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Elastic Properties of Antimony Substituted Lithium Ferrites through Ultrasonic Pulse Transmission Technique and IR Spectrum

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Abstract: ***The elastic and structural properties of antimony – substituted lithium ferrites [$Li_{0.5+x}Sb_xFe_{2.5-2x}$]O4 of various compositions sintered at 1200 ^oCwere measured at room temperature using the ultrasonic pulse transmission technique. From XRD study it confirms the elastic properties of the specimens were investigated as a function of composition. From the experimentally observed values of longitudinal (V_ℓ) and shear (V_s) wave velocities, Young's (E), Rigidity (n) and Bulk (k) moduli are calculated and found to decrease with increase of antimony content upto x = 0.4 then increased at x=0.5 similarly poission's ratio also increased upto x=0.4 and then increased at x=0.5. Ferrites under investigation are porous, the elastic moduli have been corrected to zero porosity using Hassel man and Fulrath's formulae. It is observed that the corrected values of elastic moduli are increased at x = 0.1and then gradually decreased poission ratio are corrected to zero and found to increase upto x=0.4 and finally decreased at x=0.5. Debye temperatures (θ_D) of these specimens are calculated using Anderson's formula and it is found that decrease with increasing antimony. The elastic moduli with compositions were interpreted in terms of the binding force between the atoms. The average sound velocity (V_m) is found to decreases linearly with Debye temperature (θ_D).The elastic moduli were also calculated using IR spectrum for x=0.0 and found in good agree with practical value.***

Keywords:

1. Introduction

Lithium ferrites are the spinel soft ferrites have potential applications in science and technology as electrical components,magnetic and microwave devices over wide range of frequencies due to their high resistivity,low dielectric losses,high dielectric constan,high squareness ratio, superior temperature stability of saturation magnetization,low intrinsic line width and low magnetic losses,high Curie temperature and high saturation magnetization. Inaddition to that preparation are easy and low cost. In view of the wide ranging applications in industry as well as basic research of lithium ferrites has been chosen for the present study with special reference to the dependence of its elastic behavior on sintered at high temperature. The elastic properties of ferrites are important in industry because of their elastic data are very much useful to determine the strength of the materials under various strained conditions while in basic research ,the data are useful obtaining an insight into the structure of the inter-atomic and inter-ionic forces in solids especially of the long-range type forces. A systematic study of the elastic properties of antimony substituted lithium ferrite as a function of composition has been undertaken at room temperature and verified for x=0.0 from IR spectrum ,the results are presented in this paper.

2. Experimental

The ferrite samples with compositional formula [$Li_{0.5+x}$ Sb $_xFe_{2.5-2x}$] O4 (where x = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5), were prepared by double sintering technique. Appropriate proportion of AR grade Li_2CO_3, Sb_2O_5,Fe_2O_3 were taken and thoroughly mixed in an agate mortar in the presence of methanol. The dried mixture was pre-sintered at 625 ^oC for 4 hrs. The related powder was grained again and granulated using a small amount of PVA binder. Finally samples and toroids were pressed at 5 tones / cm^2 and finally sintered at 1200^oC for 4hrs. The samples were cooled in the furnace in air atmosphere at the rate of 3^{0}C/min. The ultrasonic longitudinal (V_ℓ) and shear (V_s) wave velocities of all the ferrite samples were determined by the ultrasonic pulse transmission technique. In this method 1MHz PZT crystals and calibrated range of oscilloscope (Tektronix Model No 2221) were used with an accuracy of error +1% in velocity measurements.Fourier Transform Infrared (FTIR) Spectra of the present sample were (x=0.0)recorded in the wave number range of 300-1000 cm^{-1} using BRUKER ALPHA T, USA with software Opus 6.5 in the accuracy of ± 4 cm^{-1} . The infrared spectroscopic study for the sample were carried out in KBr medium.

3. Results and Discussion

The values of longitudinal (V_ℓ)and shear (V_s) wave velocities of all the samples were determined by using Ultrasonic pulse transmission technique (UPTT) [1] method at room temperature and these values are given in Table 1. The Young's modulus (E), rigidity modulus (n), bulk modulus (K),longitudinal modulus (L), and Poission's ratio have been calculated using the experimental values V_ℓ and V_s with the help of the formulae;

$$\sigma = (V_\ell^2 - 2V_s^2)/2(V_\ell^2 - V_s^2) \qquad (1)$$

$$L = \rho V_\ell^2 \qquad (2)$$

$$K = L - (4/3)n \qquad (3)$$

$n = V\rho_s^2$ (4)

And

$E = 2n(1+\sigma)$ (5)

The calculated values of E, n, σ are given in table (1). It can be observed from the table that the values of E, n, are decreasing continuously with increasing antimony content up to x=0.4.and finally slightly increased at x=0.5. In case of **k** are gradually decreasing with increasing antimony content. These values are almost agree with the reported values slightly higher than the reported values [2] due to sinteredat high temperature.It is observed that the Poission's ratio (σ) for all the samples are gradually increased up to x=0.4 and then decreased at x=0.5. The elastic moduli of samples depend on density of the material, after confirmed the spinel formation and calculated X-ray density, the porosity to be known with density of the sample.The X-ray density and bulk density of the samples are given in Table 1.

Table 1 Elastic data (uncorrected) of $[Li_{0.5+x}\ Sb_xFe_{2.5-2x}]\ O_4$ Ferrites

Sl.no	X	Bulk density (10^3 Kg/m^3)	Porosity (%)	V_l (m/s)	V_s (m/s)	V_m (m/s)	E (10^{10}N/m^2)	n (10^{10}N/m^2)	K (10^{10}N/m^2)	σ
1	0.0	4.6924	1.3	5983	3323	3701	13.233	5.161	9.888	0.28
2	0.1	4.3742	7.5	5842	3245	3614	11.763	4.606	8.787	0.28
3	0.2	4.37404	7.7	5732	3065	3423	10.682	4.109	8.892	0.29
4	0.3	4.3618	9.4	5536	2944	3290	9.850	3.780	8.327	0.30
5	0.4	4.5265	5.5	5025	2672	2986	8.421	3.231	7.120	0.30
6	0.5	4.5749	3.9	4983	2693	3006	8.584	3.317	6.935	0.29

The percentage of porosity is varying from 1.3% to 3.9 %, so that the elastic moduli of the measured samples will be less than non – porous samples. Hence, the observed elastic moduli of the samples have been corrected to zero porosity using Hasselman and Fulrath's formulae [3] given by ;

$n/n_0 = 1-15p(1-\sigma)/(7-5\sigma)$ (6)

And

$E/E_0 = 1-3P(1-\sigma)(9+5\sigma)/2(7-5\sigma)$ (7)

Where n_0 = corrected value of rigidity modulus, E_0 = corrected values of Young's modulus and P = volume fraction of the pores.From the values of E_0 and n_0, the corrected values of bulk modulus (K_0) and Poisson's ratio (σ_0) have also been obtained using the following relation;

$K_0 = E_0 n_0/3(3n_0 - E_0)$ (8)

And

$\sigma_0 = (E_0/2n_0) - 1$ (9)

The corrected values of E_0 , n_o , K_0 and σ_o are given in Table (2) . It can be seen from the table that the values of E_0, n_o , and K_0 are decreasing with increasing antimony content .

Table 2 Elastic data of $[Li_{0.5+x}\ Sb_xFe_{2.5-2x}]\ O_4$ corrected to Zero porosity

Sl.no	X	E_o (10^{10} N/m^2)	n_o (10^{10} N/m^2)	K_o (10^{10} N/m^2)	σ_o
1	0.0	13.598	5.319	10.022	0.28
2	0.1	13. 849	5.387	10.749	0.29
3	0.2	12.630	4.817	11.141	0.31
4	0.3	12.148	4.609	8.334	0.32
5	0.4	9.462	3.610	7.715	0.31
6	0.5	9.320	3.588	6.625	0.30

Following Woostr's work [4], the variation of elastic moduli with composition may be interpreted in terms of binding forces between the atoms. Debye temperatures (θ_D) for Li – Sb ferrites have been calculated using the simple method given by Anderson formula [5,6];

$$\text{Debye Temperatures } (\theta_D) = \left(\frac{h}{k}\right)\left(\frac{3qN\rho}{4\pi m}\right)^{1/3} V_m \quad (10)$$

Where h =Planck's constant, k = Boltzman's constant, N = Avagadro's Number, m = Molecular weight of the specimen, q = Number of atoms in molecule, ρ = Density of the Specimen and V_m = Average sound velocity which is given by:

$$V_m = \left[\frac{1}{3}\left(\frac{1}{V_l^3} + \frac{2}{V_s^3}\right)\right]^{-1/3} \quad (11)$$

The values of V_l/ρ, V_s/ρ are calculated and shown in Table 3. The calculated values of θ_D, using Eq. (10) are given in Table 3. It is evident from the table that, like the elastic moduli, the Debye temperature is also decreasing with increasing antimony content upto x= 0.4 then increased at x=0.5 . This variation also can be interpreted in terms of the binding forces between atoms related with density. The average sound velocity (V_m) for all the samples have been calculated using Eq. (11) and are also given in Table 3.

Table3 Relationship between atomic weights and velocities of $[Li_{0.5+x}\ Sb_{x}Fe_{2.5-2x}]\ O_4$ ferrites

Sl. no	X	V_l/ρ	V_s/ρ	V_m (m/s)	θ_D (K)
1	0.0	1.28	0.71	3701	504
2	0.1	1.34	0.74	3614	479
3	0.2	1.31	0.70	3423	453
4	0.3	1.27	0.67	3290	433
5	0.4	1.11	0.59	2986	397
6	0.5	1.09	0.59	3006	400

A plot of average sound velocity (V_m) against Debye temperature is shown in Fig. 1. It is interesting to note from the figure that the average sound velocity decreases linearly with the Debye temperature finally slightly/slight increased at x=0.5. This behavior clearly indicates direct relationship between the acoustic parameter (average sound velocity) and the important thermodynamic parameter (Debye temperature).

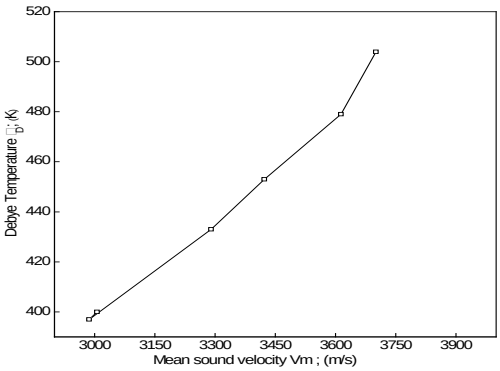

Fig 1. Variation of average sound velocity (V_m) with Debye temperature (θ_D) for antimony substituted lithium ferrites.

The elasic moduli can also be evaluated from IR study has been developed by Modi et al [7-9]. In the present study the elastic maduli were calculated only for x=0.0 and other samples are not performed due to lack of cation distribution from Mössbauer spectrometer for calculating force constants.The force constant is a second derivative of potential energy with respect to the site radius (R_A and R_B), the other independent parameter being kept constant, for tetrahedral site (K_t) and octahedral site (K_o), were calculated employing the method substituted by Waldron [10]. According to Waldron the force constants, K_t and K_o for respective sites are given by:

$K_t = 7.62 \times M_A \times \upsilon_1^2 \times 10^{-7}$ N/m (12)

$K_t = 10.62 \times M_{B/2} \times \upsilon_2^2 \times 10^{-7}$ N/m (13)

Where M_A and M_B are the molecular weights of cation on A-site and B-site calculated cation distribution $(Fe^{3+})[Li_{0.5}Fe_{2.5}]$ [11] for pure lithium ferrite (x=0). From the Fig.2 the primary absorption band ($\nu_{1)}$ is 582 cm^{-1} and the secondary absorption band ($\nu_{2)}$ is 476 cm-1.the average force constant is listed in Table 4. The elastic moduli can be evaluated using the following relation [12,13].

Bulk modulus (K) = $\frac{1}{3}(C_{11}+C_{12})$ = L — $\frac{4}{3}G$ (14)

Where C_{11} and C_{12} are the stiffness constant. But according to Waldron [10] for isotropic materials with cubic symmetry like spinel ferrites and garnets $C_{11} \approx C_{12}$. Therefore, K =C_{11}. Also, the force constant(K) is a product of lattice (a) and stiffness constant (C_{11}) i.e. K= aC_{11} [14]. And K is also average force constant (K= (K_t+K_o)/2).The value of lattice constant obtained from X-ray diffraction analysis is 8.333Å. The other elastic moduli of the ferrite specimens are calculated using following formulae [15,16] for a cubic lattice:

Stiff constant (C_{12}) = $\frac{\sigma C11}{(1-\sigma)}$ (15)

Rigidity modulus (G) = $\frac{E}{2(1+\sigma)}$ (16)

Young's modulus (E) = $2(1+\sigma)\ \rho(V_s)^2$ or

(E) = $\frac{(C11-C12)(C11+2C12)}{C11+C12}$ (17)

Poission's ratio (σ) = $\frac{3K-2G}{6K+2G}$ (18)

We have determined the value of longitudinal elastic wave velocity (V_ℓ) using the formula suggested by Waldron [10], $V\ell = \left(\frac{C_{11}}{\rho}\right)^{1/2}$ and the transverse elastic wave velocity (V_s) by general approximation [16,17] $V_l = 3^{1/2}\ V_s$. The values of $V\ell$ and V_s are further used to calculate the mean velocity and Debye temperature of the ferrite specimen using the following formula [18]:

Mean elastic Wave velocity (V_m) = $\left[\frac{v_l^3+v_s^3}{2v_l^3+v_s^3}\right]^{\frac{1}{3}}$ (19)

Debye temperature(θ_D) = $\frac{h}{k}\left[\frac{3N_A}{4\pi V_A}\right]^{\frac{1}{3}}$ (20)

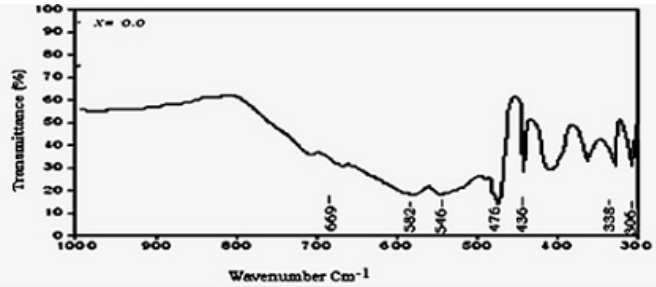

Fig.2 The IR absorption bands of $[Li_{0.5+x}\ Sb_xFe_{2.5-2x}]O_4$, where 'x' =0.0 concentration of antimony substitution

Table 4: Force constant (K), Elastic wave velocities (V_ℓ & Vs), stiffness constant (C_{ij}), Young's modulus (E), rigidity modulus (η), Bulk modulus (K), mean velocity (Vm), Poisson's ratio (σ) and Debye temperature (θ_D) of $Li_{0.5}\ Fe_{2.5}\ O_4$ ferrite.

Content x	V_ℓ (m/s)	Vs (m/s)	K (N/m^2)	η (N/m^2)	E (N/m^2)	σ	Vm (m/s)	θ_D (K)
0.0	5638.77	3255.64	8.28×10^{10}	4.97×10^{10}	12.433×10^{10}	0.25	3615.27	492

From Table 4 the calculated value of elastic moduli and Debey temperature from IR spectrum for x=0.0 are in good agreement with which are obtained from UPT technique (Table1).

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