Variation in Elastic Properties of Holmium Substituted Nickel Copper Zinc Ferrites

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Nickel copper zinc ferrites with composition of $\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6}\text{Fe}_{2-x}\text{Ho}_x\text{O}_4$ ($x=0.0$ to 0.1 in steps of 0.02) synthesized by the sol-gel auto-combustion method. Sintering temperature of precursors determined using TGA-DTA. XRD patterns indicate that all samples have single phase cubic spinel structure. The IR spectra show two major absorption bands. The microstructures of the prepared samples were studied by SEM and TEM. Elastic moduli and Debye temperature were determined using IR data and XRD data of spinel ferrite samples. The values of Debye temperature, Young's modulus (E), bulk modulus (K) and modulus of rigidity (G) and stiffness constant increased with holmium substitution.

Keywords: Ferrite, Holmium, Shearing velocity, Rigidity modulus, Bulk modulus.

INTRODUCTION

The spinel ferrite structure MeFe_2O_4 , where Me refers to the metal, can be described as a cubic close-packed arrangement of oxygen atoms, with Me^{2+} and Fe^{3+} at two different crystallographic sites. Rare earth element substituted ferrites have important significance and used for numerous industrial applications [1]. The pure and substituted nickel copper zinc ferrites have been the matter of extensive research because of their applications in electronic devices [2]. Nickel copper zinc ferrites with their ease of preparation and versatility for use in wide variety applications are commercially very attractive. Nickel copper zinc ferrites with high permeability and a high Curie temperature have been widely studied for practical and microwave applications [3,4]. 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 [5], etc. The elastic moduli represent the mechanical strength and thermal shock resistance of sample. Mostly ultrasonic pulse transmission method is used to determine the elastic constant [6]. The elastic properties of ferrites determined by using the IR spectroscopy was reported previously [7]. In this study, we presented the variation in elastic properties of holmium substituted nickel copper zinc ferrites.

EXPERIMENTAL

Holmium substituted nickel copper zinc spinel ferrites doped with holmium, with composition of $\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6}\text{Fe}_{2-x}\text{Ho}_x\text{O}_4$

($x=0.0$ to 0.1 in steps of 0.02) were synthesized by the sol-gel auto-combustion method. Analytical reagent grade metal nitrates were used for synthesis. Metal nitrates desired proportion were dissolved in the distilled water, aqueous solution of citric acid (1:3 ratio metal nitrates: citric acid) added, then the pH ≈ 7 of solution adjusted with addition of ammonia solution. The mixed solution was heated on a hot plate with continuous stirring at 90°C . The viscous gel formed further burnt with glowing flints forming brown-colored precursor. Sintering temperature is determined from TGA/DTA and prepared powders of all the precursor samples were sintered at 500°C for 4 h to obtain the final product.

TGA/DTA of precursors was carried on SDT Q600 V20.9 Build 20. The X-ray powder diffraction with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$) by Phillips X-ray diffractometer (Model 3710) used to study crystal structure. The IR spectra recorded in the range of 200 to 800 cm^{-1} using Perkin Elmer infrared spectrophotometer. Morphology and structure of the samples were studied on JEOL-JSM-5600 N Scanning Electron Microscope (SEM) and Philips (model CM 200) Transmission Electron Microscope (TEM).

RESULTS AND DISCUSSION

TG/DTA analysis: The typical TGA/DTA curves of sample ($x = 0.04$; Fig. 1) shows initial weight loss step corresponding to the temperature range of 30 - 100°C , (the loss of residual water) and second weight loss step around temperature range of 350 - 460°C (decomposition of unreacted starting citric acid).

Fig. 1. TGA-DTA plot for precursor ($x = 0.04$)

No weight loss was observed above 460 °C, therefore, all the precursors were sintered at 500 °C for 4 h to obtain the final product.

X-ray diffraction: Fig. 2 represents typical XRD pattern for sample $x = 0.06$ confirms the cubic spinel structure of single phase without additional peaks corresponding to any other phases. The lattice constant, particle size and X-ray density were increases with holmium concentration.

Fig. 2. Typical XRD patterns for sample $x = 0.06$ Fig. 3. Typical IR spectra ($x = 0.02$ and $x = 0.04$) for the series

Infrared spectroscopy: Typical IR spectra recorded in the range 200-800 cm^{-1} of samples ($x = 0.02$ and $x = 0.04$) are shown in Fig. 3. High frequency bands (574-563 cm^{-1}) assigned to the tetrahedral and low frequency bands (438-364 cm^{-1}) assigned to the octahedral complex.

The force constants corresponding to the tetrahedral and octahedral complexes are calculated by using the standard formulae given below [8]:

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

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

where, K_o is the force constant on octahedral site, K_t is the force constant on tetrahedral site, M_1 molecular weight of tetrahedral site, M_2 molecular weight of octahedral site, v_1 the corresponding center frequency on tetrahedral site, and v_2 the corresponding center frequency on octahedral site. It is to be noted that force constant ' K_o ' decreased from 1.19×10^5 to 0.82×10^5 dynes/cm and K_t decreased from 2×10^5 to 1.44×10^5 dynes/cm with the substitution of Ho^{3+} ions.

The average force constant K [$K = (K_t + K_o)/2$] is given in Table-1. The bond lengths R_A and R_B have been calculated using the formula given by Gorter [9].

$$R_A = \left(u - \frac{1}{4}\right) a_{\text{th}} \sqrt{3} - R_o \quad (c)$$

$$R_B = \left(\frac{5}{8} - u\right) a_{\text{th}} - R_o \quad (d)$$

The variation in values of R_A and R_B are given in Fig. 4. Bond lengths R_A and R_B are increased with the substitution of Ho^{3+} ions.

SEM and TEM: Typical SEM and TEM images of the sample $x = 0.4$ are shown in Fig. 5. It is observed from the SEM and TEM images that the prepared samples are amorphous and porous in nature with agglomeration.

Elastic properties: Elastic moduli and Debye temperature were determined through IR data and structural data of the series $\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6}\text{Fe}_{2-x}\text{Ho}_x\text{O}_4$ ($x=0.0$ to 0.1 in steps of 0.02) ferrite samples [7]. The stiffness constant C_{11} was calculated using relation [8]:

TABLE-1
MEAN FORCE CONSTANT, POISSON'S RATIO, STIFFNESS
CONSTANT AND DEBYE TEMPERATURE OF THE SERIES

Comp. x	Mean force constant $K \times 10^2$ (N/m)	Poisson's ratio σ	C_{11} (GPa)	C_{12} (GPa)	Debye temp. θ_E (K)
0.00	1.360	0.276	161.562	61.594	506.847
0.02	1.445	0.274	170.251	63.133	507.147
0.04	1.434	0.272	171.634	63.597	508.611
0.06	1.447	0.269	171.674	64.787	509.354
0.08	1.762	0.266	184.758	65.073	510.361
0.10	1.555	0.260	209.223	75.774	515.194

Fig. 4. Variation in values of R_A and R_B with holmium substitution

$$C_{11} = \frac{K}{a} \quad (e)$$

where, K is average force constant and a is lattice constant.

$$(C_{12}) = \frac{\sigma C_{11}}{(1-\sigma)} \quad (f)$$

where, where σ is Poisson's ratio and 'a' is the lattice constant. The Poisson's ratio is function of pore fraction. Using eqns, e

and f the stiffness constant is calculated and the variation is tabulated in Table-1. The variation in stiffness constant is illustrated in Fig. 6.

Fig. 6. Variation in stiffness constants with holmium content x

It is observed from Table-1 and Fig. 6 that both the stiffness constants were increases with increase in holmium substitution. The values of Poisson's ratio are decreased with the increasing holmium substitution. The various elastic constants such as; Young's modulus (E), bulk modulus (K) and modulus of rigidity (G) calculated using following equations [10]:

$$E = \frac{(C_{11} - C_{12})(C_{11} + 2C_{12})}{(C_{11} + C_{12})} \quad (g)$$

$$K = \frac{1}{3}(C_{11} + 2C_{12}) \quad (h)$$

$$G = \frac{E}{2(\sigma + 1)} \quad (i)$$

The variation in Young's modulus (E), bulk modulus (K) and modulus of rigidity (G) are presented in Table-1 and Fig.

Fig. 5. SEM and TEM image of sample (x = 0.4)

7. It can be observed that the values of Young's modulus (E), bulk modulus (K) and modulus of rigidity (G) increased with holmium substitution. This increase in elastic moduli correlated to the strengthening in interatomic bonding between iron and holmium ions with increase in holmium composition x.

Fig. 7. Variation in elastic modulus with holmium content x

The longitudinal wave velocity (V_L) and Shearing wave velocity (V_S) was calculated using following equations:

$$V_L = \left(\frac{C_{11}}{\rho} \right)^{1/2} \quad (j)$$

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

where, G is rigidity modulus with correct zero pore fraction. The values of V_L and V_S further used to determine mean wave velocity (V_m) [10]. The variation in shearing velocity (V_S), mean wave velocity (V_m) and longitudinal wave velocity (V_L) given in Table-1.

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

It is observed from Table-1 and Fig. 8 that the shearing velocity (V_S), mean wave velocity (V_m) and longitudinal wave velocity (V_L) increased with holmium substitution. Debye temperature (θ_E) was calculated using following equation [11]:

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

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

The variation of Debye temperature (θ_E) is given Table-1. The Debye temperature (Fig. 9) increased with holmium substitution. Debye temperature corresponds to the temperature at which nearly all modes of vibration in solid are excited. Increased values of Debye temperature indicates the increase in the rigidity of nickel copper zinc ferrite with increase in holmium composition x.

Fig. 8. Variation of shearing velocity (V_S), mean wave velocity (V_m) and longitudinal wave velocity (V_L) with holmium content x

Fig. 9. Variation in Debye temperature with holmium content x

Conclusion

$\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6}\text{Fe}_{2-x}\text{Ho}_x\text{O}_4$ ($x = 0.0$ to 0.1 in steps of 0.02) synthesized by sol gel auto combustion method. High frequency bands ($574\text{--}563\text{ cm}^{-1}$) assigned to the tetrahedral and low frequency bands ($438\text{--}364\text{ cm}^{-1}$) assigned to the octahedral complex. It is observed from SEM and TEM images that the prepared samples are amorphous and porous in nature with agglomeration. The Poisson's ratio decreases with increase in holmium substitution. The values of Debye temperature, Young's modulus (E), bulk modulus (K) and modulus of rigidity (G) and stiffness constant increased with holmium substitution. Increased values of Debye temperature indicated the increase in the rigidity of the nickel copper zinc ferrite with increase in holmium composition.

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