

IR Spectral and Elastic Moduli study of Ho⁺³ doped Co-Ni ferrites via Sol-gel auto combustion Method

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ABSTRACT

Sol-gel auto combustion method is a well-defined reacting mixture for the synthesis of nano structured and functional ferrite particles of controlled size and shape having the general chemical formula Co_{0.6}Ni_{0.4}Fe_{2-3x}Ho_xO₄ (x = 0.000 to 0.100 in the step of 0.025). The Fourier Transform Infrared Spectra (FT-IR) of the Co-Ni ferrite system have been analyzed in the frequency range of 200–800 cm⁻¹. The high frequency absorption band 'ν₁' assigned to tetrahedral complex and low frequency absorption band 'ν₂' assigned to octahedral complex. The force constant, bond length and Debye temperature were determined by infrared spectra analysis. The force constant, lattice constant and pore fraction have been used to investigate the elastic moduli such as Young's Modulus, Bulk Modulus, Rigidity Modulus.

Key words: Sol-gel, Co-Ni ferrites, IR, Elasticity.

INTRODUCTION

Nanoscience and Nanotechnology is the technology dealing with both single nanoobjects and materials, and devices based on them, and with processes that take place in the nanometer range. Ferrites are magnetic ceramics containing iron oxide as a major constituent in it. Ferrite chip inductors

are one of the important components for the latest electronics products such as cellular phones, video cameras, notebook computers, hard and floppy drives [1] etc. Ferrites are chemical compounds, ceramic with iron (III) oxide Fe_2O_3 as their principal components [2]. The presence of nonmagnetic ions in these spinel ferrites is found to alter their magnetic and electronic properties. The addition of metal cations such as trivalent or tetravalent influences the electronic and magnetic properties of the ferrite system [3–9]. The structural parameters as well as magnetic properties can be tuned by tailoring the composition of the material [10]. Now a day ferrite is used in telephone exchange, computers, and control equipment.

Many biotechnological applications have been developed based on biogenic and synthetic magnetic micro- and nanoparticles [11]. Magnetic nanoparticles have been used to guide radionuclides to specific tissues. An approach has been developed to directly label a radioisotope with ferrite particles [12] in vivo liver tissue in rats. Therapeutic applications are feasible by further conjugation with other medicals. Magnetic nanoparticles can also be used in a variety of applications: modification, detection, isolation, and study of cells [13], and isolation of biologically active compounds [14], for instance.

Co-Ni ferrite materials have gained the interest of researchers due to their remarkable properties such as high resistivity, high permeability and comparatively low magnetic losses. Co-Ni ferrites with high permeability and a high Curie temperature have been widely studied for practical and microwave applications [15–16]. The rare-earth (RE) ions substituted ferrites are becoming the promising materials for advanced applications, and addition of small amounts of rare-earth ions to ferrite samples can produce a larger improvement in their magnetic and electrical as well as structural properties.

The Ho^{+3} doped $\text{Co}_{0.6}\text{Ni}_{0.4}\text{Fe}_{2-x}\text{Ho}_x\text{O}_4$ ($x = 0.000$ to 0.100 in the step of 0.025) ferrites were synthesized by sol gel

auto combustion method to study the structural properties and elastic properties of the system.

METHODOLOGY

The nano crystalline Ho^{+3} substituted Co-Ni ferrite having chemical composition $\text{Co}_{0.6}\text{Ni}_{0.4}\text{Fe}_{2-x}\text{Ho}_x\text{O}_4$ ($x = 0.000$ to 0.100 in the steps of 0.025). Synthesized by Sol-gel auto-combustion method. The Pure (99%) AR grade corresponding nitrates Cobalt Nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), Nickel Nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Holmium Nitrate ($\text{Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), Ferric Nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$), were used to prepare. Reaction 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 $\text{pH} \approx 7$. 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.

RESULTS AND DISCUSSIONS

Infrared Spectral studies

The Typical IR spectra of the composition $\text{Co}_{0.6}\text{Ni}_{0.4}\text{Fe}_{2-x}\text{Ho}_x\text{O}_4$ ($x = 0.000$ to 0.100 in the steps of 0.025) ($x = 0.075$) as shown in Fig. 1. The spectra are recorded in the range from 200 to 800 cm^{-1} . The absorption band ' ν_1 ' around 600 cm^{-1} and ' ν_2 ' around 350 cm^{-1} are the characteristic bands of spinel ferrite and are assigned to the vibrations of the metal ion-oxygen complexes in the tetrahedral-A and octahedral-B sites, respectively [17]. The vibration frequencies ν_1 and ν_2 , respectively, corresponding to A and B sites for the investigated ferrites are given in Table 1.

Table 1 Lattice constant 'a', X ray density 'dx', Bond lengths (RA & RB), Absorption bands (v₁ and v₂) Force constant 'K' and Poisson's ratio 'σ' of Co_{0.6}Ni_{0.4}Fe_{2-x}Ho_xO₄ (x = 0.000, 0.025, 0.050, 0.075, 0.100).

Comp.x	'a' (Å)	'dx' (g/cm ³)	v ₁ (cm ⁻¹)	v ₂ (cm ⁻¹)	R _A (Å)	R _B (Å)	K ₀ × 10 ⁵ (dyne/cm)	K _t × 10 ⁵ (dyne/cm)
0.000	8.410	5.330	600.31	350.27	3.862	3.064	1.1912	2.0023
0.025	8.415	5.382	594.65	348.75	3.864	3.065	1.1245	1.9056
0.050	8.422	5.413	592.73	345.91	3.866	3.066	0.9865	1.6834
0.075	8.429	5.453	589.59	342.74	3.868	3.067	0.8723	1.5167
0.100	8.435	5.515	586.73	340.03	3.870	3.068	1.0454	1.7851

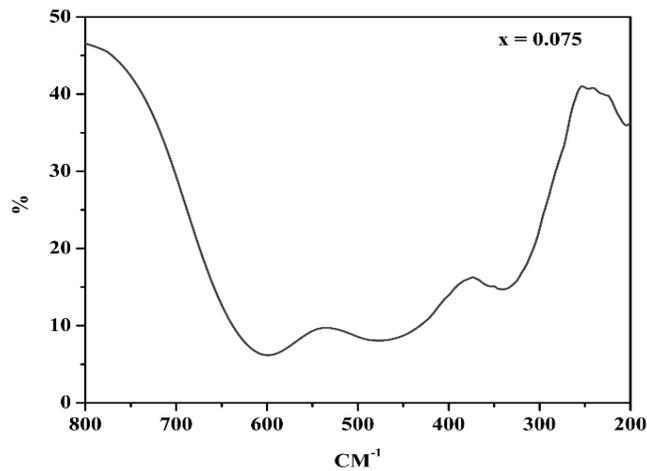


Figure 1: The typical Infrared Spectrum of Co_{0.6}Ni_{0.4}Fe_{2-x}Ho_xO₄ (x = 0.075).

The difference in band position is expected because of the difference in Fe_B³⁺ - O₂²⁻ inter-ionic distance for the octahedral and tetrahedral coordination. The vibrational frequency depends on the cation mass, cation to oxygen distance and bonding force.

The force constant is second derivative of potential energy with respect to the site radius, the other independent parameters being kept constant. The force constant for tetrahedral site (K_t) and octahedral site (K_o) were calculated employing the method suggested by Waldron [17]. According to Waldron the force constant K_t and K_o 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, M₁ and M₂ are molecular weight of cations on A and B site respectively. The bond lengths R_A and R_B

have been calculated using the formula Gorter [18].

The values of R_A, R_B and force constant K_t and K_o are listed in Table 1. The bond lengths increase as Ho⁺³ ions content increases and also the force constant K_o decreased from 1.19 × 10⁵ to 1.04 × 10⁵ dyne/cm and K_t decreased from 2 × 10⁵ to 1.74 × 10⁵ dyne/cm with the increase in substitution of Ho⁺³ ions

Elastic property Studies

Elastic moduli and Debye temperature were calculated through IR data and structural data of the presently investigated spinel ferrite samples [19–21]. These elastic moduli were calculated using the values of lattice constant 'a', X-ray density 'dx', pore fraction 'f' and force constant 'K'.

The elastic constants are of much importance because they elucidate the nature of binding forces and to understand the thermal properties of solids. The elastic moduli often used are Young's modulus, Bulk modulus, Rigidity modulus and Poisson's ratio. Among all the elastic constants of ferrites, Young's modulus is special interest because it is the decisive factor for the most widely employed core shapes, namely rods and rings [19]. The stiffness constant (C₁₁) calculated using relation [22].

$$\text{Stiffness constant } (C_{11}) = \frac{K}{a} \quad (3)$$

$$\text{Stiffness constant } (C_{12}) = \frac{\sigma}{(1 - \sigma)} C_{11} \quad (4)$$

Where, K is average force constant; 'a' is lattice constant. The variation of stiffness constants decrease with increase in Ho⁺³ ions content as shown in Figure 2.

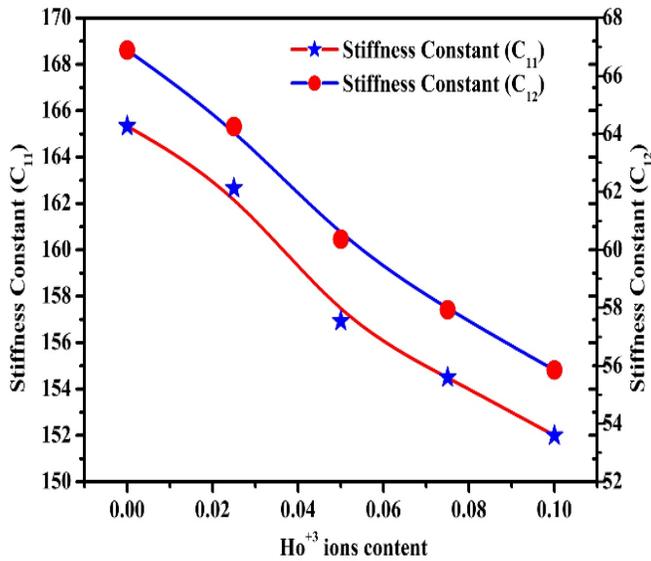


Figure 2

Figure 2: Variation of stiffness constant with Ho³⁺ ions Content.

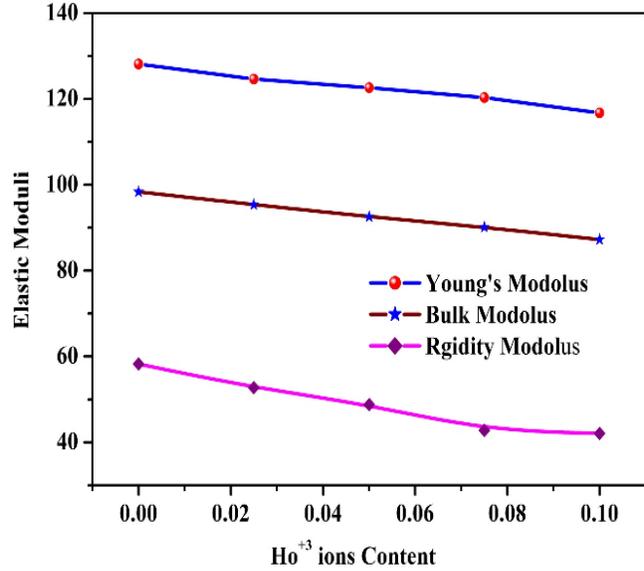


Figure 3

Figure 3: Variations of Elastic Moduli with Ho³⁺ ions Content.

The other elastic moduli for cubic structure are calculated using following relation [23],

$$\text{Young's modulus (E)} = \frac{(C_{11} - C_{12})(C_{11} + 2C_{12})}{(C_{11} + C_{12})} \quad (5)$$

$$\text{Bulk Modulus (K)} = \frac{1}{3}(C_{11} + C_{12}) \quad (6)$$

$$\text{Rigidity modulus (G}_0) = \frac{E}{2(\sigma + 1)} \quad (7)$$

The Young's modulus (E), Bulk Modulus (K) and Rigidity modulus (G₀) calculated by using above equations. The elastic moduli decreases with increase in Ho³⁺ ion content and variation of elastic moduli and Ho³⁺ ion contents as shown in Figure 3.

The longitudinal elastic wave velocity (V_L) and transverse (Shear) wave velocity (V_S) was calculated using following equations,

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

$$\text{Transverse (Shear) velocity } V_S = \left(\frac{G}{\rho} \right)^{1/2} \quad (9)$$

Where, G is rigidity modulus with correct zero pore fraction. The values of V_L and V_S used to calculate mean wave velocity (V_m) which used to calculate Debye temperature ' θ_E ' calculated using formula;

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

Where, 'h' is planks constant, k is Boltzmann's constant, M is molecular weight, 'q' is a number of an atom in the unit formula and V_m mean wave velocity.

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

The values of longitudinal velocity, shearing velocity and mean wave velocity are calculated using relation 8, 9 and 10 respectively.

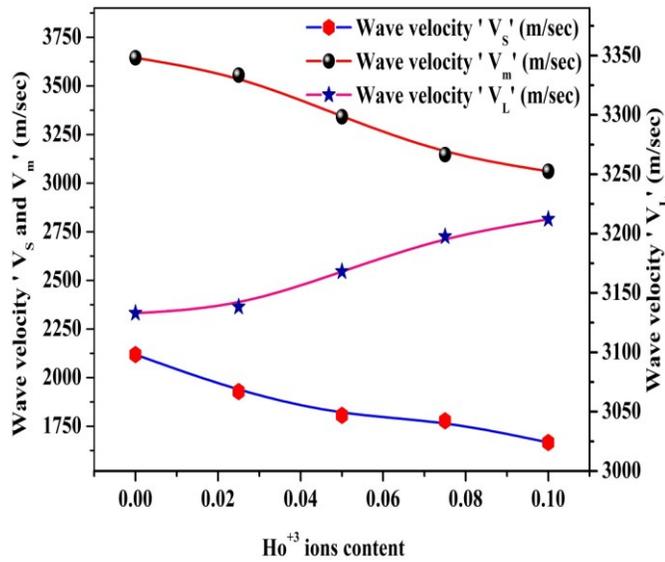


Figure 4

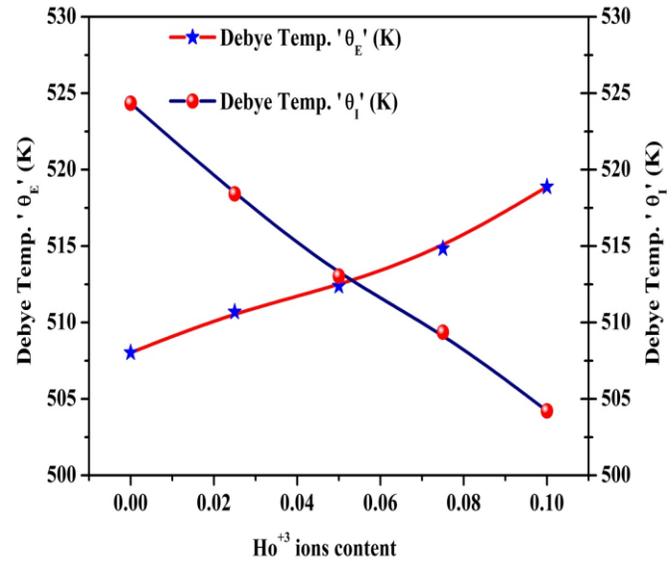


Figure 5

Figure 4: Variation of longitudinal wave velocity (V_L), shear wave velocity (V_S), *mean wave* velocity (V_m) with Ho^{+3} ions Content.

Figure 5: Variation of Debye Temperature (θ_I and θ_E) with Ho^{+3} ions Content.

Figure 4 shows that the transverse (Shear) wave velocity (V_S) and mean wave velocity (V_m) decreases whereas the longitudinal elastic wave velocity (V_L) increased with Ho^{+3} ions content. The values of wave velocities are similar to other ferrites those obtained from UPT method [24].

The Debye temperature increased with Ho^{+3} ions content increase. The Debye temperature (θ_I) obtained from IR data is compared with Debye temperature (θ_E) the variation as shown in Figure 5.

CONCLUSION

Sol-gel auto-combustion method to prepare the Ho^{+3} -doped nano ferro spinle compounds having the general formula $\text{Co}_{0.6}\text{Ni}_{0.4}\text{Fe}_{2-x}\text{Ho}_x\text{O}_4$ ($x = 0.000$ to 0.100 in the steps of 0.025). Infrared spectral shows two absorption bands ' ν_1 ' around 600 cm^{-1} is assigned to the intrinsic stretching vibrations of tetrahedral complexes and band ' ν_2 ' around 350 cm^{-1} is assigned as octahedral complexes. The bond lengths (R_A and R_B) increases with increase in Ho^{+3} ions content. Stiffness constants (C_{11} and C_{12}) decreases with increase in Ho^{+3} ions content.

Variation of Elastic Moduli Young's modulus (E), Bulk modulus (K) and Rigidity modulus (G) decreases as Ho^{+3} ions content increases. The variation of Debye temperatures (θ_E and θ_I) is increases with Ho^{+3} content and decrease in the rigidity of the ferrite.

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