

# Elastic Properties of Ho<sup>3+</sup> Substitution Co-Ferrites Synthesized by Sol-Gel Auto Combustion Method

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## Abstract:

Ho<sup>3+</sup> doped Ho<sub>x</sub>CoFe<sub>2-x</sub>O<sub>4</sub> (x = 0.0, 0.025, 0.05, 0.075, 0.1) ferrite nanoparticles prepared by using sol-gel auto combustion method. The prepared samples sintered at 600 °C for 4 hours. Infrared spectra carried out at room temperature in the wave number range of 300–800 cm<sup>-1</sup>. The IR spectra show two major absorption bands. High frequency bands 'ν<sub>1</sub>' is assigned to the tetrahedral and low frequency bands 'ν<sub>2</sub>' is assigned to the octahedral sites of complex. Force constant for the tetrahedral and octahedral site was determined by using IR data. The values of Force constant use to calculate the Stiffness constants (C<sub>11</sub> and C<sub>12</sub>). Using the values of stiffness constants; Elastic modulus such as Young's modulus, Rigidity modulus, Poisson's ratio and Debye temperature are calculated.

**Keywords** — Sol-gel method, Ferrites, infra- red spectroscopy, Elastic Properties

## I. INTRODUCTION

Spinel nano-ferrites are materials research due to their structural, dielectric, electrical and magnetic properties. [1-2] Co-ferrites are magnetic ferrite with high coercive field and high magneto crystalline anisotropy, and promised wide technological applications [3-5]. Cobalt ferrite has inverse Spinel structure and is of the most versatile Centro symmetric magnetic materials. In the inverse Spinel structure, the tetrahedral [A] sites are occupied by the Fe<sup>3+</sup> ions, and the octahedral sites (B) are occupied by the divalent metal ions (M<sup>2+</sup>) and Fe<sup>3+</sup> in equal proportions. The angle A-O-B is closer to 180° than the angles B-O-B and A-O-A; therefore, the AB pair (Fe-Fe) has a strong super exchange (anti ferromagnetic) interaction [6]. Infrared (IR) spectroscopy is one of the most versatile characterization techniques used to (i) study the occurrence of various absorption bands in the spectrum (ii) determine the local symmetry in crystalline/non-crystalline solids, ordering phenomenon, presence/absence of Jahn–Teller ions (iii) determine force constants, elastic moduli,

Debye temperature and molar heat-capacity[7]. The elastic moduli represent the mechanical strength and thermal shock resistance of sample [8]. The nano ferrite CoHo<sub>x</sub>Fe<sub>2-x</sub>O<sub>4</sub> (x = 0.0, 0.025, 0.05, 0.075, 0.1) were synthesized by Sol-gel Auto-Combustion method and also examine the effect of Ho<sup>3+</sup> ions substitution in Co-ferrites on the infra-red spectra and study of their elastic properties.

## II. EXPERIMENT

The ferrite powders were synthesized through sol-gel auto-combustion route to achieve homogeneous mixing of the chemical constituents on the atomic scale and better sinter ability. AR grade Cobalt Nitrate (Co(NO<sub>3</sub>)<sub>2</sub>•3H<sub>2</sub>O), Holmium Nitrate (Ho(NO<sub>3</sub>)<sub>3</sub>•5H<sub>2</sub>O), Iron Nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O) and Citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>•H<sub>2</sub>O), were used to prepare the Ho<sub>x</sub>CoFe<sub>2-x</sub>O<sub>4</sub> (x = 0.0, 0.025, 0.05, 0.075, 0.1) ferrite compositions. Reaction procedure was carried out in air atmosphere without protection of inert gases. The molar ratio of metal nitrates to citric acid was taken as 1:3. The metal nitrates were dissolved together in a minimum amount of double distilled water to get a clear solution. An aqueous solution of citric acid

was mixed with metal nitrates solution, then ammonia solution was slowly added to adjust the pH at 7. Then the solution was heated at 90 °C to transform into gel. When ignited at any point of the gel, the dried gel burnt in a self-propagating combustion manner until all gels were completely burnt out to form a fluffy loose powder. The auto-combustion was completed within a minute, yielding the brown-colored ashes termed as a precursor. The as prepared powder then annealed at 600 °C for 4 hrs.

Sol-gel auto-combustion synthesized powder samples were the infrared spectra of all the samples were recorded at room temperature in the range 300 cm<sup>-1</sup> to 800 cm<sup>-1</sup> using Perkin Elmer infrared spectrophotometer.

### III. RESULT AND DISCUSSION

#### A. Infrared spectroscopy

The room temperature IR spectra of the all the composition are shown in Figure 1. The spectra are recorded in the range from 300 to 800 cm<sup>-1</sup>. The band positions for all the investigated composition are given in Table 1. The spectra show two main absorption bands ‘v<sub>1</sub>’ and ‘v<sub>2</sub>’ as a common feature of all the ferrites. The high-frequency band v<sub>1</sub> lies in the range 702-725 cm<sup>-1</sup> while the low-frequency band v<sub>2</sub> is varying in the 486-497 cm<sup>-1</sup> range.

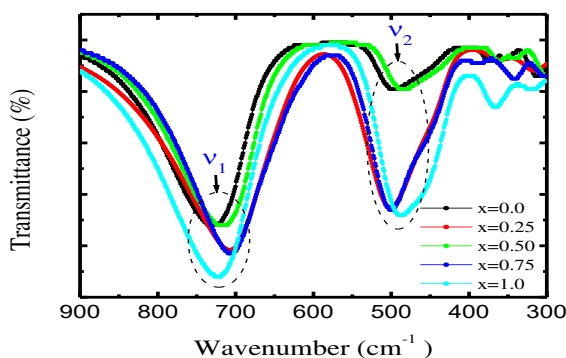


Figure.1. Infrared spectra of Ho<sub>x</sub>CoFe<sub>2-x</sub>O<sub>4</sub> (x = 0.0, 0.025, 0.05, 0.075, 0.1)

The difference in the band position is expected because of the difference in Fe<sup>3+</sup>- O<sup>2-</sup> distance for the octahedral and tetrahedral compounds. From the IR spectra it is noticed that the frequency ‘v<sub>1</sub>’ and ‘v<sub>2</sub>’ are slightly shifted with an increasing Ho<sup>3+</sup> concentration and consequently with decreasing Fe ions concentration. Waldron [9] studied the vibration spectra of ferrites and attributed the v<sub>1</sub> band to the intrinsic vibrations of the tetrahedral groups and ‘v<sub>2</sub>’ band to the octahedral groups. Thus, the replacement of Ho<sup>3+</sup> with Fe<sup>3+</sup> ions (having larger ionic radius and higher atomic weight than Fe<sup>3+</sup>) at octahedral site in the ferrite lattice affects the Fe<sup>3+</sup>- O<sup>2-</sup> stretching vibration. This may be reason for the observed change in v<sub>1</sub> and v<sub>2</sub> band positions [10].

According to Waldron the force constant K<sub>t</sub> and K<sub>o</sub> for respective sites are given by:

$$K_t = 7.62 \times M_1 \times v_1^2 \times 10^{-3} \quad (1)$$

$$K_o = 10.62 \times \frac{M_2}{2} \times v_2^2 \times 10^{-3} \quad (2)$$

Where, K<sub>o</sub> = force constant on octahedral site,

K<sub>t</sub> = force constant on tetrahedral site,

M<sub>1</sub> = Molecular weight of tetrahedral site,

M<sub>2</sub> = Molecular weight of octahedral site,

v<sub>1</sub> = Corresponding frequency on tetrahedral site,

v<sub>2</sub> = Corresponding frequency on octahedral site.

TABLE 1.

LATTICE CONSTANT (a), X-RAY DENSITY (dx), BAND POSITION (v<sub>1</sub> and v<sub>2</sub>), FORCE CONSTANT (K<sub>o</sub> and K<sub>t</sub>) Ho<sub>x</sub>CoFe<sub>2-x</sub>O<sub>4</sub>.

Comp . x	'a' (Å)	'd <sub>x</sub> ' (g/cm <sup>3</sup> )	Band position		Force constant	
			v <sub>1</sub> (cm <sup>-1</sup> )	v <sub>2</sub> (cm <sup>-1</sup> )	K <sub>o</sub> x 10 <sup>5</sup> (dyne/cm)	K <sub>t</sub> x 10 <sup>5</sup> (dyne/cm)
0.00	8.355	5.345	725	497	1.550	2.239
0.025	8.363	5.392	708	499	1.490	2.115
0.05	8.373	5.436	714	491	1.376	2.123
0.075	8.379	5.484	702	496	1.326	2.053
0.10	8.383	5.536	725	486	1.186	2.030

The values of force are summarized in above Table 1. The force constant  $K_t$  decreasing with the increasing  $\text{Ho}^{3+}$  content whereas  $K_0$  decreases with the increasing in  $\text{Ho}^{3+}$ . This variation can be related with the difference in ionic radii of  $\text{Fe}^{3+}$  and  $\text{Ho}^{3+}$  ions and their occupancy at A and B sites. Analysis of IR spectra with crystallographic knowledge helps us to determine the Debye temperature and elastic properties. The Debye temperature ( $\theta_D$ ) of all samples was calculated using the wave number of IR bands [9].

$$\theta_D = hCV_{ac}/k \tag{3}$$

Where,  $h = h/2\pi$ ,

$k =$  Boltzman constant,

$C =$  velocity of light ( $3 \times 10^8$  cm/s)

$V_{ac} =$  average wave number of bands

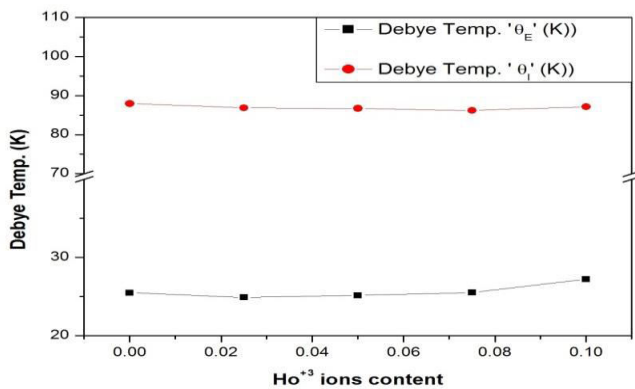


Figure 2. Variation of Debye temperature calculated from infrared ( $\theta_i$ ) and elastic ( $\theta_e$ ) with  $\text{Ho}^{3+}$  content

### B. Elastic properties

The elastic properties were determined using infrared spectroscopy [11-12] These elastic moduli were calculated using the values of lattice constant 'a', X-ray density 'dx', pore fraction 'f' and force constant 'K'. Values of lattice constant, X-ray density and pore fraction are listed in Table 1. The average force constant (K) was calculated using the following relation:

$$K = K_t + K_0/2 \tag{4}$$

The bulk modulus of term stiffness constant  $C_{11}$  was calculated using relation [13]

Stiffness constant

$$C_{11} = \frac{K}{a} \tag{5}$$

Where, K is average force constant and 'a' is lattice constant.

Stiffness constant

$$(C_{12}) = \frac{\sigma \times C_{11}}{(1 - \sigma)} \tag{6}$$

Where, 'σ' is Poisson ratio and 'a' is the lattice constant.

The Poisson ratio is function of pore fraction ( $\sigma = 0.324 \times 1 - 1.043f$ ). Values of Poisson ratio are described in Table 2. The Poisson ratio is ranges in between 0.276 and 0.266; these values are lying in the range of -1 to 0.5, which is in conformity with the theory of isotropic elasticity. [12].

Variation of stiffness constants ( $C_{11}$  and  $C_{12}$ ) as a function of  $\text{Ho}^{3+}$  content is shown in Table 2. It is observed from Table 2; both the stiffness constant was decreases with increase in  $\text{Ho}^{3+}$  substitution.

TABLE 2

MEAN FORCE CONSTANT (K), PORE FRACTION STIFFNESS CONSTANT ( $C_{11}$  and  $C_{12}$ ), of  $\text{Ho}_x\text{CoFe}_{2-x}\text{O}_4$ .

Comp. x	Mean Force constant (K) ( $K_t + K_0$ )	Pore Fraction	Poisson's ratio σ	$C_{11}$	$C_{12}$
0.00	1.8943	0.141	0.276	226.73	86.58
0.025	1.88029	0.147	0.274	215.58	81.50
0.05	1.7498	0.154	0.272	209.01	78.07
0.075	1.6899	0.160	0.269	201.68	74.57
0.10	1.7080	0.168	0.266	203.75	74.30

The values of Poisson's ratio were calculated using the relation discussed elsewhere [14] and the values are presented in Table 2. Stiffness constant are affected by two factors; i.e. the tightness of bonding between the atoms and force constant. In present system bonds between  $\text{Fe}^{3+}$  and  $\text{Ho}^{3+}$  atoms is residual bond and due to this stiffness constant are decreases with increasing

Ho content. These two stiffness constants are further used to calculate the various elastic constants such as; Young’s modulus (E), bulk modulus (K) and modulus of rigidity (G) [14]. The other elastic moduli for cubic structure are calculated using following relation [15].

$$\text{Rigidity modulus } (G) = \frac{E}{2(\sigma + 1)} \quad (7)$$

The rigidity modulus (G) is calculated using the relation 7 and the variation are presented in Figure 3 as shown below.

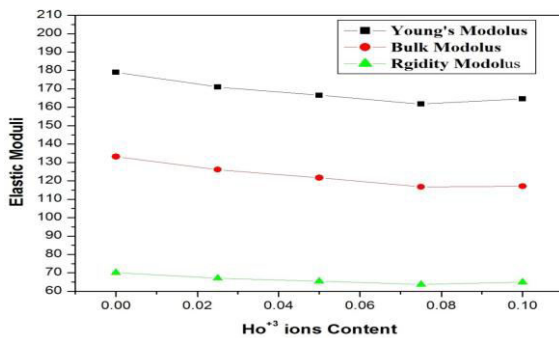


Figure 3. Variation of Young’s modulus (E), bulk modulus (K) and modulus of rigidity (G) with Ho³⁺ content.

Young’s modulus (E), bulk modulus (K) and modulus of rigidity (G) decrease with increase in both Ho³⁺. It indicates that deformation of the solid is easy and the solid has fewer tendencies to spring back to its equilibrium position. The Young’s modulus, Bulk modulus and Modulus of rigidity decrease with the increasing Ho³⁺ content. The decreases in elastic moduli may be due to the interatomic binding between various atoms in the spinel lattice [15]. The inter-atomic bonding between the various atoms weakens continuously with the addition of Ho³⁺ content and therefore elastic moduli decreases with the increasing Ho³⁺ content. In Fe³⁺-Ho³⁺ ferrite repulsion between electrons may be increased with the increasing Ho³⁺ content [16].

The longitudinal elastic wave velocity (V<sub>L</sub>) and transverse (Shear) wave velocity (V<sub>S</sub>) were calculated using following equations.

$$\text{Longitudinal velocity } V_L = \left( \frac{C_{11}}{\rho} \right)^{1/2} \quad (8)$$

Transverse (Shear) velocity

$$V_s = \left( \frac{G}{\rho} \right)^{1/2} \quad (9)$$

Where, G is rigidity modulus with correct zero pore fraction. The values of V<sub>L</sub> and V<sub>S</sub> used to calculate mean wave velocity (V<sub>m</sub>) which used to calculate Debye temperature was calculated using formula.

Debye temperature

$$\theta_E = \frac{h}{k} \left[ \frac{3\rho q N_A}{4\pi M} \right]^{1/3} \times V_m \quad (10)$$

Where, h is planks constant, k is Boltzmann’s constant, M is molecular weight, q is number if atom in the unit formula and V<sub>m</sub> mean wave velocity.

$$\frac{3}{V_m^3} = \frac{1}{V_L^3} + \frac{2}{V_s^3} \quad (11)$$

The values of longitudinal wave, shearing wave and mean wave velocity are calculated using relation 8, 9 and 10 respectively. It is observed shown in Figure 4 the longitudinal elastic wave velocity is decreases whereas transverse (Shear) wave velocity increased with Ho³⁺ substitution.

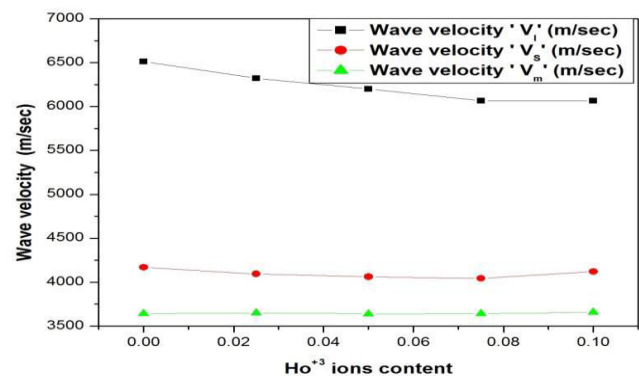


Figure 4. Variation of shearing velocity (V<sub>S</sub>), mean wave velocity (V<sub>m</sub>) and longitudinal wave velocity (V<sub>L</sub>) with Ho³⁺ content.

The values of wave velocities are similar to other ferrites those obtained from UPT method [17]. The variation of Debye temperature ( $\theta_E$ ) is shown in the Figure 2. The Debye temperature increased with  $\text{Ho}^{3+}$  substitution. It suggested that lattice vibrations are hindered due to  $\text{Ho}^{3+}$  substitution. This may be due to the fact that strength of interatomic bonding increases with concentration ( $x$  and  $y$ ) as supported by our results on the variation of elastic moduli [18].

The variation of Debye temperature ( $\theta_E$ ) calculated by using the relation 12. Given in Figure.2. The values of  $V_l/p$  and  $V_s/p$  are calculated by Anderson equation [19] shown in Figure .5. This behaviour clearly indicates the direct relationship between the acoustic parameter (average sound velocity) and the important thermodynamic parameter Debye temperature [20].

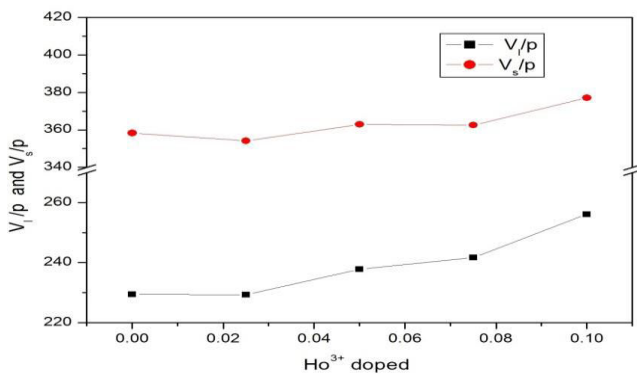


Figure 5.  $V_l/p$  and  $V_s/p$  against  $\text{Ho}^{3+}$  ion content.

#### IV. CONCLUSIONS

The  $\text{Ho}^{3+}$  substituted Co ferrite nanoparticles were prepared by using the sol-gel auto-combustion method. IR spectra confirmed the formation of Spinel structure and gave information about the distribution of ions between the two sites, tetrahedral (A-site) at  $702\text{-}725\text{ cm}^{-1}$  and octahedral (B-site) at  $486\text{-}497\text{ cm}^{-1}$ . The Elastic properties such as elastic wave velocity, elastic constant and Debye temperature calculated using IR data. The elastic constants decreased with the increase in  $\text{Ho}^{3+}$  content. The elastic moduli decreasing with increasing  $\text{Ho}^{3+}$  content and Debye Temperature are found to increasing with increasing  $\text{Ho}^{3+}$  content.

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