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### **Effect of Al<sup>3+</sup> Substituent on Elastic Properties of Ni-Cu-Zn Ferrites**

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#### **ABSTRACT:**

Al<sup>3+</sup> substituted Ni-Cu-Zn ferrites synthesized by the wet chemical co-precipitation method. Sintering temperature determined by TGA-DTA. XRD patterns illustrate sintered ferrites in single phase with cubic spinel structure. The IR spectra recorded in the range 200-800 cm<sup>-1</sup> indicates 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 complex. SEM image illustrates the prepared samples are amorphous. Elastic moduli and Debye temperature were calculated using IR data and XRD data of prepared ferrite samples. The values of Young's modulus (E), bulk modulus (K) and modulus of rigidity (G) decreased while Debye temperature and stiffness constant increased with Al<sup>3+</sup> substitution.

**KEYWORDS:** Ni-Cu-Zn Ferrite, XRD, TGA-DTA, Elastic moduli.

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## **INTRODUCTION**

Ferrites are complex magnetic oxides with the ferric oxide ( $\text{Fe}_2\text{O}_3$ ) as their basic magnetic component. The spinel ferrites have the general formula  $\text{MFe}_2\text{O}_4$  with M as divalent metal ions such as Co, Ni, Mg, Fe, Cd, Zn etc. Ferrites having spinel structure are ferromagnetic and have semiconductor properties of type p or n<sup>1,2</sup>. The spinels are cubic in structure with 8 formula units and possess two sub-lattices. Polycrystalline ferrites exhibiting low hysteresis loss and high resistivity at room temperature are used in microwave applications and radio electronics.<sup>3</sup> The Ni-Zn ferrites are the mainly adaptable ferrites for their high resistivity and low eddy current losses. The high frequency applications and further miniaturization of magnetic components enable the use of NiZn or NiCuZn ferrites, because both of them have high electrical resistivity and can miniaturize magnetic components without a bobbin.<sup>4,5</sup> The ferrites prepared by different methods such as wet chemical co-precipitation<sup>6</sup>, Sol-gel method<sup>7</sup>. Wet chemical methods require low temperature. The elastic moduli represent the mechanical strength and thermal shock resistance of sample. The mostly Ultrasonic pulse transmission method is used to determine the elastic constant.<sup>8</sup> The elastic properties of ferrites determined by using the IR spectroscopy was reported.<sup>9</sup> This article, focused on by the wet chemical co-precipitation method and detailed study of the elastic properties of  $\text{Al}^{3+}$  substituted  $\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.65}\text{Fe}_{2-x}\text{Al}_x\text{O}_4$  ferrites.

## **EXPERIMENTAL:**

$\text{Al}^{3+}$  substituted Ni-Cu-Zn ferrites, with nominal composition of  $\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6}\text{Fe}_{2-x}\text{Al}_x\text{O}_4$  ( $x=0.0$  to  $0.1$  in steps of  $0.02$ ) were synthesized by the wet chemical co-precipitation method. The metal sulphates in desired composition dissolved in deionized water to yield clear solution; the initial pH of solution was 3. The 2M NaOH solution used as precipitant, in oxygen atmosphere at  $80^\circ\text{C}$ , temperature, brownish precipitate of precursor obtained when pH of solution becomes 12. The precipitate was filtered, washed with deionized water till free from sodium sulphates and then dried. Prepared precursors were sintered at  $700^\circ\text{C}$  for 4 h to obtain the ferrites.

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 diffract meter (Model 3710) used to study crystal structure. The IR spectra recorded in the range  $200$  to  $800 \text{ cm}^{-1}$  using Perkin Elmer infrared spectrophotometer. Morphology and structure of the samples were studied on JEOL-JSM-5600 N Scanning Electron Microscope (SEM).

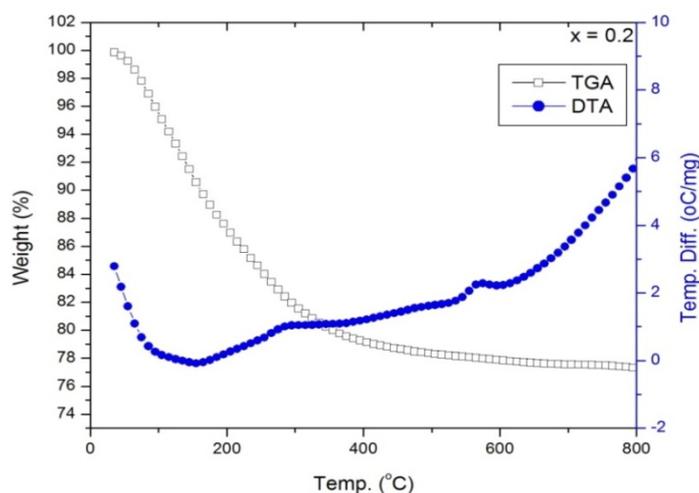


Figure 1: TGA-DTA plot for precursor ( $x = 0.04$ )

## RESULTS AND DISCUSSION:

The typical TGA/DTA curves of sample ( $x = 0.04$ ; Fig. 1) shows precursor were dehydrated completely at temperature  $175\text{ }^{\circ}\text{C}$ , and the oxidation takes place in the temperature range  $430\text{ }^{\circ}\text{C}$  and converted in to nano ferrites. No weight loss was observed above  $620\text{ }^{\circ}\text{C}$ , therefore, the all the precursors were sintered at  $700\text{ }^{\circ}\text{C}$  for 4 hour to obtain the final product.

Figure 2 represents typical XRD pattern for sample  $x=1.0$  illustrate sintered ferrites in single phase with cubic spinel structure without additional peaks corresponding to any other phases. Lattice constant ( $a$ ), x-ray density and crystallite size of all the samples was determined. The lattice constant, particle size and X-ray density were increases with  $\text{Al}^{3+}$  concentration.

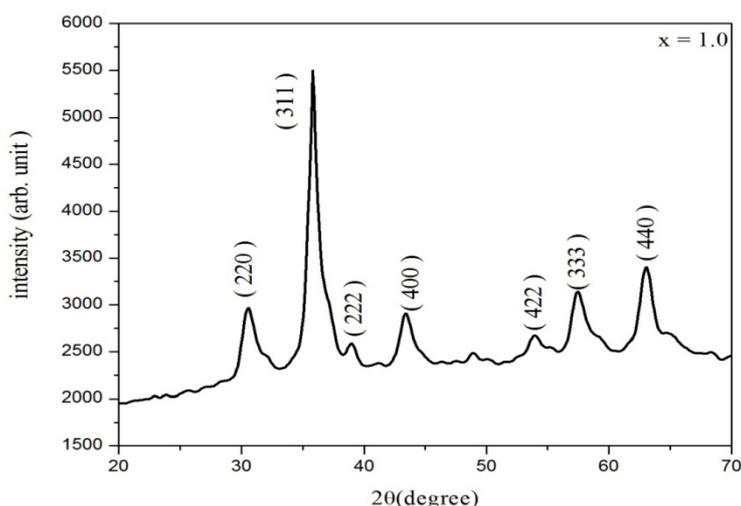


Figure 2. Typical XRD patterns for sample  $x=1.0$

Typical IR spectra recorded in the range  $200\text{--}800\text{ cm}^{-1}$  of samples ( $x=0.8$ ) is shown in Fig. 3. High frequency bands ( $565\text{--}593\text{ cm}^{-1}$ ) assigned to the tetrahedral and low frequency bands ( $433\text{--}463\text{ cm}^{-1}$ ) assigned to the octahedral complex.

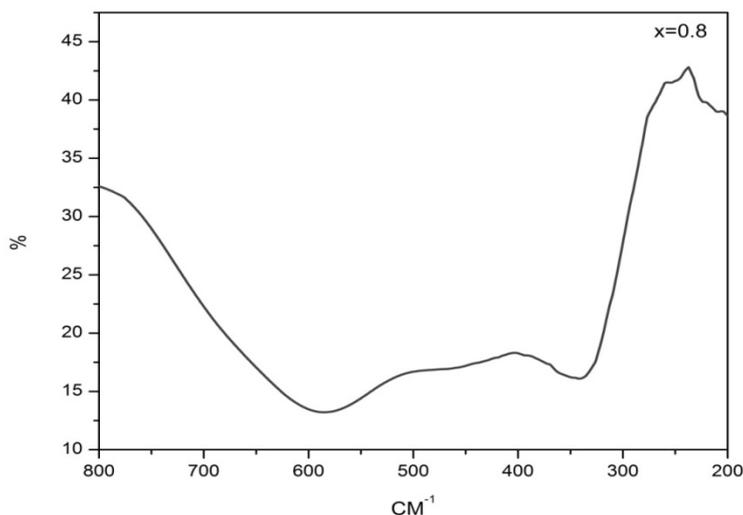


Figure 3: Typical IR spectra  $x=0.8$  for the series

The force constants corresponding to the tetrahedral and octahedral complexes are calculated by using the standard formulae given below<sup>10</sup>:

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

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

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  $2.3818 \times 10^5$  to  $2.3249 \times 10^5$  dyne/cm and  $K_t$  decreased from  $2.1451 \times 10^5$  to  $1.9529 \times 10^5$  dyne/cm with the substitution of  $Al^{3+}$  ions.

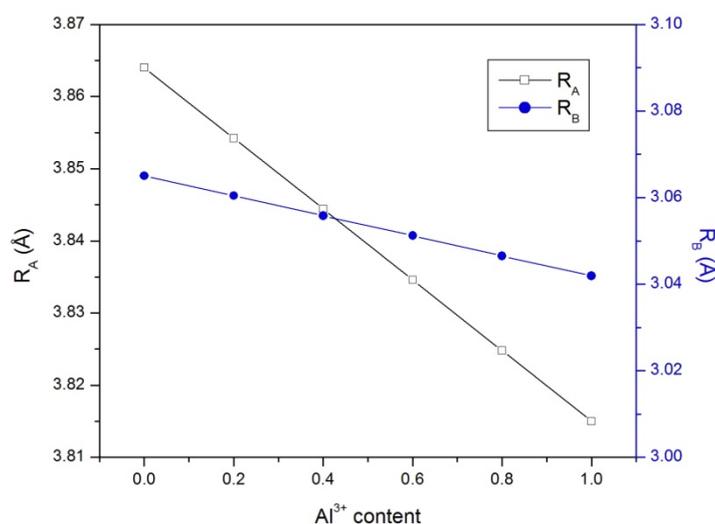


Figure 4: Variation in values of  $R_A$  and  $R_B$  with  $Al^{3+}$  substitution

Table 1 : Mean K, poissons ratio, stiffness constant, elastic moduli and Debye temperature the series.

Comp. x	Mean Force constant $K \times 10^2$ (N/m)	Pore Fraction	Poisson's ratio $\sigma$	$C_{11}$ (GPa)	$C_{12}$ (GPa)	Youngs modulus	Bulk modulus	Rigidity modulus	Debye Temp. (K)
0.0	1.3385	0.142	0.2760	158.614	60.470	129.404	93.185	50.787	504.34
0.2	1.3661	0.148	0.2740	163.140	61.567	126.802	95.425	50.085	504.368
0.4	1.3127	0.154	0.2720	157.269	58.748	125.316	91.588	49.365	506.589
0.6	1.3013	0.163	0.2689	156.177	57.447	125.28	90.357	49.261	506.831
0.8	1.3083	0.172	0.2659	157.046	56.877	125.232	90.267	49.14	507.487
1.0	1.2639	0.188	0.2605	151.715	53.435	123.879	86.195	49.072	512.483

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<sup>11</sup>.

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

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

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

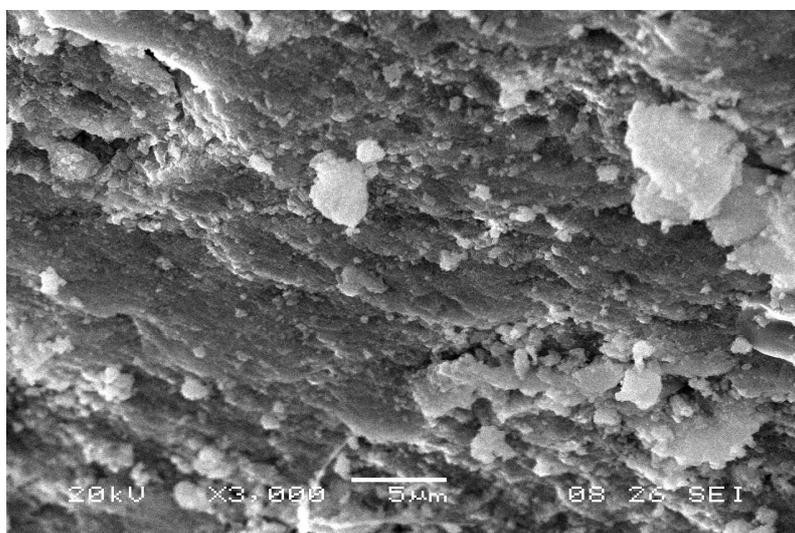


Figure 5: SEM image of sample (x=1.0)

Typical Scanning electron micrograph (SEM) of the sample x=1.0 is shown in Fig. 5. It is observed from the SEM image that the prepared samples are amorphous and porous in nature with agglomeration.

**Elastic properties:**

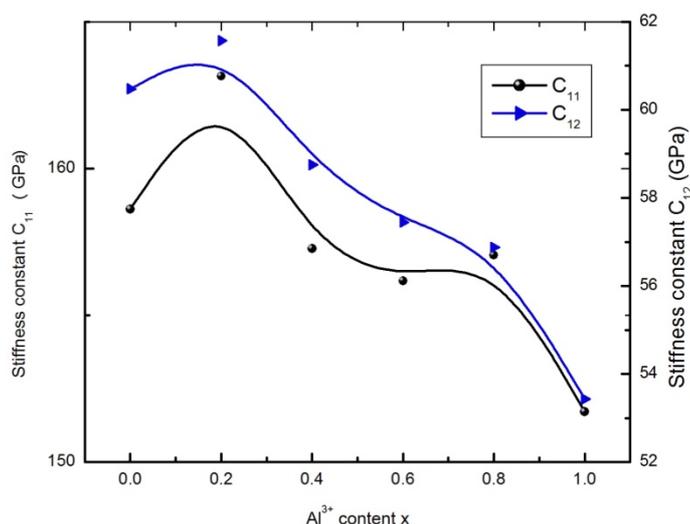
Elastic moduli and Debye temperature were determined through IR data and structural data of the series  $Ni_{0.2}Cu_{0.2}Zn_{0.6}Fe_{2-x}Al_xO_4$  ( $x=0.0$  to  $0.1$  in steps of  $0.02$ ) ferrite samples [9]. The stiffness constant  $C_{11}$  was calculated using relation<sup>10</sup>,

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

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

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

Where, where  $\sigma$  is Poisson ratio and ‘a’ is the lattice constant. The Poisson ratio is function of pore fraction. Using equation 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.



**Figure 6: Variation in stiffness constants with Al<sup>3+</sup> content x**

It is observed from Table 1 and Fig. 6 that both the stiffness constants were decreases with increase in Al<sup>3+</sup> substitution. The values of Poisson’s ratio are decreased with the increasing Al<sup>3+</sup> substitution. The various elastic constants such as; Young’s modulus (E), bulk modulus (K) and modulus of rigidity (G) calculated using following equations<sup>12</sup>.

$$E = \frac{(C_{11}-C_{12})(C_{11}+2C_{12})}{(C_{11}+C_{12})} \tag{vii}$$

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

$$G = \frac{E}{2(\sigma+1)} \tag{ix}$$

The variation in Young's modulus (E), bulk modulus (K) and modulus of rigidity (G) are presented in Table 1 and Fig. 7. It can be observed from Fig. 7 that the values of Young's modulus (E), bulk modulus (K) and modulus of rigidity (G) modulus decreased with Al<sup>3+</sup> substitution. The decrease in magnitude of elastic moduli with Al content suggests that the strengthening of interatomic bonding.

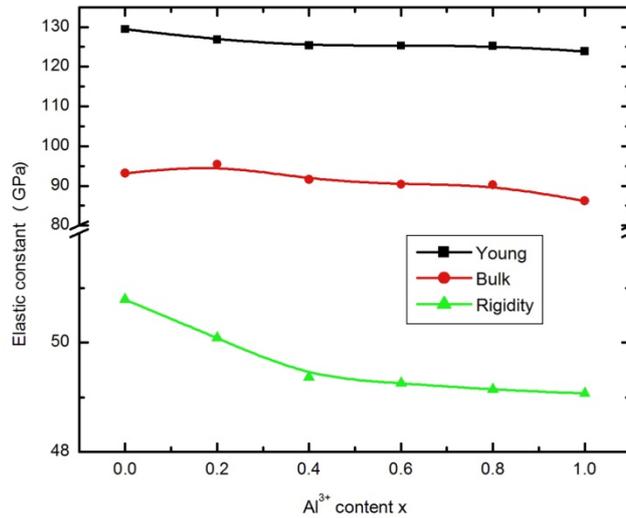


Figure 7: Variation in elastic modulus with Al<sup>3+</sup> content x

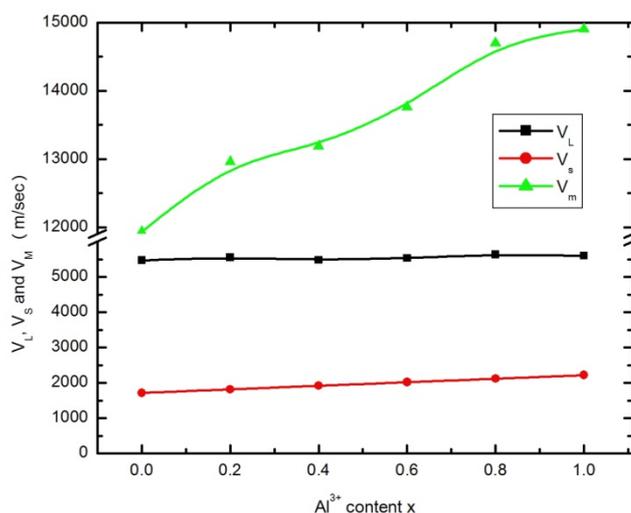
The longitudinal wave velocity (V<sub>L</sub>) and Shearing wave velocity (V<sub>S</sub>) was calculated using following equations,

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

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

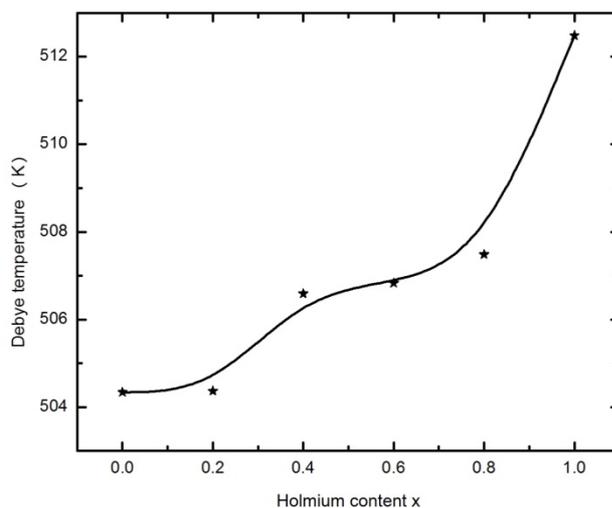
Where, G is rigidity modulus with correct zero pore fraction. The values of V<sub>L</sub> and V<sub>S</sub> further used to determine mean wave velocity (V<sub>m</sub>).<sup>12</sup> The variation in shearing velocity (V<sub>S</sub>), mean wave velocity (V<sub>m</sub>) and longitudinal wave velocity (V<sub>L</sub>), are given in table 1 and Fig. 8.

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



**Figure 8: Variation of shearing velocity (V<sub>S</sub>), mean wave velocity (V<sub>m</sub>) and longitudinal wave velocity (V<sub>L</sub>) with Al<sup>3+</sup> content x**

It is observed from Table 1 and Fig. 8, that the shearing velocity (V<sub>S</sub>), mean wave velocity (V<sub>m</sub>) and longitudinal wave velocity (V<sub>L</sub>) increased with Al<sup>3+</sup> substitution.



**Figure 9: Variation in Debye temperature with Al<sup>3+</sup> content x**

Debye temperature (θ<sub>E</sub>) was calculated using following equation<sup>13</sup>.

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

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.

The variation of Debye temperature (θ<sub>E</sub>) is given Table 1 and Fig. 9, the Debye temperature increased with Al<sup>3+</sup> 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 the Nickel copper zinc ferrite with increase in Al<sup>3+</sup> composition x.

#### 4. CONCLUSION:

$\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6}\text{Fe}_{2-x}\text{Al}_x\text{O}_4$  ( $x=0.0$  to  $0.1$  in steps of  $0.02$ ) synthesized by wet chemical co-precipitation method. High frequency bands ( $565\text{-}593\text{ cm}^{-1}$ ) assigned to the tetrahedral and low frequency bands ( $433\text{-}463\text{ cm}^{-1}$ ) assigned to the octahedral complex. It is observed from the SEM image that the prepared samples are amorphous and porous in nature with agglomeration. The Poisson's ratio was decreases with increase in  $\text{Al}^{3+}$  substitution. The values of Young's modulus (E), bulk modulus (K) and modulus of rigidity (G) decreased while Debye temperature and stiffness constant increased with  $\text{Al}^{3+}$  substitution. Increased values of Debye temperature indicated the increase in the rigidity of the nickel copper zinc ferrite with increase in  $\text{Al}^{3+}$  composition.

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