Elastic constants determination for Fe^{3+} substituted YIG through infra-red spectroscopy and heterogeneous metal mixture rule

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In engineering practice, the elastic moduli often used are the Young's modulus, rigidity modulus, Bulk modulus and Poisson's ratio. Elastic data are used in industry to determine strength of the materials. When, we think about an application of any polycrystalline material (viz. spinel ferrites, garnets, superconductors, perovskites) subjected to some sort of mechanical stresses, the knowledge of its magnetic, electric/dielectric response and elastic properties help to decide suitability of the material for specific application. From fundamental research points of view the knowledge of elastic constants elucidate the nature of interatomic and interionic forces in solids.

The most conventional technique for elastic constants and Debye temperature determination is the ultrasonic pulse transmission technique [1]. The sample size required for such measurements is around 1 cm in length. In the study of elastic properties of nanoparticles, single crystal, irradiated or specially treated materials, where sample quantity is very small, such technique may not be useful. We have developed a new method to study the elastic properties of spinel ferrite material through infrared spectroscopy [2, 3], where only a few milligram of material is sufficient for the characterization.

The survey of literature shows that there is a scarcity of adequate data on elastic properties of garnet system except Debye temperature of single crystal YIG [4]. The present work reports the method of elastic constants and Debye temperature determination for substituted garnet system in general and Fe^{3+} substituted YIG: $Y_{3-x}Fe_{5+x}O_{12}$ ($x = 0.00, 0.15, 0.30$, and 1.0) in particular for the first time. To our knowledge no information has been reported in literature regarding elastic properties of $Y_{3-x}Fe_{5+x}O_{12}$ system. This work is in continuation of our work on structural properties [5] and infrared spectral study [6] of the system.

The values of lattice constant, a, X-ray density, ρ, and pore fraction, f, through X-ray diffraction analysis [5] and band positions, υ, through IR spectral analysis [6] (Table I) are used to calculate elastic constants corrected to zero porosity. The applicability of heterogeneous metal mixture rule [7, 8] has been tested. The experimental details regarding sample preparation, X-ray diffractometry and infrared spectroscopy have been given elsewhere [5, 6].

The room temperature (300 K) infrared spectra for $Y_{3-x}Fe_{5+x}O_{12}$ were found to exhibit three bands in the range 400–700 (10^2 m^{-1}). The high frequency band (υ_d) is caused by the stretching vibrations of the tetrahedral (d-site) metal-oxygen bond, the mid frequency band (υ_a) is caused by the metal–oxygen vibrations in octahedral (a-site) sites and the lower frequency band (υ_c) is due to the dodecahedral (c-site) metal–oxygen bond [6].

The force constant is a second derivative of potential energy with respect to the site radius the other independent parameters kept constant. The force constant in terms of reduced mass (μ) and wave number (υ) is given by:

$$k = 4\pi^2 c^2 \cdot \upsilon^2 \cdot \mu \tag{1}$$

where c is the velocity of light (3×10^8 m/sec) and μ is reduced mass of the composition calculated by considering atomic weight and concentration of the cations involved to the molecular weight of the composition (Table II). The force constants, for tetrahedral site, k_d, octahedral site, k_a, and dodecahedral site, k_c, were calculated from Equation (1) using corresponding band position value (Table I), and same are present in Table II. The shifting of band towards lower frequency side is accompanied with decrease in force constant with Fe-substitution in the system; suggest weakening of strength of interatomic bonding.

The bulk modulus B of solid in terms of stiffness constant is defined as $B = 1/3[C_{11} + 2C_{12}]$, but according to Waldron *et al*. [9] for isotropic materials with cubic symmetry like spinel ferrites and garnets $C_{11} = C_{12}$, therefore B is simply given by C_{11}. Further, force constant (k) is a product of lattice constant and stiffness constant [1]. The value of lattice constant obtained from X-ray diffraction analysis (Table I) and average force constant ($\bar{k} = (k_d + k_a + k_c)/3$) has been used for calculating B and is given in Table III. We have determined the value of longitudinal elastic wave

TABLE I Lattice constant (a), X-ray density (ρ), bulk density (d), pore fraction (f) and band position (υ) for Y-Fe-O system

Content x	a (nm) ± 0.0002 nm	$(kg/m^3) \times 10^3$ ρ	d	f	$(m^{-1}) \times 10^2$ υ_d	υ_a	υ_c
0.00	1.2332	5.23	4.30	0.178	656.5	604.1	572.5
0.15	1.2334	5.19	4.40	0.152	656.6	605.8	566.3
0.30	1.2330	5.16	4.44	0.139	656.8	606.0	565.9
1.00	1.2317	5.01	4.05	0.190	648.0	596.0	538.1

TABLE II Reduced mass (μ), force constant (k) and elastic wave velocity (V) for Y-Fe-O system

Content x	$\mu \times 10^{-26}$ (kg/mole)	(N/m) $\times 10^2$				(m/s)		
		k_d	k_a	k_c	$\bar{k}$	V_l	V_s	V_m
0.00	1.1176	1.71	1.45	1.30	1.48	4799.82	2771.18	3076.56
0.15	1.1043	1.69	1.44	1.26	1.46	4778.73	2759.0	3063.04
0.30	1.0908	1.67	1.37	1.24	1.43	4738.31	2735.66	3037.13
1.00	1.0250	1.53	1.29	1.05	1.29	4572.92	2640.18	2931.12

TABLE III Bulk modulus (B), Young's modulus (E), rigidity modulus (G), Poisson's ratio (σ) and Debye temperature (θ) for Y-Fe-O system

Content x	(GPa)			σ	θ (K)
	B	E	G		
0.00	120.49	108.44	40.16	0.35	403.11
0.15	118.52	106.68	39.51	0.35	401.22
0.30	115.85	104.27	38.62	0.35	397.95
1.00	104.83	94.34	34.94	0.35	384.5

velocity V_l using the formula suggested by Waldron [9]: $V_l = (C_{11}/\rho)^{1/2}$ and the transverse elastic wave velocity (V_s) by general approximation: $V_l = 3^{1/2} \cdot V_s$ [2, 3]. The value of V_l and V_s are in the same order obtained for various spinel ferrite systems [2, 3 and reference there in].

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

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

$$\text{Poisson ratio}(\sigma) = \left(\frac{3B - 2G}{6B + 2G}\right)$$

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

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

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

and the Debye temperature (θ) value of all the garnets have been calculated using the Anderson's formula [10]

$$\theta = \frac{h}{k_B}\left[\frac{3N_A}{4\Pi V_A}\right]^{\frac{1}{3}} v_m$$

where V_A and N_A are mean atomic volume given by $(M/q)/\rho$, M, the molecular weight and q is the number atoms (i.e., 20) in the formula unit, N_A is Avogadro's number, h and k_B are Plank's and Boltzmann's constant, respectively. The values of G, σ, E, V_m and θ for all the compositions are included in Tables II and III. It can be seen from Table III that B, E, G and θ decrease continuously with increasing Fe^{3+} content (x). The Poisson's ratio however remains constants for different compositions. The value of σ 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 [11], the variation of B, E, G and θ with increasing Fe^{3+}-content (x) may be interpreted in terms of interatomic bonding. Thus, it can be inferred from the decrease in elastic moduli and Debye temperature with concentration (x) that the interatomic bonding between various atoms is getting weakend continuously.

In general, the samples prepared by solid-state reaction method are found to be porous. The measured elastic moduli do not have much significance unless they are corrected to zero porosity. As the garnet specimens under study are porous (pore fraction $\approx$ 0.14–0.19), the values of elastic moduli have been corrected to zero porosity using Hosselman and Fulrath's formula [12] given by

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

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

$$B_0 = \rho(2V_s^2/(1-2\sigma) + V_s)^2$$

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

The corrected values of Young's modulus (E_0), rigidity modulus (G_0), bulk modulus (B_0) and Poisson's ratio (σ_0) for different compositions are given in Table IV. The value of E_0, G_0 and B_0 show regular variation similar to that E, G and B (Table III).

Recently we have developed and successfully implemented heterogeneous-metal-mixture rule (MMMR) to estimate elastic constants of various spinel ferrites, superconductors and perovskites [7, 8]. The validity of this model for estimating elastic moduli of various garnet compositions has been tested. It is always desirable

TABLE IV Elastic moduli (corrected to zero porosity) (B_0, E_0, G_0) and from MMMR (B^*, E^*, G^*, θ^*) for Y-Fe-O system

Content x	(GPa)				(GPa) (MMMR)			
	B_0	E_0	G_0	σ_0	B^*	E^*	G^*	θ^* (K)
0.00	157.21	168.21	59.99	0.40	119.85	155.87	61.00	398.75
0.15	154.62	153.16	55.05	0.39	124.13	158.63	62.5	402.31
0.30	151.13	144.32	52.06	0.39	124.84	161.38	63.1	405.87
1.00	136.63	151.99	53.99	0.41	137.75	174.25	68.0	422.5

to have general idea of elastic constants value before synthesis and its characterization, in order to tailor the properties. According to this model "The elastic constant and Debye temperature value of polycrystalline oxide material (K'_{pm}) is equal to the average stoichiometric compositional addition of elastic constant values of metallic elements present in the material". The elastic moduli such as bulk modulus, rigidity modulus, Young's modulus and Debye temperature values of various metallic elements (Y and Fe in present case) are taken from the literature [13–15] and are used to estimate K'_{pm}. The elastic constant value, to be estimated, for a given garnet system can be given as:

$$K'_{pm} = 1/n \infty \sum C_{in} \cdot K_n \quad i > 0, \quad n = 1$$

where, K'_{pm} is either Bulk modulus (B), Young's modulus (E), rigidity modulus (G) or Debye temperature (θ) of the polycrystalline system $Y_{3-x}Fe_{5+x}O_{12}$ to be estimated, n is the total concentration of metallic cations involved in the chemical formula of the polycrystalline material ($n = 8$), C_{in}, concentration of the nth cation in the formula unit while K_n is the corresponding modulus of the metallic element.

The values of elastic moduli (B^*, E^*, G^*) and Debye temperature (θ^*) obtained from MMM rule are summarized in Table IV. The results of our calculations are in conformity with the elastic constant values obtained from IR spectral analysis with adequate accuracy.

In conclusion, the elastic moduli and Debye temperature can be determined through IR spectral analysis. The observed decrease of elastic constants with Fe-substitution suggests weakening of interatomic bonding. The reasonable agreement between elastic moduli corrected to zero porosity and calculated using metal-mixture rule, validates of the method used for the garnet system.

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Appendix

Illustrative calculations for elastic constant and Debye temperature determination through MMM rule.

(i) $Y_2Fe_6O_{12}$ ($x = 1.0$)
$B'_{pm} = 1/8[(2)\ 41.6\ \text{GPa} + (6)\ 169.8\ \text{GPa}]$ Ref. [15]
$B'_{pm} = 137.75$ GPa (MMMR)
$B_0 = 136.63$ GPa (IR)

(ii) $Y_{2.85}Fe_{5.15}O_{12}$ ($x = 0.15$)
$\theta'_{pm} = 1/8[(2.85) \cdot 280\ \text{K} + (5.15) \cdot 470\ \text{K}]$ Ref. [14]
$\theta'_{pm} = 402.31$ K (MMMR)
$\theta = 401.22$ K (IR)

References

1. S. L. KAKANI and C. HEMRAJANI, "Textbook of Solid State Physics" (Sultan Chand & Sons, New Delhi, 1997).
2. K. B. MODI, *J. Mater. Sci.* **39** (2004) 2884.
3. K. B. MODI, U. N. TRIVEDI, M. P. PANDYA, S. S. BHATU, M. C. CHHANTBAR and H. H. JOSHI, "Proc. Nat. Conf. Microwaves and Optoelectronics" (Anamaya Publishers, New Delhi, 2004) p. 223.
4. LALITHA SIRDESHMUKH, K. KRISHNAKUMAR, S. BALAXMAN, A. RAMAN KRISHNA and G. SATHAIAH, *Bull. Mater. Sci.* **21**(3) (1998) 219.
5. R. P. VARA, H. J. SHAH, M. P. PANDYA, M. C. CHHANTBAR and K. B. MODI, *Ind. J. Pure Appl. Phys.* **42** (2004) 117.
6. K. B. MODI, R. P. VARA, H. G. VORA, M. C. CHHANTBAR and H. H. JOSHI, *J. Mater. Sci.* **39** (2004) 2187.
7. K. B. MODI and H. H. JOSHI, *Mat. Lett*. (2004) (Communicated).
8. K. B. MODI, M. C. CHHANTBAR and H. H. JOSHI, *J. Mater. Sci Lett.* (2004) (Communicated).
9. R. D. WALDRON, *Phys. Rev.* **99** (1955) 1727.
10. O. L. ANDERSON, in "Physical Acoustics," edited by, W. P. Mason (Academic Press, New York, 1965) vol. 3B, p. 63.
11. W. A. WOOSTER, *Rep. Prog. Phys.* **16** (1953) 62.
12. D. P. H. HOSSELMAN and R. M. FULRATH, *J. Amer. Ceram. Soc.* **47** (1964) 52.
13. www.webelements.com/webelements/elements/text/phys.html.
14. C. KITTEL, "Introduction to Solid State Physics," 5th ed. (Wiley Eastern, New York, 1976) p. 126.
15. MICHEL DE PODESTA, "Understanding the Properties of Matter," 2nd ed. (Taylor and Francis, New York, 2002) p. 183.

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