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Effect of Zr^{4+} ions on structural and electrical porperties of Ni-Cd ferrite

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ABSTRACT

The distinct compositions of $Ni_{0.7+x}Cd_{0.3}Zr_xFe_{2-2x}O_4$(where x=0.0,0.1,0.2,0.3,0.4,0.5) samples were prepared by using solid state ceramic method and characterized to understand their structural and electrical properties. The X-ray diffraction (XRD) analysis shows the existence of single phase spinel structure with the increase of lattice constant and density with increasing tetravalent Zr ions contents. The temperature dependence of DC electrical resistivity of all the samples of the series $Ni_{0.7+x}Cd_{0.3}Zr_xFe_{2-2x}O_4$(where x=0.0,0.1,0.2,0.3,0.4,0.5) was studied in the temperature range of 300-800K using by two-probe method. The activation energies were calculated in ferromagnetic and paramagnetic regions and are found in between 0.205 and 0.071 eV. The transition temperature is obtained in the range 653 to 688 K which shows the two parts of the curve namely paramagnetic region and ferromagnetic region.

Key words: Ceramic method, X-ray diffraction, lattice constant, activation energy

INTRODUCTION

Ferrites are widely used in many electronic devices because of their high electrical resistivity, chemical stability, mechanical hardness and reasonable cost [1]. These important properties of ferrites are the basis of its technological importance in many fields. These are also useful to prevent and eliminate radio frequency interference to audio systems. Ferrites are well-known technological magnetic materials finding their applications in various electronic devices such as transformer core, antenna rods, memory chips, magnetic sensors, drug delivery etc [2]. The physical properties of the ferrite are very sensitive to the method of preparation, the amount and type of dopants or substitutions cation distribution etc. [3, 4]. On the basis of crystal structure, spinel ferrites are represented by the formula AFe_2O_4, where A is a divalent metal ion. The crystal structure of ferrite consists of two interstitial sites, tetrahedral (A) and octahedral [B] sites; in which cations are occupied.

In this work, attempt has been made to synthesize nickel ferrite with Zr^{4+} substitution with the chemical formula $Ni_{0.7+x}Cd_{0.3}Zr_xFe_{2-2x}O_4$ (where x=0.0, 0.1, 0.2, 0.3, 0.4, 0.5). The structural and electrical properties were investigated by means of X-ray diffractometry, d. c. electrical resistivity measurements.

METHODOLOGY

The polycrystalline samples of $Ni_{0.7+x}Cd_{0.3}Zr_xFe_{2-2x}O_4$(where x=0.0, 0.1, 0.2, 0.3, 0.4, 0.5) were prepared by double sintering ceramic technique [5]. The A.R. grade oxides (SD ine) of corresponding ions were mixed in stoichiometric proportions. Each sample was wet ground for 6 hours using agate mortar. The samples were pre-sintered in a muffle furnace at 500°C for 24 hours. The pre-sintered samples was reground and compressed into a pellet form using hydraulic press with a pressure of 6 ton per inch^2. These pellets were sintered at 1100°C in air for 24 hours and were slowly cooled to room temperature.

X-ray diffraction (XRD) patterns were recorded at room temperature in the 2θ range of 20^0 to 80^0 to confirm the single phase cubic spinel structure. The cation distribution was estimated through X-ray diffraction technique. DC electrical resistivity of all the samples of the series was studied in the temperature range of 300-800K using by two-probe method.

RESULTS AND DISCUSSIONS

Structural Porperties

X-ray diffraction patterns of a typical samples x=0.1 is recorded at room temperature represented in **Fig.1.**

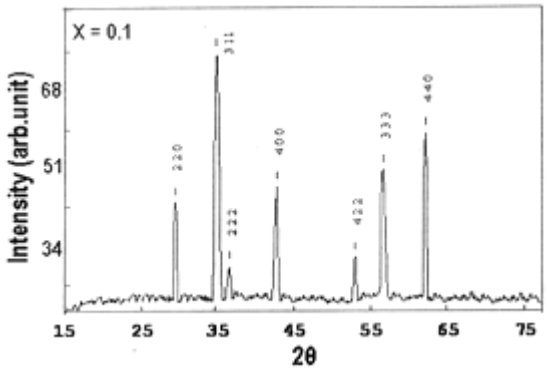

Fig.1: X-ray diffraction patterns of a typical samples x=0.1 of $Ni_{0.7+x}Cd_{0.3}Zr_xFe_{2-2x}O_4$ ferrite

From **Fig.1;** represents well defined peaks and (311) reflection appears to be more intense in all the samples. All the planes are allowed planes which confirm the formation of single phase cubic spinel structure without appearance of any extra peaks. The Inter- planer spacing (d) values were calculated for the recorded peaks using Bragg's law and the lattice constant 'a' was calculated for each plane using the relation.

$$a = d\sqrt{N}$$

where, d- inter planner spacing, $N = (h^2+k^2+l^2)$; (h, k, l) being the Miller indices. The values of lattice parameter calculated from XRD data are given in **Table 1**.

Table 1. Variation in Lattice constant 'a', X-ray density 'dx' and particle size't' with Zr^{4+} content x

Comp. x	Lattice constant 'a' Å	X-ray density 'dx' (gm/cm^3)	Particle size 't' Å
0.0	8.315	5.785	206.0
0.1	8.326	5.850	238.6
0.2	8.336	5.917	208.7
0.3	8.345	5.983	203.9
0.4	8.356	6.084	202.4
0.5	8.361	6.124	210.7

Table 2: Variation in activation energy in paramagnetic region, ferromagnetic region and change in activation energy with Zr^{4+} content x

Comp. x	Transition temperature T_s 'K'	Activation energy (eV)		
		E_p	E_f	ΔE
0.0	688	0.805	0.599	0.205
0.1	683	0.288	0.176	0.112
0.2	675	0.367	0.270	0.092
0.3	666	0.591	0.500	0.090
0.4	657	0.406	0.327	0.079
0.5	653	0.888	0.817	0.071

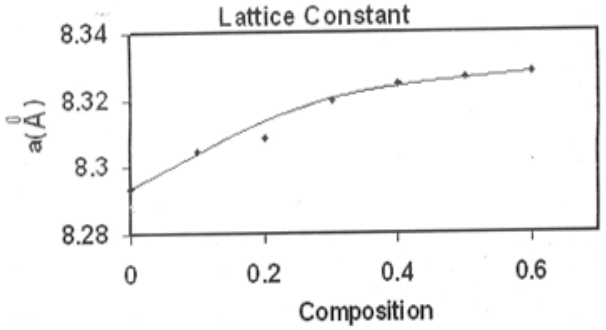

Fig. 2: Variation in lattice constant of $Ni_{0.7+x}Cd_{0.3}Zr_xFe_{2-2x}O_4$ ferrite

The variation of lattice parameter as a function of Zr^{4+} content x is depicted in **Fig. 2,** which reveals that as Zr^{4+} content x increases, lattice constant decreases from 8.3612 Å - 8.315Å. The increasing nature of lattice constant can be explained on the basis of ionic radii of the constituent ions, namely Fe^{3+}, Ni^{2+} and Zr^{4+} ions. It is well known that, ions of smaller ionic radii when replaced by larger ionic radii, lattice constant of the samples decreases [6]. Thus, the decreasing nature of lattice constant with Zr^{4+} substitution quite resembles with the theoretical considerations and similar nature of lattice constant was reported in literature [7].

The crystal size't' of all the samples of the spinel ferrite system $Ni_{0.7+x}Cd_{0.3}Zr_xFe_{2-2x}O_4$ (where x=0.0, 0.1, 0.2, 0.3, 0.4, 0.5) was estimated using Scherrer formula [8] given by,

$$t = \frac{0.9\lambda}{\beta \cos\theta}$$

In the XRD pattern, (311) peak is found to be most intense and is used to estimate the crystallite size. The values of crystallite size determined through XRD data are presented in **Table 1.** The X-ray density 'd_x' of all the samples was calculated using the relation,

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

where, M-Molecular weight, N-Avogadro's number, a-lattice constant. **Table 1.** gives the values of X-ray density. From **Table 1**, it is observed that, X-ray density increases with Zr^{4+} content x. The increase in X-ray

density is attributed to the fact that increase in volume overtakes the decrease in molecular weight.

D.C. electrical resistivity

The D.C. electrical resistivity measurement was performed on disc shaped pellets. The value of energies is listed in Table 2. From Table 2, it is observed that that the activation energy in paramagnetic region Ep is higher than that in ferromagnetic region Ef. This agrees well with the theory of magnetic semiconductors or Irkhin and Turov theory [9]. It is expected that there is a reduction in activation energy as the system undergoes the transition from the paramagnetic state to the ferromagnetic region. The difference in the activation energy continueously decreases as Ni^{2+} and Zr^{4+}ion substitution increases. The transition temperature decreases on increasing Ni^{2+} and Zr^{4+} ions content. It is know that the conduction mechanism in ferrite occurs mainly through the hopping between Fe^{2+} and Fe^{3+} in the B-sites could be understood in terms of exchange interaction [10].

CONCLUSION

The experimental results on structural and magnetic properties of Zr^{4+} substituted nickel ferrite system leads us to draw the following conclusions:

1. The prepared samples are single phase in nature with cubic spinel structure.
2. The lattice constant increases with Zr^{4+} substitution.
3. DC electrical resistivity shows semiconducting nature of the prepared material.
4. Curie temperture the substance change its state from ferromgnetic to parmagnetic region.

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