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Infrared spectral studies of Zn-substituted CuFeCrO_4 spinel ferrite system

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Abstract : The spinel solid solution series $\text{Zn}_x\text{Cu}_{1-x}\text{FeCrO}_4$ with $x = 0.0, 0.2, 0.4$ and 0.6 has been studied by infrared absorption spectroscopy. The IR-spectrum showed two main absorption bands ν_1 and ν_2 in the range $400\text{-}600\text{ cm}^{-1}$ arising from tetrahedral (A) and octahedral (B) interstitial sites in the spinel lattice. The absence of ν_4 band suggests that lattice vibrations are insignificant. No shoulder or splitting is observed around ν_1 and ν_2 bands confirming absence of Fe^{2+} ions in the system. The sharpening of band with Zn- content (x) is due to the fact that the system changes from inverse to normal spinel structure. The structural and optical properties are correlated and the bulk modulus, compressional and shear velocity values determined through IR spectral analysis are in good agreement to those obtained through ultrasonic pulse transmission technique.

Keywords : Ferrites, infrared spectra, inter-ionic distances.

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1. Introduction

The electrical and magnetic properties of spinels depend on the chemical composition, cation distribution, and the method of preparation. The vibrational, electronic, and magnetic dipole spectra can give information about the position and valency of the ions in the crystal lattice.

The infrared spectroscopic technique is based upon the fact that a chemical substance shows marked selective absorption in the infrared region. Various bands present in IR spectrum correspond to the characteristic functional groups and bonds present in the chemical substance. Hence, an IR spectrum of a chemical substance is the finger print for its identification. Unfortunately, very scanty information exists in literature on infrared spectral study of pure and substituted- ferrite systems [1-10].

Earlier, for the first time, Waldron[1] had reported the infrared spectra of several ferrite systems and assigned the high frequency band to the tetrahedral group complexes and low frequency band to the octahedral complexes. He had reported detailed calculation for determining force constants and elastic constants. Josyulu and Sobhanadri *et al* [2] in their communication, have reported the IR spectra of some

mixed Co-Zn and Mg-Zn ferrites. Far-infrared spectral studies of mixed Li-Zn ferrites were made by Ravinder *et al* [3]. He had correlated ν_1 , ν_2 and ν_3 bands to the Fe^{2+} ion concentration. Amer *et al* [4,5] have carried out the infrared absorption spectrum along with Mössbauer spectral studies for $\text{CuCr}_x\text{Fe}_{2-x}\text{O}_4$ and $\text{Co}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ ferrite systems. Fourier transfer spectral studies in the range of $200\text{-}1200\text{ cm}^{-1}$ at room temperature was done by Mazen *et al* [6] along with some physical properties of Ti^{4+} -substituted CuFe_2O_4 . A comparative study on infrared spectroscopy in addition to X-ray, SEM and bulk magnetic properties of Zn^{2+} -substituted CuFeO_4 ferrite synthesized by wet-chemical method before and after high temperature annealing was performed by Parmar *et al* [7]. They have assigned IR absorption band at 3400 cm^{-1} to adsorbed water and 1100 cm^{-1} to sulphate ions. Beside these, reports are also available on Cu-less system like $\text{MgAl}_x\text{Fe}_{2-x}\text{O}_4$ [8,9], Li-Cd ferrite [10] and Li-Ni ferrite [11]. They have explained shift in ν_1 band due to the charge imbalance of A-sites, which makes the oxygen ions shift towards Li^{1+} ions, while splitting of B-site absorption band is due to the presence of three kinds of cations at the B-site.

In this work, we report a detailed analysis of the infrared spectra of the $\text{Zn}_x\text{Cu}_{1-x}\text{FeCrO}_4$ spinel ferrite system with $x = 0.0, 0.2, 0.4$ and 0.6 , which is a part of our work on magnetic

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[12,13], structural [14] and electrical [15] properties of the $Zn_xCu_{1-x}FeCrO_4$ system.

2. Experimental details

The four samples of the spinel series $Zn_xCu_{1-x}FeCrO_4$ ($x = 0.0, 0.2, 0.4$ and 0.6) were prepared by the usual double sintering ceramic method. The starting materials were AR grade (99.3% pure supplied by E. Merck) oxides ZnO , CuO , Fe_2O_3 and Cr_2O_3 . These oxides were mixed in proper proportion and pre-sintered at $950^\circ C$ for 12 h. In the final sintering process, the materials were held at $1100^\circ C$ for 12 h and slowly cooled to room temperature. The X-ray diffractograms were recorded using CuK_α radiation on a Philips X-ray diffractometer (model PM 9220). The infrared spectrum for all the compositions at room temperature was recorded in the wave number range of $400 - 1000\text{ cm}^{-1}$. For the present samples, BRUKER IFS 66v FT-IR spectrometer was used to carry out the infrared spectroscopic studies in the KBr medium. The analysis was carried out at RSIC, IIT, Chennai.

3. Results and discussion

Typical X-ray diffraction patterns for the system $Zn_xCu_{1-x}FeCrO_4$ with $x = 0.2, 0.4$ and 0.6 at 300K is shown in Figure 1. The diffraction lines were found to be sharp corresponding to single-phase cubic spinel structure. No other phase has been detected for all the samples. The lines are indexed using a computer program, which are consistent with face-centered cubic spinel structure.

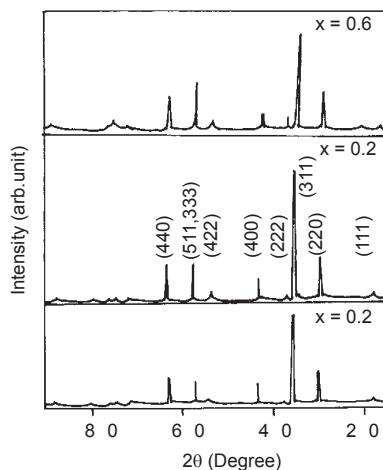


Figure 1. Typical X-ray diffractograms (300K) for Zn-Cu-Fe-Cr-O system.

The values of lattice constant ' a ' were determined with an accuracy of $\pm 0.002\text{ \AA}$. As in the present system, smaller Cu^{2+} ions (0.69 \AA) are replaced by slightly larger Zn^{2+} ions (0.70 \AA), one can expect no change in lattice constant as a function of x . In the present case, the lattice constant increases linearly with increasing x (Table 1), thus obeying the Vegard's Law [16]. Usually in a solid solution of spinels within the miscibility range, a linear change in lattice constant with the concentration of the component is observed [16]. The slow linear increases

in lattice constant with x can not be explained on the basis of replacement of smaller ions by larger ones. In the present case, this may be due to the fact that Cu^{2+} has B-site preference while Zn^{2+} has strong A-site preference as confirmed by earlier study [14]. When larger Zn^{2+} occupy smaller tetrahedral (A) sites, it results in lattice expansion which in turn, increases lattice constant (Table 1).

Table 1. Lattice constant (a), X-ray density (ρ), oxygen positional parameter (u), site radii (R_A, R_B) and force constants (K_t, K_o) for $Zn_xCu_{1-x}FeCrO_4$ system.

x	$a(\text{\AA})$ $\pm 0.002\text{ \AA}$	$\rho(\text{g/cm}^3)$	$u(\text{\AA})$	$R_A(\text{\AA})$	$R_B(\text{\AA})$	$K_t \times 10^5$ dynes/cm	$K_o \times 10^5$ dynes/cm
0.0	8.372	5.330	0.255	1.921	2.030	1.32	0.84
0.2	8.377	5.325	0.256	1.922	2.031	1.39	0.86
0.4	8.381	5.325	0.257	1.923	2.032	1.43	0.90
0.6	8.386	5.324	0.258	1.924	2.034	1.46	0.91

The X-ray density for each composition was calculated using the relation [17]

where Z is the number of molecules per unit cell (here $Z = 8$) of spinel lattice, M the molecular weight of the ferrite sample, N is Avogadro's number and a the lattice constant of the ferrite. The variation of X-ray density (ρ) with Zn-content (x) is shown in Table 1.

The X-ray diffraction data was further used to calculate the tetrahedral and octahedral site radii (R_A and R_B). The site radii, R_A and R_B , were calculated using the relations

$$(1)$$

where

$$u_{\text{system}} = \text{oxygen parameter} = (u_1 + u_2)/2 \quad \text{and} \quad u_{\text{ideal}} = 0.250\text{ \AA},$$

u_1 and u_2 are oxygen parameters of two end members of the system respectively.

The value of oxygen positional parameters (u) of each composition was estimated assuming the values of u for $ZnFe_2O_4$ (0.260 \AA) and $CuFe_2O_4$ (0.255 \AA) [18]. These values hold true for $CuFeCrO_4$ ($x = 0.0$) and $ZnFeCrO_4$ ($x = 1.0$) because of the slender difference in the ionic radii of Fe^{3+} (0.64 \AA) and Cr^{3+} (0.63 \AA) ions and the values are summarized in Table 1.

The values of site radii calculated from above eq. (1) are given in Table 1. It can be seen that both R_A and R_B increase linearly with Zn-content, which can be attributed to the fact that the lattice parameter increases linearly with zinc concentration

(x) (Table 1). Similar results have been reported for substituted lithium ferrites [19,20]. The site radius R_B is greater than R_A .

Levine [21] has correlated the decrease in site radius to an increase in covalent character. In the present system, the increase in Zn^{2+} -content decreases Cu^{2+} -content, which results in decrease of covalent character of the ferrite. The site radius exhibits a sensitive dependence on covalency and composition [22,23].

Ferrites possess the structure of mineral spinel (MgAl_2O_4) that crystallizes in the cubic form with space group $\text{Fd}\bar{3}\text{m}-\text{O}_h^7$ [24]. It is generally known that the spinel ferrites exhibit four IR active bands, designated as ν_1 , ν_2 , ν_3 and ν_4 . The occurrence of these four bands has been rationalized on the basis of group theoretical calculations employing space group and point symmetries, both in normal and inverse spinels. The first three IR bands are due to tetrahedral and octahedral complexes while the fourth one is due to some type of lattice vibrations.

The room temperature (300K) infrared spectra for $\text{Zn}_x\text{Cu}_{1-x}\text{FeCrO}_4$ system with $x = 0.0, 0.2, 0.4$ and 0.6 are shown in Figures 2 and 3. It can be seen from the figures that the IR spectrum of zinc-substituted copper-ferri-chromates are found to exhibit two bands in the range $400\text{--}600\text{ cm}^{-1}$.

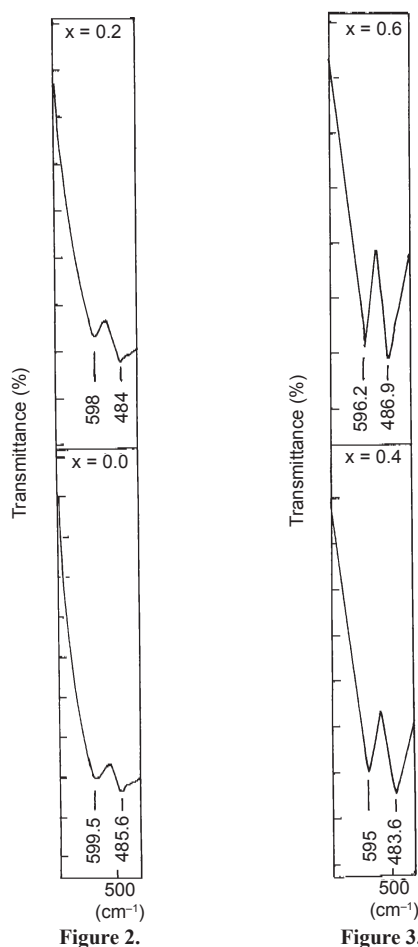


Figure 2.

Figure 3.

Figure 2. Infrared spectra of Zn-Cu-Fe-Cr-O system with $x = 0.0$ and 0.2 .

Figure 3. Infrared spectra of Zn-Cu-Fe-Cr-O system with $x = 0.4$ and 0.6 .

No absorption bands were observed above 600 cm^{-1} . The high frequency band ν_1 is in the range of $595\text{--}600\text{ cm}^{-1}$ and the lower frequency band ν_2 is in the range of $480\text{--}490\text{ cm}^{-1}$. These bands are common features of all the ferrites [1]. According to Waldron's classification [1], the vibrations of the unit cell of cubic spinel can be constructed in the tetrahedral (A-) site and octahedral (B-) site. So, the absorption band ν_1 is caused by the stretching vibration of the tetrahedral metal-oxygen bond, and the absorption band ν_2 is caused by the metal-oxygen vibrations in octahedral sites. The band positions and intensities are given in Table 2. The shift in band positions is observed as function of content (x). The difference in band position is expected because of the difference in the $\text{Fe}^{3+}\text{--O}^{2-}$ for the octahedral and tetrahedral complexes. It was found that Fe-O distance of A-site (1.89 \AA) is smaller than that of the B-site (1.99 \AA) [25]. This can be interpreted by the more covalent bonding of Fe^{3+} ions at the A-sites than B-sites. The center frequency of the bands ν_1 and ν_2 show a slight variation. The bands ν_1 and ν_2 shift slightly towards lower frequency side for $x = 0.0 - 0.4$ while for $x = 0.6$, they shift towards higher frequency (Table 2). It is known that increase in site radius (Table 1) reduces the fundamental frequency and therefore, the center frequency should shift towards lower frequency side. Among the zinc-substituted copper-ferri-chromates of different concentrations, the one with a zinc concentration of 0.4 mole

Table 2. Position of IR absorption bands (ν_1, ν_2) and intensity (I_1, I_2), bulk modulus (B) and velocity (v_1, v_2) for $\text{Zn}_x\text{Cu}_{1-x}\text{FeCrO}_4$ system.

x	$\nu_1(\text{cm}^{-1})$	$\nu_2(\text{cm}^{-1})$	$I_1(\%)$	$I_2(\%)$	B (dynes/ cm^2)	$v_1 = v_s \times 10^5$ (cm/sec)
0.0	599.5	485.6	13.0	14.8	1.58	5.44
0.2	598.0	484.0	14.3	14.8	1.66	5.58
0.4	595.0	483.1	34.0	48.0	1.71	5.67
0.6	596.2	486.9	50.0	56.0	1.74	5.72

has the minimum value of absorption bands. This result is corroborated by the a.c. susceptibility and magnetization measurements [13] which have provided evidence of cluster formation in the samples with $x > 0.4$ mole. It is believed that the clusters cause local lattice distortion of the grain boundaries and act as charge traps at various depths. The process of trap recharging affects the absorption bands in IR spectra. The observed band positions for unsubstituted system CuFeCrO_4 ($x = 0.0$) are in very good agreement with reported band positions for $\text{CuCr}_x\text{Fe}_{2-x}\text{O}_4$ system [4]. The shifting of ν_1 and ν_2 bands towards lower frequency is in agreement with results reported for Zn-substituted CoFe_2O_4 [2].

One can notice that the spectra for $x = 0.0$ and 0.2 are different from those for $x = 0.4$ and 0.6 indicating change in cation distribution, in support to earlier results [14]. It is important to note that on increasing Zn-content in the system, bands become more and more sharp (Figures 2 and 3). The broadening of bands has been reported earlier by many workers.

Patil *et al* [26] have observed more and more broadening for higher content of cobalt in case of Cd-Co ferrites. They have reported that such broadening is commonly observed in inverse spinel ferrites and has been attributed to statistical distribution of Fe^{3+} ions on A - and B-sites. In the present case, system transfer from inverse (CuFeCrO_4) ($x = 0.0$) to normal (ZnFeCrO_4) ($x = 1.0$) spinel structure, results in sharpening of bands. Furthermore, the intensity of bands is found to increase with increase in Zn-concentration (x). The increase in intensity is accompanied by the sharpening of bands (Figures 2 and 3). This may be attributed to changes in the $\text{Fe}^{3+}-\text{O}^{2-}$ complexes by $\text{Cu}^{2+}-\text{O}^{2-}$ complexes in the tetrahedral and octahedral sites on the substitution of Zn^{2+} ions in the system.

It is known that the intensity ratio is a function of the change of dipole moment with the inter-nuclear distances ($d\mu/dr$) [27]. This value represents the contribution of the ionic bond Fe-O in the lattice. So one can conclude that the IR spectra can give an idea about the change of the molecular structure of the ferrites due to the perturbation occurring in Fe-O bond by introducing the Zn^{2+} ion, on the other hand, the electronic distribution of Fe-O bonds is greatly affected when Zn^{2+} ion with ($3d^{10}, 4s^2$) orbitals are introduced in its neighborhood, and this consequently affects ($d\mu/dr$) of the Fe-O bond, as measured by their IR absorption bands.

One can also obtain information about the presence/absence of Fe^{2+} ions in the sample from IR spectra in addition to the valency and the band position. The presence of Fe^{2+} ions in the ferrite can cause a shoulder or splitting of the absorption band. Local deformations can occur due to Jahn-Teller effect [28] in Fe^{2+} ions which can lead to a non-cubic component of the crystal field potential and hence to splitting of the band. Since such effect is not observed in present case, around ν_1 as well as ν_2 band, confirming absence of Fe^{2+} ions in tetrahedral and octahedral sites.

To see the presence/ absence of ν_3 band, spectra in the frequency range of $50\text{cm}^{-1}-400\text{cm}^{-1}$ was carried out and such IR spectra of typical composition $x = 0.4$ is shown in Figure 4. Earlier it has been reported that the band ν_3 is assigned to the divalent metal ion-oxygen complexes in the octahedral sites [2]. The intensity of ν_3 band is found to decrease with increase in concentration of zinc as the content of Cu^{2+} ions decreases with increase in zinc concentration. Consequently, the decrease in the intensity of ν_3 band is confirmed by the results. Thus, the band ν_3 can be assigned to $\text{Cu}^{2+}-\text{O}^{2-}$ octahedral complexes.

Preudhomme and Tarte [29] reported that the band ν_4 depends on the mass of the divalent tetrahedral cations and assigned ν_4 band to some type of vibrations involved in a displacement of the tetrahedral cation. It is seen from the Table 2 that the ν_4 band remains totally absent including the parent composition ($x = 0.0$). The ν_4 band does not seem to evolve on substitution of Zn^{2+} for Cu^{2+} on A-site due to slender difference

in the atomic mass values of Zn (65.39 g/mole) and Cu (62.55 g/mole). Thus, the substitution of Zn^{2+} does not cause significant vibrations that can be observed in the IR spectra.

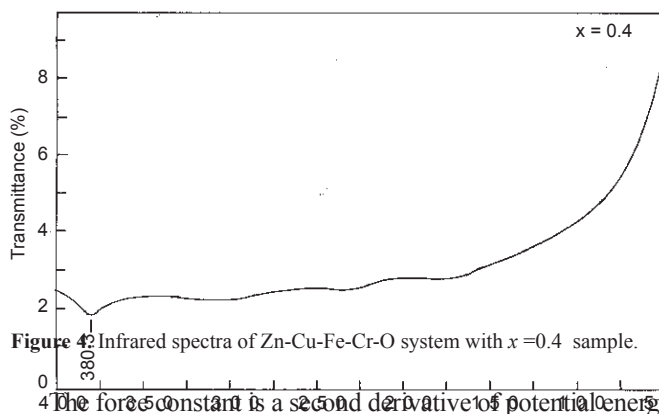


Figure 4. Infrared spectra of Zn-Cu-Fe-Cr-O system with $x=0.4$ sample.

The force constant is a second derivative of potential energy with respect to the site radii, the other independent parameters being kept constant. The force constant for tetrahedral and octahedral sites, K_t and K_o , respectively were calculated using the standard procedure and formulae suggested in the literature [1,30].

The variation of force constants with site radii is shown in Figure 5. Table 1 lists the values of site radii R_A , R_B and force constants K_t and K_o . The force constants are found to increase with site radii as shown in Figure 5 that suggests strengthening of interatomic bonding. Normally, increase in site radius leads to decrease in force constants. This can be attributed to the fact that under favourable conditions, oxygen can form stronger bonds with metal ions even at larger inter-nuclear separations [20,26,31].

The configuration of ion pairs in spinel ferrites with favourable distances and angles for effective magnetic

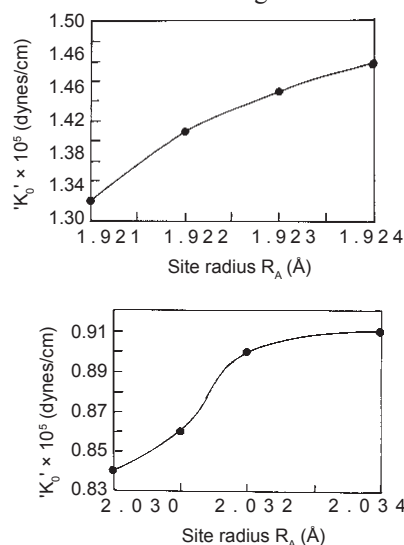


Figure 5. Variation of force constants, K_t , K_o with site radii R_A , R_B .

interactions are shown in Figure 6. The inter-ionic distances between the cations (b, c, d, e and f) (M_e-M_e) and between the cations and anion (p, q, r and s) (M_e-O) were calculated using the experimental values of lattice constant and oxygen positional parameter (u) (Tables 1) by the relations [32] :

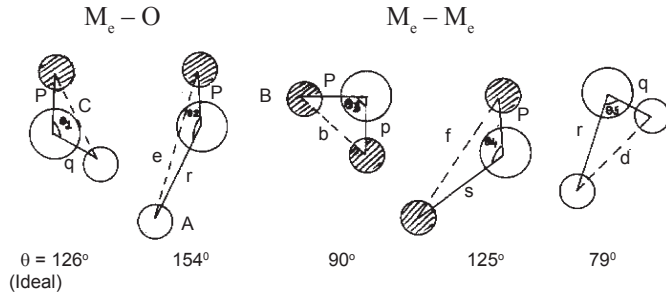


Figure 6. The configuration of ion pairs with favourable distances and angles for effective magnetic interactions.

$$\begin{aligned}
 p &= a(1/2 - u), & b &= (a/u) 2^{1/2}, \\
 q &= a(u - 1/8) 3^{1/2}, & c &= (a/8) 11^{1/2}, \\
 r &= a(u - 1/8) 11^{1/2}, & d &= (a/4) 3^{1/2}, \\
 s &= a/3(u + 1/2) 3^{1/2}, & e &= (3a/8) 3^{1/2}, \\
 & & f &= (a/4) 6^{1/2}.
 \end{aligned}$$

From the Table 3, it is seen that both inter-ionic distances between the cation-anion and between cations, increase with increasing zinc- concentration (x). These results are rather unexpected, and cannot be explained on the basis of difference of ionic radius of substituent cations and for which it is substituted (Cu^{2+}). The increase in M_e-O and M_e-M_e distances should result in the weakening of the strength of interatomic bonding.

Table 3. Inter-ionic distances between cation-anion (M_e-O), cation-cation (M_e-M_e) and angles (θ) for $\text{Zn}_x\text{Cu}_{1-x}\text{FeCrO}_4$ system.

	$x = 0.0$	$x = 0.2$	$x = 0.4$	$x = 0.6$
P	2.0511	2.0440	2.0366	2.0294
Q	1.8851	1.9007	1.9161	1.9318
R	3.6097	3.6396	3.6691	3.6991
S	3.6493	3.6564	3.6629	3.6700
B	2.9599	2.9617	2.9629	2.9649
C	3.4708	3.4729	3.4746	3.4766
D	3.6252	3.6273	3.6291	3.6312
E	5.4378	5.4410	5.4436	5.4469
F	5.1268	5.1298	5.1323	5.1353
θ_1	123.65°	123.35°	123.02°	122.70°
θ_2	146.39°	144.95°	143.50°	142.22°
θ_3	85.15°	84.16°	83.18°	82.16°
θ_4	125.81°	125.91°	126.03°	126.13°
θ_5	74.44°	74.20°	75.93°	76.67°

constants are increased with increasing Zn-content (x). Now, this can be explained in the light of bond angles ($\theta_1, \theta_2, \theta_3, \theta_4$ and θ_5) (Figure 6), calculated by simple trigonometry principles using the values of inter-ionic distances. It is seen that angles θ_1, θ_2 and θ_3 decrease while θ_4 and θ_5 increase with x (Table 3). The observed decrease in $\theta_1, \theta_2, \theta_3$ angles suggest strengthening of A-B and B-B interactions, consistent with the above results. The increase in angle θ_5 , which is related with A-A interactions, may not have effect on strength of interatomic bonding because A-A interactions are considered to be weakened.

The most conventional technique for bulk modulus, other elastic moduli and Debye temperature determination is the ultrasonic pulse transmission technique (UPT) ; but information regarding parameters like force constant, heat capacity *etc.* cannot be obtained from the same. For such purpose, IR spectral analysis proved better which can give idea about above parameters along with those obtained from UPT technique [33].

The bulk modulus (B) of solids in terms of stiffness constants is defined as $B = 1/3[C_{11} + 2C_{12}]$, but according to Waldron *et al* [1] $C_{11} = C_{12}$ and thus B is simply given by C_{11} . Further, force constant (k) is a product of lattice constant (a) and stiffness constant C_{11} [33]. The values of lattice constant obtained from X-ray diffraction pattern analysis and force constant for tetrahedral (A-) site, (K_t) (Table 1) from the IR spectral analysis of $\text{Zn}_x\text{Cu}_{1-x}\text{FeCrO}_4$ system, have been used for the determination of B and the same are included in Table 3. The values of Bulk modulus B are in the same order to those reported for Ni - Cd spinel ferrites system obtained from ultrasonic pulse transmission technique [34]. This suggests validity of present technique. It is seen that B increases with increasing Zn - content (x). The observed increase in B with x can be explained on the basis of 'a' and K_t values. It can be seen from Table 1 that the rate of increase of K_t is higher than rate of increase of a , which results in increase in B with concentration (x). The increase in B with zinc content (x) suggests strengthening of the interatomic binding. A similar result has been reported for Mn - Zn ferrites system. We have also determined the values of compressional or longitudinal velocity (v_l) and shear velocity (v_s) using the formula suggested by Waldron [1] :

(with $v_l = v_s$) where ρ is X-ray density (Table 1). The values of v_l and v_s are also in the same order obtained from IR spectral analysis [1] and ultrasonic pulse transmission technique [34] and same are summarized in Table 3.

4. Conclusions

The results obtained from various structural parameters and infrared spectral studies of $\text{Zn}_x\text{Cu}_{1-x}\text{FeCrO}_4$ show that

- (i) The absorption bands ν_1 and ν_2 are found in the

expected range and difference in band positions is due to the difference in the $\text{Fe}^{3+}\text{-O}^{2-}$ for the octahedral and tetrahedral complexes.

- (ii) The absence of ν_4 band suggest that the substitution of Zn^{2+} does not cause significant vibrations that can be observed in the IR spectra.
- (iii) Absence of shoulder or splitting around ν_1 and ν_2 bands confirm absence of Fe^{2+} ions in the system.
- (iv) The sharpening of bands with Zn-content is due to the fact that the system transfers from inverse to normal spinel structure.
- (v) Structural and optical properties are correlated.

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