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Synthesis and Thermoelectric behavior in Nanoparticles of doped Co Ferrites

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Abstract**—**Samples of $CoFe_{2-x}Cr_xO_4$ where x varies from 0.0 to 0.5 were prepared by co-precipitation route. These samples were sintered at 750°C for 2 hours. These particles were characterized by X-ray diffraction (XRD) at room temperature. The FCC spinel structure was confirmed by XRD patterns of the samples. The crystallite sizes of these particles were calculated from the most intense peak by Scherrer formula. The crystallite sizes lie in the range of 37-60 nm. The lattice parameter was found decreasing upon substitution of Cr. DC electrical resistivity was measured as a function of temperature. The room temperature thermoelectric power was measured for the prepared samples. The magnitude of Seebeck coefficient depends on the composition and resistivity of the samples.

Keywords**—**Ferrites, Crystallite size, Drift mobility, Seebeck coefficient, Thermopower

I. Introduction

FERRITES having low resistivity and low eddy current losses have been found to be the most versatile to be used for technological applications as in the case of stress sensors and recording media. Cobalt ferrite possesses an inverse spinel structure and the degree of inversion depends upon the heat treatment [1],[2]. The physical properties of the spinel ferrite developed due to distribution of cations among the tetrahedral A site and octahedral B sites. The dielectric properties and conductivity of the ferrites depend on preparation method, chemical composition and grain size, frequency and temperature [3], [4].DC resistivity of ferrites as a function of temperature and drift mobility and activation energy was reported by different authors [5]-[7]. Several researchers reported the magnetic properties of spinel ferrites as well [8]-[12].Ferrites are low mobility semiconductors. To know about the conduction mechanism in ferrites thermoelectric measurement is done. The thermo e.m.f. and its sign gives appropriate information about the type of conduction in semiconductors, i.e., they are p-type or n-type. There has been considerable interest during the past 10 years in finding new materials and structures for use in clear, highly efficient cooling and energy conversion systems [13]-[16].

II. Experimental Methods

Samples of $CoFe_{2-x}Cr_xO_4$ spinel ferrites having fine particles with x varying from 0.0 to 0.5, was prepared by co-precipitation method. The chemical reagents used in this work were ferric nitrate Fe $(NO_3)_3.9H_2O$, cobalt nitrate CO $(NO_3)_2.6H_2O$ and Cr $(NO_3)_3.9H_2O$. All reagents were of analytical grade and were used without further purification. The aqueous solutions of the chemicals $Co(NO_3)_2.6H_2O$, Fe $(NO_3)_3.9H_2O$ and Cr $(NO_3)_3.9H_2O$ were mixed, in alkaline medium (NaOH). The molarity of the co-precipitation agent (NaOH) used was 0.4M. Then heating of solution was done up to 70^0C with constant stirring. Dehydration is required for the formation of ferrites from the hydro-oxides of chemicals. For that purpose, heating at 70 ^{0}C was continuously done for 45 min to remove the water molecules. By fixing the co-precipitation step, the size of the precipitated particles was controlled. For all values of Cr concentration, the stirring speed was kept constant. The pH of the reactions was kept from 12.5 to 13. The precipitates were thoroughly washed with distilled water until solutions were free from sodium and nitrate ions.After washing samples were dried in an electric oven at a temperature of 105 ^{0}C over night to remove water contents. The dried form of the samples was homogenously grinded with agate mortar and pestle for 15 min then this powder was converted into pellets by using hydraulic press. The pellets were sintered at 750 ^{0}C for 2 hours. Then furnace was cooled down to room temperature. X-ray powder diffraction of the prepared sample was done in order to investigate the structure of the prepared samples. Grain size of the prepared samples was calculated as

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

Where ‘D’ is grain size, ‘0.9’ is symmetry constant, ‘λ’ is wavelength of Cu source of incident ray, ‘β’ is full width at half maxima, and ‘ϴ’ is diffraction angle. X-ray density of the prepared samples was measured as

$$\rho_x = \frac{n\,M}{Na3} \quad (2)$$

where n is number of atoms per unit cell, M is molecular weight of the sample, ‘N’ is Avogadro’s number and ‘a’ is lattice constant. Measured density was calculated as

$$\rho_m = \frac{m}{\pi r2\, h} \quad (3)$$

Where ‘m’ was mass of the sample, ‘r’ was the radius and ‘h’ was the thickness of the sample in pellet form [17].

DC resistivity and drift mobility of the prepared sample was done as a function of temperature by two probe method. DC electrical resistivity for all the prepared samples were calculated by using formula

$$\rho = \frac{R\,A}{L} \quad (4)$$

‘R’ is resistance of the sample, ‘A’ is the area of the pellet and ‘L’ thickness of sample.

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Resistivity as a function of temperature and the results could be fitted by using the relation

$$\rho = \rho_0 \, e^{\frac{\Delta E}{k_B T}} \quad (5)$$

'ρ' is electrical resistivity at temperature T (K), 'k_B' is Boltzmann constant and 'ΔE' is activation energy for electrical conduction process. The drift mobility 'μ' of the charge carrier in the synthesized sample is calculated by following equation

$$\mu = \frac{1}{n \, e \, \rho} \quad (6)$$

'n' is number of charge carriers, e the charge on electron and 'ρ' is the resistivity at a given temperature.

Seebeck coefficient as a function of composition was measured and calculated as

$$S = \frac{\Delta V}{\Delta T} \quad (7)$$

Where 'S' is Seebeck coefficient, 'ΔV' is emf developed across the sample and ΔT is temperature.

III. Results and Discussion

A. Structural and Morphological Properties

The XRD patterns in figure 1 show that the structure is cubic spinel structure with no additional phase (ICSD 01-076-2496).

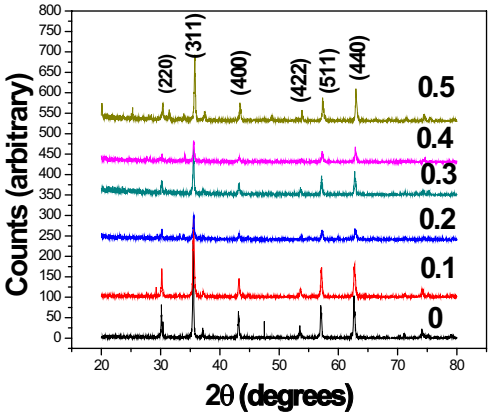

Fig. 1 XRD patterns for $CoFe_{2-x}Cr_xO_4$ where x= 0.0, 0.1, 0.2, 0.3, 0.4, 0.5(sintered)

Table I shows the X-ray and measured density of the prepared samples. The decrease in 'a' was due to Cr concentration. Ionic radius of Cr^{+3} is 0.63 Å which was less than the ionic radius of Fe^{+3} which is 0.645 Å [18]. The size of octahedral B site was greater than tetrahedral A site. The addition of smaller ionic radii at B site results in decrease lattice constant.

TABLE 1
X-RAY DENSITY 'ρ_x' AND MEASURED DENSITY 'ρ_m' OF SAMPLES $COFe_{2-x}Cr_XO4$ where X=0-0.5

Parameter	x=0	x=0.1	x=0.2	x=0.3	x=0.4	x=0.5
$\rho(x)(g/cm^3)$	5.2	5.44	5.20	5.21	5.30	5.33
$\rho(m)\ (g/cm^3)$	3.99	2.68	2.75	2.95	2.60	2.98

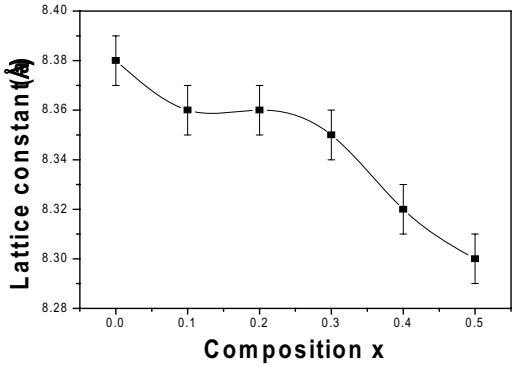

Fig. 2 Variation of lattice constant 'a' with composition x

B. DC Properties

The observed decrease in the value of dc-electrical resistivity with increase in temperature in figure 3 shows the similar trend as that of semiconductor materials. Plot of resistivity with $1/k_BT$ provides activation energy of the hopping E_a.

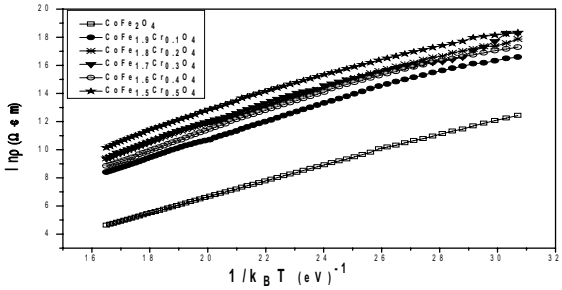

Fig. 3 Graph between resistivity (lnρ) and temperature for $CoFe_{2-x}Cr_xO_4$ where x=0.0, 0.1, 0.2, 0.3, 0.4, and 0.5

Exchange of electrons between Fe^{+2} and Fe^{+3} result in conduction mechanism in ferrites. So as a result there is local displacement of charges causing polarization. The magnitude of this exchange depends on $Fe^{+3}$and Fe^{+2} ion pairs on octahedral sites [18]. The decrease in activation energy is due to reduction of ion pairs. Figure 4 shows that drift mobility increases with increase in temperature.

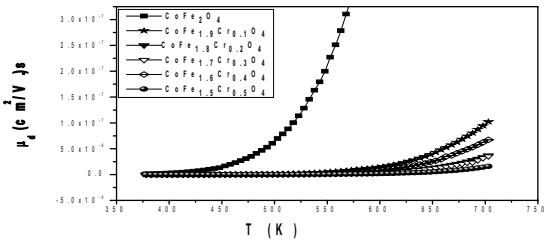

Fig.4 Graph between drift mobility (μ_d) and temperature for $CoFe_{2-x}Cr_xO_4$ where x=0.0, 0.1, 0.2, 0.3, 0.4 and 0.5

This is due to enhanced mobility of the charge carriers due to thermal activation and it is not due to generation of charge carriers by increase of temperature. Also charge carrier concentration is reported to be constant throughout the temperature range [18].

C. Thermoelectric Properties

Thermoelectric effects give conversion of energy between heat and electricity directly. Thermoelectric power of Cr doped Co ferrite nanoparticles as a function of composition was measured at room temperature. The conduction mechanism in Cr doped Co ferrite is due to electrons because sign of seebeck is negative for all the prepared samples. Seebeck coefficient as a function of Cr concentration for all the prepared samples is given in figure 5. All the samples were sintered at 750 ^{0}C.

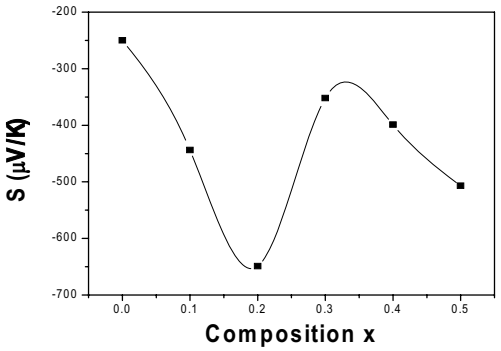

Fig. 5 Variation of Seebeck coefficient 'S' with composition $CoFe_{2-x}Cr_xO_4$ where x=0-0.5

The decrease in Seebeck coefficient 'S' is due to fact that if resistivity of the material increases, motion of charges becomes slow and as a result of which emf developed across the sample was low. Due to decrease in emf the Seebeck coefficient also decreases.The reported value of the Seebeck coefficient for the cobalt ferrite was in good agreement with our measured value . The difference in measured value was due to porosity of the samples, purity of the samples and surrounding temperature of the atmosphere. The Seebeck coefficients for the other compositions are an addition to the existing literature.

IV. Conclusions

Nanoparticles of Cr doped Co ferrite $CoFe_{2-x}Cr_xO_4$ where x=0 to 0.5 were prepared. These nanoparticles were prepared by co-precipitation method and were homogenous. The addition of Cr in Co ferrite creates changes in structure, electrical, and thermoelectric properties. The patterns of XRD show that the structures of all the samples were cubic spinel. The lattice constant 'a' decreased with the increase in the concentration of Cr. DC electrical properties of the samples were done by two probe method in a temperature range of 300K to 673K. The resistivity for all the prepared samples was decreased with increase in temperature. The decrease in resistivity with temperature was due to the fact that at elevated temperatures the hopping between Fe^{+2} and Fe^{+3} was increased as a result of which resistivity decreased. Sign of Seebeck coefficient show that charge carriers were electrons in our prepared samples. The decrease in Seebeck coefficient was due to increase in resistivity for that particular composition.

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