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Elastic moduli determination through IR spectroscopy for zinc substituted copper ferri chromates

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The elastic constants are of much importance because they elucidate the nature of binding forces in solids. In engineering practice the elastic constants often used are the Young modulus, Bulk modulus, Rigidity modulus and Poisson's ratio.

The most conventional technique for bulk modulus, other elastic moduli and Debye temperature determination is the ultrasonic pulse transmission technique (UPT) [1]. Infrared spectroscopy is a technique which can give information regarding parameters like force constant, molar heat capacity, bulk modulus, longitudinal velocity, Debye temperature etc. [2].

The bulk modulus and longitudinal velocity values determined through IR spectral analysis, X-ray density and pore fraction values through X-ray diffraction analysis, are used to calculate other elastic moduli, Debye temperature, shear and mean sound velocities. The observed variation of elastic moduli with composition has been interpreted in terms of strength of interatomic bonding. The Debye temperature obtained from elastic constant data is higher than that of the X-ray Debye temperature. The agreement of the results obtained from the present method with the results of the other methods confirm the validity of the method used. This work is in continuation of our work on magnetic [3, 4], structural [5] electrical [6] and infrared spectral studies [7] of the $Zn_xCu_{1-x}FeCrO_4$ system.

To our knowledge no such work has been reported in the literature except for the study of elastic behavior of various ferrites like Ni-Cd, Cu-Zn, Li-Mg, Li-Zn, Mn-Zn, Ni-Zn [8, 9 and references therein] through conventional ultrasonic pulse transmission technique.

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 usual double sintering ceramic technique. The starting materials were AR grade (99.3% pure supplied by E. Merck) oxides ZnO, CuO, Fe_2O_3, Cr_2O_3. The oxides were mixed in proper proportion and pre-sintered at 950 °C for 12 h. In final sintering process the materials were held at 1100 °C for 12 h and slowly cooled to room temperature. The X-ray diffraction patterns were recorded using Cu K_α radiation on a Philips X-ray diffractrometer (model: PM 9220).

Typical X-ray diffraction patterns for the system $Zn_x Cu_{1-x}FeCrO_4$ with $x = 0.2$, 0.4 and 0.6 at 300 K are shown in Fig. 1. The diffraction lines were found to be sharp corresponding to single phase spinel structure. No other phase has been detected for all the samples. The lines were indexed using a computer program and are consistent with face centered cubic spinel structure. The values of lattice constant a were determined with an accuracy of ±0.0002 nm. As in the present system smaller Cu^{2+} ions (0.069 nm) are replaced by only slightly larger Zn^{2+} ions (0.070 nm), one can expect no change in lattice constant as a function of substitution (x). In the present case the lattice constant increases linearly with increasing x, (Table I), thus obeying the Vegard's law [10]. Usually in a solid solution of spinels within the miscibility range linear change in lattice constant with the concentration of the component is observed [10]. The slow linear increase in lattice constant can not be explained on the basis of the replacement of smaller ions by larger ones. In the present case this may be due to the fact that Cu^{2+} ions have B-site preference while Zn^{2+} ions have strong A-site preference as confirmed by earlier study [5]. The occupancy of larger Zn^{2+} in smaller tetrahedral (A-) sites results in the lattice expansion, which is reflected in the increase of lattice constant (Table I).

The X-ray density for each composition was calculated using the relation [11]:

$$\rho = \frac{ZM}{Na^3}$$

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 I. In order to determine the bulk density (d) of a specimen in pellet form, the precise values of weight measured through electronic balance and the volume measured by using traveling microscope were used. The X-ray density (ρ) and bulk density (d) decrease with increase in Zn-content i.e., the bulk density nearly reflects the same behavior of the theoretical density (Table I). The pore fraction (f) was calculated using the relation [11]:

$$f = (1 - d/\rho)$$

The change of pore fraction f with zinc content (x) is shown in Table I.

The bulk modulus (K) of solids in terms of stiffness constants is defined as $K = 1/3\ [C_{11} + 2C_{12}]$, but according to Waldron *et al.* [2] $C_{11} = C_{12}$ therefore, K is simply given by C_{11}. Further, force constant (k) is a product of lattice constant (a) and stiffness constant

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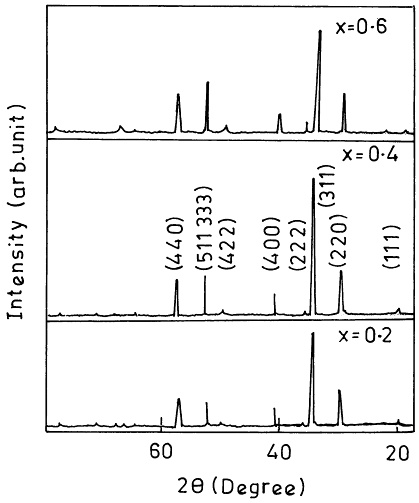

Figure 1 Typical X-ray diffraction patterns at 300 K.

[1]. The values of lattice constant obtained from X-ray diffraction analysis and average force constant (k) using force constant for tetrahedral (A-) site, (k_t) and octahedral (B-) site (k_o) obtained from IR spectral analysis of $Zn_xCu_{1-x}FeCrO_4$ system [7] have been used for the determination of K and the same are included in Table I. The values of bulk modulus K are of the same order of magnitude when compared to those reported for Ni-Cd and Cu-Zn spinel ferrite systems obtained from ultrasonic pulse transmission technique [8, 9]. We have determined the value of longitudinal velocity (V_l) using the formula suggested by Waldron *et al.* [2]: $V_l = (C_{11}/\rho)^{1/2}$ and the transverse velocity (V_s) by general approximation : $V_s \sim 3^{1/2} V_l$ [8]. The values of V_l and V_s are in the same order obtained from IR spectral analysis [2] and ultrasonic pulse transmission technique [8, 9], and are summarized in Tables I and II, respectively.

The elastic moduli of the ferrite specimens are evaluated using the following formulae

$$\text{Rigidity modulus } (G) = \rho \cdot V_s^2$$

$$\text{Poisson's ratio } (\sigma) = \frac{3K - 2n}{6K + 2n}$$

$$\text{Young's modulus } (E) = (1 + \sigma)2G$$

The values of V_l and V_s were further used to calculate mean sound velocity (V_m) using the relation:

$$V_m = \left[3\left(\frac{V_s^3 \cdot V_l^3}{V_s^3 + 2V_l^3}\right)\right]^{1/3}$$

TABLE I Lattice constant (a), molecular weight (M), X-ray density (ρ), pore fraction (f), average force constant (k), bulk modulus (K) and longitudinal velocity (V_l) of $Zn_xCu_{1-x}FeCrO_4$ system

Content (x)	a (nm) ±0.0002 nm	M (kg)	ρ (kg/m^3) ×10^3	F	k (N/m)	K (GPa)	V_l (m/s)
0.0	0.8372	0.2354	5.330	0.1726	1.080	129	4920
0.2	0.8377	0.2357	5.325	0.1735	1.125	134.3	5022
0.4	0.8381	0.2361	5.325	0.1770	1.165	139	5109
0.6	0.8386	0.2365	5.324	0.1830	1.185	141.31	5152

TABLE II Shear velocity (V_s), Poisson's ratio (σ), rigidity modulus (G), Young's modulus (E), mean sound velocity (V_m) and Debye temperature (θ) for $Zn_xCu_{1-x}FeCrO_4$ system

Content (x)	V_s (m/s)	σ	G (GPa)	E (GPa)	V_m (m/s)	θ_E (K)	θ_M (K)
0.0	2841	0.35	43.00	116.1	3154	429	–
0.2	2899	0.35	44.75	121.0	3219	438	125
0.4	2950	0.35	46.34	125.1	3275	445	139
0.6	2975	0.35	47.12	127.2	3303	449	–

The calculated values of G, σ, E, V_s and V_m for the compositions with $x = 0.0$, 0.2, 0.4 and 0.6 (Table II) are in good agreement to those obtained from UPT technique. This validates the present method of elastic moduli determination.

As the ferrite specimens under study are porous, (pore fraction ≈ 0.17), the values of elastic moduli have been corrected to zero porosity using Hosselman and Fulrath's formulae [12], given by:

$$\frac{1}{E_0} = \frac{1}{E}\left(1 - \frac{3f(1-\sigma)(9+5f)}{2(7-5f)}\right)$$

$$\frac{1}{G_0} = \frac{1}{G}\left[1 - \frac{15f(1-\sigma)}{(7-5\sigma)}\right]$$

$$K_0 = \frac{E_0 G_0}{3(3G_0 - E_0)}$$

$$\sigma_0 = \frac{E_0}{2G_0} - 1$$

The corrected values of Young's modulus (E_0), rigidity modulus (G_0), bulk modulus (K_0) and Poisson's ratio (σ_0) for different compositions are given in Table III. The values of E_0, n_0, and K_0 show regular variation similar to that of E, G, and K.

It can be seen from the Table II that, E, G and K increase continuously with increasing zinc content. The Poisson's ratio, however remains constant for different compositions. The value of Poisson's ratio is found to be 0.35 for all the compositions. This value lies in the range from -1 to 0.5 which is in conformity with the theory of isotropic elasticity. Following Wooster's work [13], the variation of E, G and K with increasing zinc content (x) may be interpreted in terms of interatomic bonding. Thus, it can be inferred from the increase of elastic moduli with concentration (x) that the inter atomic bonding between various atoms is being strengthened continuously. This compositional variation of the elastic moduli is similar to that has been observed in Cu-Zn, Li-Ti and Mg-Al ferrites [8]. These

TABLE III Elastic data (zero porosity) for of $Zn_xCu_{1-x}FeCrO_4$ system

Content x	E_0 (GPa)	G_0 (GPa)	σ_0	K_0 (GPa)
0.0	175.75	62.84	0.40	288.30
0.2	185.12	66.02	0.40	314.82
0.4	193.46	69.03	0.40	326.47
0.6	200.42	71.38	0.40	347.57

results are consistent with our recent work on infrared spectral study of the system [7] in which the bond angles between cations and cation-anion are found to decrease with increase in zinc content, suggested strengthening of inter ionic bonding.

The Debye temperature (θ_{E}) value of all the ferrites have been calculated using the Anderson's formula [14]:

$$\text{Debye temperature } (\theta_{\mathrm{E}}) = \frac{h}{k}\left[\frac{3N_{\mathrm{A}}}{4\pi V_{\mathrm{A}}}\right]^{1/3} V_{\mathrm{m}}$$

where h and k are Plank's and Boltzmann's constant respectively, N_{A} is Avogadro's number and V_{A} is mean atomic volume given by $(M/q)/\rho$, where M, the molecular weight (Table I) and q is the number atoms (i.e., 7) in the formula unit. The value of θ_{E} for each composition is presented in Table II. It is seen that θ_{E} increases with increasing Zn-constant (x). The Debye temperature is the temperature at which maximum lattice vibrations take place. The observed increase in θ_{E} with content (x) suggested that lattice vibrations are hindered due to zinc substitution. This may be due to the fact that strength of inter atomic bonding increases with the replacement of Cu^{2+} by Zn^{2+} in $\mathrm{Zn}_x\mathrm{Cu}_{1-x}\mathrm{FeCrO}_4$ system, as supported by our results on variation of elastic moduli with content (x). The magnitude of Debye temperature in the present work is consistent with those obtained for various ferrite systems [8, 9] and pure yttrium iron garnet [15].

The Debye temperature plays an important role in the study of a large number of solid-state problems involving lattice vibrations. A number of physical parameters such as mean square atomic displacements, elastic constants, are known to depend upon the Debye temperature of a solid. It has been shown that the Debye temperature obtained through different physical properties will not, in general, be equal.

Attempt has been made to extract the X-ray Debye temperature θ_{M} for typical the compositions of $\mathrm{Zn}_x\mathrm{Cu}_{1-x}\mathrm{FeCrO}_4$ system. The θ_{M} thus obtained is compared with the Debye temperature obtained from the elastic constant data. A method which depends on the principle of measuring the integrated intensities of a large number of Bragg reflections at a fixed temperature was first outlined by Buerger [16].

The Debye-Waller factor is defined as

$$M(T) = \frac{6h^2T}{mk\theta_{\mathrm{M}}^2}\left\{\phi(x) + \frac{x}{4}\right\}\frac{\sin^2\theta}{\lambda^2} \quad \text{or}$$
$$M(T) = B\frac{\sin^2\theta}{\lambda^2} \quad \text{where } B = \frac{6h^2T}{mk\theta_{\mathrm{M}}^2}\left\{\phi(x) + \frac{x}{4}\right\} \tag{1}$$

Here, m is the mass of atom (taken as the mean mass) (Table I), θ_{M} is the X-ray Debye temperature, T is the temperature, θ is Bragg's angle, $x = \theta_{\mathrm{M}}/T$ and λ is the wave length of X-ray; the function $(\phi(x) + x/4)$ is tabulated by James *et al.* [16].

The average vibration amplitudes are related to the Bragg intensities, within the quasi-harmonic approximation, through the Debye-Waller theory. The integrated intensity, *I*, from a cubic powder sample can be expressed as follows,

$$I = L_{\mathrm{p}}P|F|^2 \tag{2}$$

where L_{p} is function of the Bragg angle known as the Lorentz-polarization factor; *P* is multiplicity; and $|F|$ is the modulus of the structure factor. The structure factor for present system (space group $Fd3m\text{-}O_{\mathrm{h}}^{-7}$) can be written as

$$\begin{aligned} F(hkl) = {} & xf_{\mathrm{Zn}}F_{\mathrm{Zn}} \cdot e^{-\mathrm{MZn}} + (1-x)f_{\mathrm{Cu}}F_{\mathrm{Cu}} \cdot e^{-\mathrm{MCu}} \\ & + f_{\mathrm{Cr}}F_{\mathrm{Cr}} \cdot e^{-\mathrm{MCr}} + f_{\mathrm{Fe}}F_{\mathrm{Fe}} \cdot e^{-\mathrm{MFe}} \\ & + 4f_{\mathrm{o}} \cdot F_{\mathrm{o}} \cdot e^{-\mathrm{Mo}} \end{aligned} \tag{3}$$

The exponential term in Equation 3 represents the Debye-Waller factor for the five constituent atoms of zinc, copper, chromium, iron and oxygen; $f_{\mathrm{Zn}}, f_{\mathrm{Cu}}, f_{\mathrm{Cr}}, f_{\mathrm{Fe}}$ and f_{o} are their respective atomic scattering factors; $F_{\mathrm{Zn}}, F_{\mathrm{Cu}}, F_{\mathrm{Cr}}, F_{\mathrm{Fe}}$ and F_{o} are their respective structure factors which are sine and cosine functions of *hkl* values.

As the mass of zinc, copper, chromium, iron and oxygen atoms are different, the respective Debye-Waller factors will also be different. The mean mass of different compositions of the system is listed in Table I. To first approximation let M_{Zn}, M_{Cu}, M_{Cr}, M_{Fe} and M_0 be equal to each other, Equation 3 therefore becomes

$$\begin{aligned} F(hkl) &= (xf_{\mathrm{Zn}}F_{\mathrm{Zn}} + (1-x)f_{\mathrm{Cu}}F_{\mathrm{Cu}} + f_{\mathrm{Cr}}F_{\mathrm{Cr}} \\ &\quad + f_{\mathrm{Fe}}F_{\mathrm{Fe}} + 4f_{\mathrm{o}}F_{\mathrm{o}})e^{-\mathrm{M}} \\ &= \Sigma f e^{-\mathrm{M}} \end{aligned} \tag{4}$$

where

$$\begin{aligned} \Sigma f = {} & xf_{\mathrm{Zn}}F_{\mathrm{Zn}} + (1-x)f_{\mathrm{Cu}}F_{\mathrm{Cu}} + f_{\mathrm{Cr}}F_{\mathrm{Cr}} \\ & + f_{\mathrm{Fe}}F_{\mathrm{Fe}} + 4f_{\mathrm{o}}F_{\mathrm{o}} \end{aligned}$$

Equation 2 may be written using Equations 1 and 4, as

$$I = L_{\mathrm{p}}P|\Sigma f|^2 e^{-2\mathrm{B}}\sin^2\theta/\lambda^2 \tag{5}$$

The experimental structure factor, F_{corr}, may be obtained from Equation 5 using measured integrated intensity, *I*, as

$$|F_{\mathrm{corr}}|^2 = \frac{I}{L_{\mathrm{p}}P} = |\Sigma f|^2 e^{\frac{-2B\sin^2\theta}{\lambda^2}} \tag{6}$$

It follows from Equation 6, that the slope $\ln(|F_{\mathrm{corr}}|^2/|\Sigma f|^2)$ against $\sin^2\theta/\lambda_2$ yields the temperature factor B and hence θ_{M} can be obtained. The plots of $\ln(|F_{\mathrm{corr}}|^2/|\Sigma f|^2)$ against $\sin^2\theta/\lambda^2$ for typical compositions $x = 0.2$ and 0.4 at $T = 300$ K is shown in Fig. 2. It is apparent from Fig. 2 that the even-even ($h + k = 2n$, $1 + k = 2n$), even-odd ($h + k = 2n$,

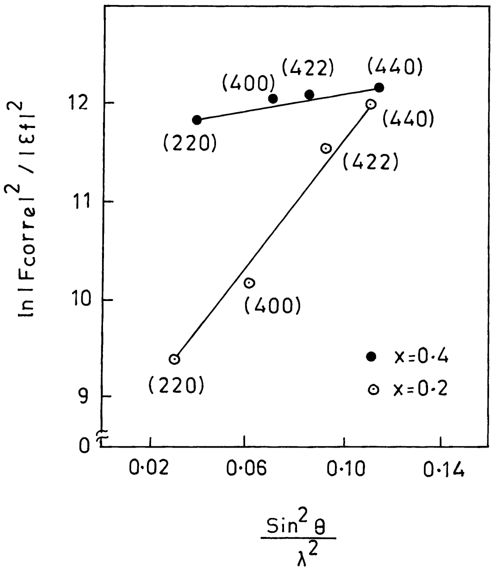

Figure 2 Plot of ln($|F_{\text{corr}}|2/|\Sigma f|^2$) versus $\sin^2\theta/\lambda^2$ at 300 K.

$1 + k = 2n + 1$), odd-even ($h + k = 2n + 1, 1 + k = 2n$) and odd-odd ($h + k = 2n + 1, 1 + k = 2n + 1$) reflections lie on the same straight line. The solid line in Fig. 2 is least squares fit to the experimental data points. The Debye temperatures derived from the slope of $\ln(|F_{\text{corr}}|^2/|\Sigma f|^2)$ against $\sin^2\theta/\lambda^2$ curves for the compositions with $x = 0.2$ and 0.4 and 0.6 are given in Table II. The Debye temperature, θ_{M}, obtained at 300 K from X-rays lies between 100–110 K range, while the Debye temperature θ_{E} from elastic constant data is ranging from (430–450 K) (Table II) for $x = 0.0$–0.6. This suggests that the Debye temperature obtained from elastic constant is higher than that of the X-ray diffraction analysis.

The discrepancy between the two can be explained on the basis of vibrational spectra. Possibly the elastic constant value θ_{E} is higher than the X-ray θ_{M} value mainly due to the existence of peaks in the vibrational spectra at low frequencies. The fact that the even-even, even-odd, odd-even and odd-odd reflections lie on the same straight line (Fig. 2) indicates that $M_{\text{Zn}} \approx M_{\text{Cu}} \approx M_{\text{Fe}} \approx M_{\text{Cr}} \approx M_{\text{o}}$. Thus, the experiment has not distinguished between the individual Debye temperatures or mean square atomic displacements appropriate to the atoms of zinc, copper, chromium, iron and oxygen in the system.

In conclusion, the elastic moduli, transverse and mean sound velocities and Debye temperature can be determined through infrared spectral analysis. The observed increase of elastic constants with zinc content suggest strengthening of inter atomic bonding. The Debye temperature obtained from elastic constant data is higher than that of the X-ray Debye temperature, mainly due to the existence of bands in the vibration spectra at low frequencies.

References

1. S. L. KAKANI and C. HEMRAJANI, *Solid State Phys.* C. CHAND & Sons (1997).
2. R. D. WALDRON, *Phys. Rev.* B **99** (1995) 1727.
3. K. B. MODI, H. H. JOSHI and R. G. KULKARNI, *Ind. J. Pure Appl. Phys.* **34** (1996) 92.
4. K. B. MODI, V. T. THANKI and H. H. JOSHI, *Ind. J. Phys.* **70A**(4) (1996) 497.
5. K. B. MODI, P. V. TANNA, S. S. LAGHATE and H. H. JOSHI, *J. Mater. Sci. Lett.* **19** (2000) 1111.
6. K. B. MODI and H. H. JOSHI, *Ind. J. Phys.* **76A**(6) (2002) 541.
7. M. C. CHHANTBAR, U. N. TRIVEDI, P. V. TANNA, H. J. SHAH, R. P. VARA, H. H. JOSHI and K. B. MODI, *ibid.* (2003) (in press).
8. D. RAVINDER, K. VIJAYA KUMAR and B. S. BOYANOV, *Mater. Lett.* **38** (1999) 22 and references there in.
9. D. RAVINDER and T. ALIVELU MANGA, *ibid.* **41** (1999) 254 and references therein.
10. L. VEGARD, *Z. Phys.* **5** (1921) 17.
11. J. SMITH and H. P. J. WIJN, Ferrites, Philips, Eindhoven, 1959.
12. D. P. H. HASSELMAN and R. M. FULRATH, *J. Amer. Ceram. Soc.* **47** (1964) 52.
13. W. A. WOOSTER, *Rep. Prog. Phys.* **16** (1953) 62.
14. O. L. ANDERSON, in "Physical Acoustics" edited by W. P. Mason, Vol. 3B (Academic Press, New York, 1965) p. 45.
15. L. SRIDESHMUKH, K. KRISHNA KUMAR, S. B. LAXMAN, A. R. KRISHNA and G. SATHAIAH, *Bull. Mater. Sci.* **21**(3) (1998) 219.
16. R. W. JAMES, "The Optical Principles of the Diffraction of X-ray" (Bell, Londan, 1967) p. 216.

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