All the peaks in the XRD pattern were indexed using Bragg's law. The XRD patterns reveal all the peaks belonging to cubic spinel structure suggesting that, the prepared samples possess single phase nature. All the peaks observed in the XRD patterns are intense and slightly broader reflecting nanocrystalline nature. The XRD pattern of pure nickel ferrite sample is well matched with that of reported in the literature and JCPDS Card No. #22-1086 [7].

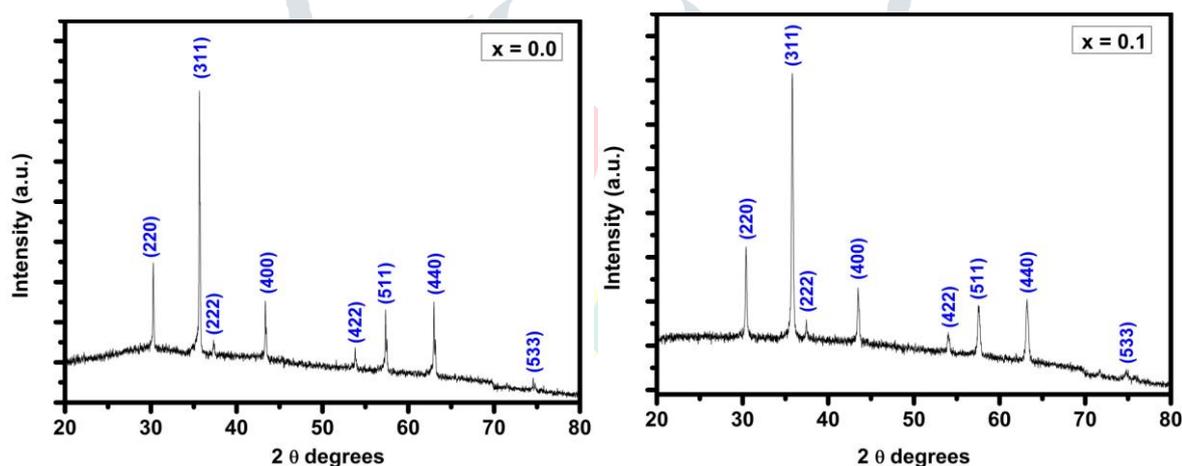


Fig. 1 X-ray diffraction pattern of $\text{NiAl}_x\text{Cr}_x\text{Fe}_{2-2x}\text{O}_4$ ($x = 0.0$ and 0.1)

Crystallite size (t)

The most intense peak (311) was used to determine full width at half maxima (FWHM). Using FWHM values and Scherrer's formula, the crystallite sizes for $\text{NiAl}_x\text{Cr}_x\text{Fe}_{2-2x}\text{O}_4$ ($x = 0.0$ and 0.1) were obtained. The crystallite size varies between 55 nm to 38 nm, which confirms that, the prepared nanoparticles are of nanometer dimensions.

Lattice constant (a)

Using the value of interplanar spacing (d) and Miller indices (hkl), the average lattice constant was calculated using the relation $a = d\sqrt{h^2+k^2+l^2}$. The lattice constant of the pure i.e. nickel ferrite sample closely agree with the reported values. The lattice constant found to decrease after Al-Cr co-doping. The observed decrease in lattice constant is attributed to difference in ionic radii of Fe^{3+} (0.67 Å), Al^{3+} (0.57 Å) and Cr^{3+} (0.64 Å). In the present case, the larger Fe^{3+} ions are replaced by smaller Al^{3+} and Cr^{3+} ions.

Unit cell volume (V)

The values of lattice constant were used to obtain unit cell volume. The unit cell volume found to decrease after Al-Cr co-doping. The decrease in unit cell volume is obviously due to decrease in lattice constant.

Hopping length (L_A and L_B)

The hopping length corresponding to tetrahedral (A) and octahedral [B] sites i.e. L_A and L_B were calculated using the following relations [8];

$$L_A = a\sqrt{3/4} \quad \dots 1$$

$$L_B = a\sqrt{2/4} \quad \dots 2$$

The values of hopping length L_A and L_B are given in table 1.

Ionic radii (r_A and r_B)

The tetrahedral A-site ionic radii can be calculated using the value of lattice constant 'a' and oxygen positional parameter 'u' ($u = 0.381\text{\AA}$) as:

$$r_A = \left(u - \frac{1}{4}\right) a\sqrt{3} - r(O^{2-}) \quad \dots 3$$

Where, r_A represents radius of tetrahedral (A) site cation, u- Oxygen positional parameter, r (O)- represents radius of oxygen anions.

The values of tetrahedral ionic radius are given in table 1 and it is found that it increases with increase in zinc content x.

The octahedral B-site ionic radii can be calculated using the equation:

$$r_B = \left(\frac{5}{8} - u\right) a - r(O^{2-}) \quad \dots 4$$

Where, r_B represents radius of octahedral [B] site cation

Bond lengths

The tetrahedral bond length (d_{AX}), octahedral bond length (d_{BX}), tetra edge (d_{AXE}) and octa edge (d_{BXE}) were also determined for all the samples by using standard relations given below [9].

$$d_{AX} = a\sqrt{3\left(u - \frac{1}{4}\right)} \quad \dots 5$$

$$d_{BX} = a\sqrt{3u^2 - \frac{11}{4}u + \frac{43}{64}} \quad \dots 6$$

$$d_{AXE} = a\sqrt{2\left(2u - \frac{1}{2}\right)} \quad \dots 7$$

$$d_{BXE} = a\sqrt{2(1 - 2u)} \quad \dots 8$$

$$d_{BEU} = a\sqrt{4u^2 - 3u + \frac{11}{16}} \quad \dots 9$$

The values of all these structural parameters are given in table 2.

Table 1

Values of molecular weight (M.W.), Lattice constant (a), crystallite size (t), Unit cell volume (V), hopping lengths (L_A and L_B) and interstitial radii (r_A and r_B) for $\text{NiAl}_x\text{Cr}_x\text{Fe}_{2-2x}\text{O}_4$ ($x = 0.0$ and 0.1) nanoparticles

Parameters	x = 0.0	x = 0.1
M.W.	234.38	231.10
a (Å)	8.3402	8.3281
t (nm)	54.57	37.45
V (Å ³)	580.13	577.61
L_A (Å)	3.6114	3.6061
L_B (Å)	2.9482	2.9439
r_A (Å)	0.5723	0.5696

r_B (Å)	0.7150	0.7120
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Table 2

Values of Tetrahedral bond (d_{AX}), Octahedral bond length (d_{BX}), Tetraedge shared (d_{AXE}), Octaedge shared (d_{BXE}), Octaedge unshared (d_{BXEU}) for $NiAl_xCr_xFe_{2-2x}O_4$ ($x = 0.0$ and 0.1) nanoparticles

Parameters	$x = 0.0$	$x = 0.1$
d_{AX} (Å)	1.8923	1.8896
d_{BX} (Å)	2.0362	2.0332
d_{AXE} (Å)	3.0902	3.0857
d_{BXE} (Å)	2.8071	2.8030
d_{BXEU} (Å)	2.9504	2.9461

IV. CONCLUSION

Pure and Al-Cr co-doped nanocrystalline nickel ferrite samples were prepared successfully using sol-gel auto combustion method. All the samples are single phase with cubic spinel structure. The crystallite size of both the samples is of the order of 55 nm and 38 nm exhibits nanocrystalline nature. The structural parameters like lattice constant, hopping lengths, bond lengths etc. were decreased after Al-Cr co-doping.

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