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Research Article

Physical, Elastic and Thermal Characterization of Ni-Cd Nano Ferrites

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Abstract: The soft spinel ferrite system $Ni_{1-x}Cd_xFeO4$ (x=0.0, 0.2, 0.4, 0.6) have been synthesized by the co-precipitation method. The prepared samples are characterized by the x-ray diffraction (XRD) and FTIR techniques. The XRD data have been used to obtain lattice constants, average crystallite size, specific surface area, dislocation density and strain of the nanoferrites. The data also provided the cation distribution, indicating that Fe^{3+} occupies both the A and B-sites. The elastic properties of this system are studied through infra-red spectroscopy and XRD data. The force constants for tetrahedral (k_t) and octahedral (k_0) sites are estimated along with the Poisson's ratio and the Debye temperature (Θ_D).

Keywords: Co-precipitation synthesis, x- ray diffraction, Debye temperature, specific surface area, elastic properties, magnetic materials, metallic ferrites

1. INTRODUCTION

Spinel nanoferrites are considered superior to other magnetic materials because they have low eddy current losses due to high electrical resistivity. The possibility of preparing ferrites at the nano-scale has extended the application in biotechnology as well as in medicines. Polycrystalline nanoferrites are important because of their well-defined structural, electrical and magnetic properties that depend upon several factors like synthesis techniques, cation substitution and their microstructure. In these polycrystalline materials, doping of minor cations can alter the properties of the entire final product. The ferrites constitute of iron oxide along with other metal with a general formula $MeFe_2O_4$, where Me is divalent metal ion such as Cd^{2+}, Mn^{2+}, Mg^{2+}, Ni^{2+} and Co^{2+} etc.[1]. It is well defined that in inversed spinel structure the Me^{II} divalent metal cation (likeCd^{2+}) occupies the tetrahedral A-site. Recently, a study of Cd-Ni nanoferrites describing the fabrication, structural and electrical studies has been carried-out by Arshad *et. al.* [1]. There is a very little work on the elastic properties of Cd-Ni spinel nanoferrites as compared to their dielectric and magnetic properties. In continuation of this work, the investigation of the elastic properties of Cd^{2+} substituted Ni^{2+} nanoferrites is reported. In the present work, a technique discussed by Modi *et. al.* [2] based on IR-spectroscopy was used to investigate the elastic behaviour of spinel nanoferrites. Infrared or IR spectroscopy deals with the IR region of the electromagnetic spectrum with a larger wavelength compared to visible light. The IR spectrum of a sample under study is recorded by passing a beam of IR light through the sample. When the frequency of the IR matches with the vibrational frequency of a bond or collection of bonds, absorption occurs. An instrument called Fourier Transform Infrared Spectroscopy (FTIR) is used to record the wavelength/energy at which the absorption occurs. This technique is mainly used to determine the functional groups in molecules. More detail is available on the Wikipedia. The results of that study are presented in this paper.

2. EXPERIMENTAL

2.1 Preparation of Materials

The Cd doped nanoferrites with the formula $Ni_{1-x}Cd_xFe_2O_4$ (x= 0.0, 0.2, 0.4, 0.6) were prepared by a co-precipitation technique. The detail is already published by the authors [1] along with dielectric

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characterization of these samples. In summary, the prepared material was characterized by the x-ray diffraction technique at room temperature. The lattice was fcc with the lattice constants varying between 8.351 to 5.595 Å depending upon the replacement of Cd^{2+} in $Ni_{1-x}Cd_xFe_2O_4$. Similarly the average crystallite size varied in the range of 21 to 28nm. The x-ray density, porosity, dislocation density, strain on the lattice and specific surface area of the nanocrystallites were also determined using the standard relations [1]. The obtained values of these parameters are tabulated in Table 1.

2.2 Characterization

The x-ray diffraction patterns of the samples were made using CuK_{alpha} radiation source for determining crystal structure and related properties at room temperature. FTIR spectra were recorded from 300 cm^{-1} to 900 cm^{-1} for all the samples by taking KBr and sample in the ratio 99:1 respectively at room temperature.

3. RESULTS AND DISCUSSION

3.1 Cation Distribution and Structural Related Properties

Fig. 1 shows the x-ray diffraction patterns of all the samples and it confirmed the single phase spinel structure. A nonlinear increase in lattice constant is observed with increasing cadmium concentration. This increase in lattice constant is expected in view of the larger size of Cd as compared to Ni and is already discussed by Arshad *et. al* [1]. Here the cation distribution in the Cd-Ni nanoferrites sample is under taken. $NiFe_2O_4$ is reported to be inversed spinel structure. In inversed spinel structure the cadmium and nickel ions due to their high crystal field stabilization prefer tetrahedral and octahedral sites respectively while the iron ions are equally distributed among A and B-sites [2]. The distribution of cations for the initial composition was achieved using equations (1-3) and is presented in Table 1.

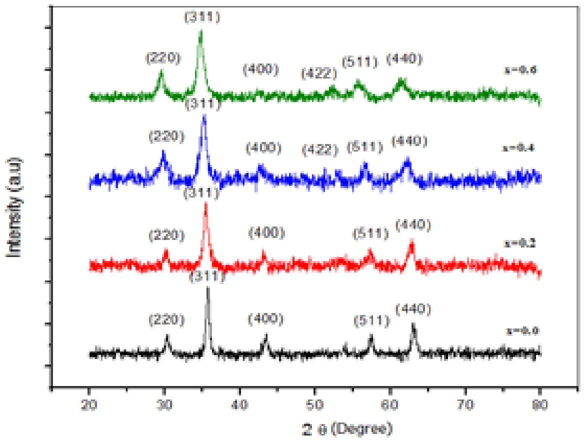

Fig. 1. Indexed XRD pattern of Cd-Ni nanoferrites

The average cation radii as a function of Cd^{2+} concentration of A-site and B-site can be calculated using the relation [3].

$$r_A = \left[x\, r_{Cd(A)} + (1-x) r_{Fe(A)}\right] \tag{1}$$

$$r_B = \frac{1}{2}\left[(1-x) r_{Ni(B)} + (1+x) r_{Fe(B)}\right] \tag{2}$$

where r_{Cd}, r_{Ni} and r_{Fe} are the radii of Cd, Ni and Fe respectively. Ionic radii values used in the calculations are: Cd^{2+} (0.86 Å), Ni^{2+} (0.69 Å), Fe^{3+} (0.49 Å) and Fe^{+2} (0.645 Å) as mentioned by Desai et.al [3].

Using the above values oxygen positional parameter (u) can be estimated through the following expression [3].

$$r_A = (u - 0.25)\, a(1.732) - R_o \tag{3}$$

where a is the measured lattice constant and R_o (1.40 Å) is the oxygen ionic radius.
The lattice constant can be calculated using the formula [4]

$$a_{th} = \left(\frac{8}{3}/\sqrt{3}\right)\{[r_A + R_0] + \sqrt{3}\,[r_B + R_0]\} \tag{4}$$

Table 1. Cation distribution for $(Cd_x^{2+} Fe_{1-x}^{3+})_A\, [Ni_{1-x}^{2+} Fe_{1+x}^{3+}]_B\, O_4^{2-}$

Composition (x)	*A-Site*	*B-Site*
0.0	Fe_1^{3+}	$Ni_1^{2+}Fe_1^{3+}$
0.2	$Cd_{0.2}^{2+}\, Fe_{0.8}^{3+}$	$Ni_{0.8}^{2+}\, Fe_{1.2}^{3+}$
0.4	$Cd_{0.4}^{2+}\, Fe_{0.6}^{3+}$	$Ni_{0.6}^{2+}\, Fe_{1.4}^{3+}$
0.6	$Cd_{0.6}^{2+}\, Fe_{0.4}^{3+}$	$Ni_{0.4}^{2+}\, Fe_{1.6}^{3+}$

The observed (a) and theoretical (a_{th}) lattice constants, r_A, r_B, u and R_o are tabulated in Table 2. For completeness of the parameters that could be determined from the x-ray diffraction data, the

Table 2. X-ray diffraction related parameters: Observed lattice constant (a), theoretical lattice constant (a_{th}), average crystallite size ($\tau_{(311)}$), measured density (ρ_m), x-ray density(ρ_x), volume of unit cell (Vol.), specific surface area (S.s),avg. cation radius (r_A), avg. cation radius (r_B), oxygen position parameter (u), dislocation density and strain on the lattice of $Ni_{1-x}Cd_xFe_2O_4$ nanoferrites. The detail is already published by the authors [1].

Composition (x)	*x=0.0*	*x=0.2*	*x=0.4*	*x=0.6*
Observed lattice constant a_o (Å)	8.351	8.354	8.465	8.595
Theoretical lattice constant a_{th} (Å)	8.419	8.515	8.610	8.706
Average crystallite size $\tau_{(311)}$ (nm)	24.24	21.21	28.24	28.18
Measured density ρm (g.cm^{-3})	2.173	2.182	2.188	2.191
X-ray density ρx (g.cm^{-3})	5.352	5.586	5.604	5.578
Vol. of the unit cell (Å)^3	582	583	607	635
Specific surface area S.s (m^2 g^{-1})	114.09	129.68	97.22	97.44
Average cation radius r_A (Å)	0.490	0.561	0.633	0.702
Average cation radius r_B (Å)	0.667	0.663	0.658	0.654
Oxygen position parameter u	0.381	0.385	0.388	0.391
Dislocation density (m^2)x10^{15}	1.17	2.22	1.25	1.26
Strain %	0.1432	0.1635	0.1229	0.1233

average crystallite size, density related properties, specific surface area, dislocation density and strain on the lattice are also mentioned in the same table. The detailed investigation is already published by our group [1].

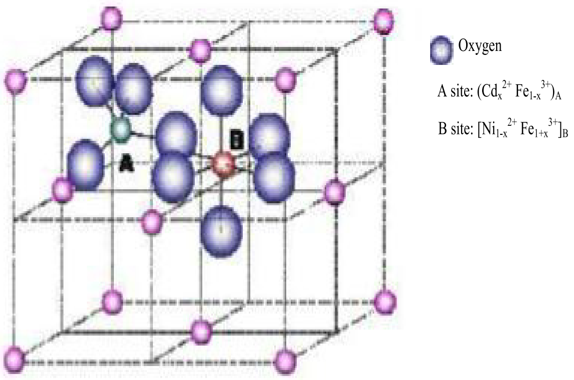

Fig. 2. Diagram of crystal structure of Cd- Ni spinel ferrite, showing tetrahedral (A) and octahedral (B) sites. Ref: Crystallization in Spinel Ferrite Nanoparticles, Advances in Crystallization Processes, Yitzhak Mastai (Ed.), ISBN: 978-953-51-0581-7, Intech

3.2 Force Constants, Elastic Moduli and Debye Temperatures

The crystal structure of Cd-Ni spinel ferrite is shown in Fig.2 along with A and B- sites. The distribution of cations is tabulated in Table1 for different values of 'x'. Fig. 3 shows the FTIR spectra of pure Ni-Cd ferrite and the composition with x = 0.2, 0.4 and 0.6 in the range 300 cm^{-1} to 900 cm^{-1}. The absorption band at 397 cm^{-1} is attributed to stretching vibration of Fe-O bond at octahedral sites. The absorption

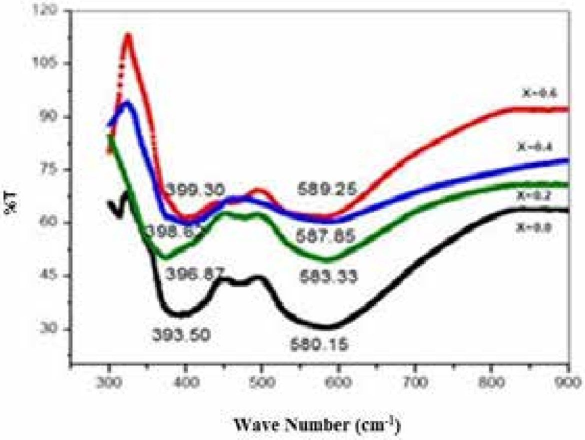

Fig. 3. FTIR spectrum of Cd-Ni nanoferrite.

band near 580 cm^{-1} is characteristics of intrinsic stretching vibration of metal-oxygen (Me-O) bonds present at tetrahedral sites [3, 5]. However, the absorption bands at tetrahedral and octahedral sites are shifted to slightly higher wave number with increasing the cadmium concentration and may be due to distortion in the structure because the lattice constant increased.

Using the values of vibration frequencies, force constant can be estimated [5]. Force constant (k) is the second derivative of potential energy with respect to inter nuclear separation. They are associated with the unit displacement of a Me-O in the tetrahedral A-site and octahedral B-sites. The force constant for A-site (k_t) and B-site (k_o) are estimated using the relations [2, 6].

$$k_t = 7.62 \times M_1 \times v^2{}_1 \times 10^{-7}\, N/m \tag{5}$$

$$k_o = 10.62 \times \left(\frac{M_2}{2}\right) \times v^2{}_2 \times 10^{-7}\, N/m \tag{6}$$

where M_1 and M_2 are estimated from the cation distribution equations and are the molecular weight of cations on tetrahedral A and octahedral B-sites respectively. The values of force constants are shown in Table 3. It can be observed that the values of force constant k_t and k_o both increased with the increase in cadmium concentration. This increase in the force constants may be due to the difference of ionic radii of Cd^{2+}, Ni^{2+} and Fe^{3+} ions. The combined radii of Cd^{2+} and Ni^{2+} are greater than the Fe^{3+} ion. A similar result has been discussed by Modi *et. al.*[2].They introduced a new technique to study the elastic properties of spinel nano ferrites based on infrared spectroscopy. The bulk modulus (B), the elastic or the Young's modulus (Y) and Rigidity (R) modulus as well as Debye temperature (θ_D) and Poisson's ratio (σ) of $Ni_{1-x}Cd_xFe_2O_4$ where x = 0.0, 0.2, 0.4, 0.6, were calculated from the longitudinal elastic wave velocity V_L and transverse elastic wave velocity V_T and x-ray density, using the following relations taken from [3,5,7]. The results are indicated in Table 3.

The bulk modulus (B) of solids in-terms of

Table 3. FTIR related elastic parameters: tetrahedral band position (v_1), octahedral band position (v_2) tetrahedral force constant (k_t), octahedral force constant (k_o), average force constant (k_{avg}), longitudinal elastic wave velocity (v_L), transverse elastic wave velocity (v_T), mean elastic wave velocity (v_M), mean atomic volume (v_A), bulk modulus (B), rigidity modulus (R), Young's modulus (Y), Poisson ratio (σ) and Debye temperature (θ_D) of Ni_{1-x} Cdx Fe_2O_4.

Composition (x)	*x=0.0*	*x=0.2*	*x=0.4*	*x=0.6*
Tetra. band position v_1 ×10^2 (m^{-1})	580.15	583.3	587.85	589.25
Octa. band position v_2 ×102 (m^{-1})	393.50	396.87	398.62	399.30
Tetra. force constant k_t ×102 (Nm^{-1})	1.431	1.739	2.064	2.375
Octa. force constant k_o ×102 (Nm^{-1})	0.941	0.952	0.956	0.955
Avg. force constant k_{avg} ×102 (Nm^{-1})	1.186	1.345	1.510	1.663
Long. Elastic wave velocity v_L (ms^{-1})	5150.9	5368.6	5640.6	5888.2
Trans. Elastic wave velocity v_T (ms^{-1})	2973.8	3099.5	3256.6	3399.6
Mean Elastic wave velocity v_m (ms^{-1})	3301.5	3441.1	3615.4	3774.2
Mean atomic volume v_A ×10^{-6} (m^3)	6.255	6.268	6.522	6.827
Bulk modulus B (GPa)	142.01	161.02	178.31	193.41
Rigidity modulus R (GPa)	47.34	53.66	59.43	64.46
Young's modulus Y (GPa)	127.71	144.88	160.46	174.04
Poisson ratio σ	0.35	0.35	0.35	0.35
Debye temp. θ_D (K)	450.58	469.47	486.59	500.50

stiffness constants may be given by:

$$B = \frac{1}{3}[C_{11} + 2C_{12}] \tag{7}$$

The stiffness constants C_{11} and C_{12} were defined by Waldron [5, 8] that with cubic symmetry like in garnets and spinel ferrites $C_{11} \approx C_{12}$ for isotropic materials therefore, $B = C_{11}$. The force constant (*k*) is associated to the stiffness constant [5, 8]:

$$C_{11} = \frac{k}{a} \tag{8}$$

where *k* is the average force constant estimated as:

$$k_{avg} = \left(\frac{k_t + k_o}{2}\right) \tag{9}$$

The values of the transverse elastic wave velocity (V_T) and the longitudinal elastic wave velocity (V_L) can be calculated as follows [5, 8]:

$$V_L = (C_{11}/\rho_X)^{1/2} \tag{10}$$

$$V_T = V_L/\sqrt{3} \tag{11}$$

The distinction in transverse elastic wave velocity (V_T) and longitudinal elastic wave velocity (V_L) as a function of Cd^{2+} composition are shown in Table 3. It can be seen that both V_T and V_L increase with the substitution of Cd^{2+} ions. The values of V_T and V_L are used to compute the elastic moduli of the spinel nanoferrites samples using the following relations [5, 8]:

$$3/{V^3}_m = 1/{V^3}_L + 2/{V^3}_T \tag{12}$$

$$\theta_D = \frac{h}{k_B}\left[{}^{3N_a}\!/_{4\pi V_A}\right]^{\frac{1}{3}} \cdot V_m \tag{13}$$

$$R = \rho_x {V^2}_T \tag{14}$$

$$\sigma = \frac{(3B - 2R)}{2(3B + R)} \tag{15}$$

$$Y = (1 + \sigma)2R \tag{16}$$

Table 3 shows the measured values of different elastic moduli for the nano-ferrites. It shows that R, B and Y-moduli increased with increasing the Cd^{2+} concentration. It is due to the strengthening of interatomic binding between the various atoms of the spinel lattice with increasing Cd^{2+} content. According to Modi *et. al.*[2] the strengthening of interatomic bonding suggests that the deformation in given solids is difficult and they have the strong affinity to spring (analogues to planes with in a solid held to-gather by atomic bond), back to its equilibrium position [6]. Similar results are reported by Mazen *et. al.* in Li-Mn ferrites [8].

However, the Poisson's ratio (σ) remains constant for different compositions of ferrite samples and equal to 0.35. This value lies between the range (-1 to 0.5) which is in agreement with the theory of isotropic elasticity as discussed by Wooster [9]. The Debye temperature (θ_D) was estimated by using equation (13) as stated above, where V_A is the mean atomic volume given by:

$$V_A = \left({}^{M}\!/_{\rho_x}\right)/q \tag{17}$$

'M' is the molecular weight, ρ_x is the x-ray density, q is the number of atoms in the formula units (i.e. 7) and N_a is the Avogadro's number.

The measured values are listed in Table 3. The increase in 'θ_D' suggests that due to cadmium ion substitution the lattice vibrations are hindered. This might be the reason that length of interatomic bonding increase with the replacement of nickel ions by cadmium ions. An increase in the size of the lattice constants was noticed from the x-ray diffraction (Table 1) in confirmation with the above statement. It is interesting to note that the average mean sound velocity increases almost linearly with the Debye temperature (Table 3). Similar results were also reported by Mazen *et. al.* [8] for Li-Mn ferrite system and Ravinder *et. al* [10] for Ni-Cd ferrite system. This confirmed the relationship between acoustic parameter (i.e., average mean sound velocity) and the thermodynamic parameter (θ_D) in this system.

4. CONCLUSIONS

The $Ni_{1-x}Cd_xFe_2O_4$ ($0 \leq x \leq 0.6$ samples with the step size of 0.2) nano-sized particles were prepared successfully with co-precipitation method and the detail is published by the authors already [1]. The cation distribution has been estimated by x-ray diffraction. The process of functional group has been identified by Fourier transform (FTIR) spectra and the tetrahedral and the octahedral bond positions are determined. The force constants corresponding to tetrahedral (k_t) and octahedral (k_o) positions are estimated. Both k_t and k_o increase with Cd concentration. The elastic bulk modulus (B), Young's modulus (Y) and rigidity modulus (R) are dependent on Cd concentration and approximately increase linearly.

5. ACKNOWLEDGEMENTS

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