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Ceramics International 32 (2006) 111–114

CERAMICS INTERNATIONAL

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Study of elastic behaviour of magnesium ferri aluminates

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Received 4 October 2004; received in revised form 29 November 2004; accepted 7 January 2005
Available online 21 March 2005

Abstract

The elastic behaviour of $MgAl_xFe_{2-x}O_4$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0) has been studied by infrared spectroscopy and X-ray diffraction analysis. The force constants for tetrahedral and octahedral sites determined by IR spectral analysis, lattice constant and X-ray are used to calculate elastic moduli-like bulk modulus, Young's modulus, rigidity modulus, Poisson's ratio and Debye temperature. The observed variation of elastic constants has been interpreted in terms of strength of interatomic bonding and electronic configuration of the cations involved in the system. The applicability of heterogeneous metal mixture rule has been tested; the agreements of the results obtained from the present method with the results of the other method confirm the validity of the methods used.

Keywords: D. Ferrites; Infrared spectra; Elastic properties

1. Introduction

The knowledge of elastic properties, besides magnetic, electric/dielectric response of given solids help to decide the suitability of a given material for the specific application. From the fundamental points of view the elastic constants are important to elucidate the nature of binding forces and to understand the thermal properties like specific heat and Debye temperature of the solids.

The most conventional technique for elastic constants and Debye temperature determination is the ultrasonic pulse transmission technique (UPT) [1]. The limitation of such technique is that it requires sample size having length ~1 cm in pellet form. In the study of nanoparticles, single crystal, irradiated or specially treated materials, where sample quantity is very small or it is not possible to pelletize them, such technique may not be useful. We have developed a new method to study the elastic properties of spinel ferrites material by infrared spectroscopy [2,3] where a few milligrams of material is sufficient.

It is always desirable to have general idea of elastic moduli values before synthesis and its characterization, in order to tailor the properties. We have developed a model based on heterogeneous mixture of metallic elements, which made modestly successful predictions for the elastic moduli: bulk modulus, Young's modulus and rigidity modulus of a given polycrystalline composition using corresponding elastic modulus of the metallic element [4].

2. Experimental

The samples of the spinel solid solution series $MgAl_xFe_{2-x}O_4$ for $x = 0.0$–1.0 with steps of $x = 0.2$, were prepared by the standard ceramic method. The X-ray diffraction patterns for all the samples were recorded at 300 K with a Philips (PM 9220) diffractometer using Fe Kα radiation. The values of lattice constant 'a' were determined with an accuracy of ± 0.0002 nm, which in turn used to calculate X-ray density ($\rho = 8\ M/Na^3$; M = molecular weight of the sample, N = Avogadro's number) [5]. The infrared spectra for all the compositions at 300 K were recorded in the wave number range of 400–4000 cm^{-1}. No absorption bands were observed above 1000 cm^{-1}. For the present study, a BRUKER IFS 66v FT-IR spectrometer was used for the infrared spectroscopic studies in KBr medium.

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0272-8842/$30.00
doi:10.1016/j.ceramint.2005.01.005

Table 1
Lattice constant (a), X-ray density (ρ), molecular weight (M), band position (υ) and force constant (k) for $MgAl_xFe_{2-x}O_4$ system

Content (x)	a (nm) ± 0.0002 nm	ρ (kg/m^3) $\times 10^3$	M_1 (kg) $\times 10^{-3}$	M_2 (kg) $\times 10^{-3}$	υ_1 (m^{-1}) $\times 10^2$	υ_2 (m^{-1}) $\times 10^2$	k_t (N/m) $\times 10^2$	k_o (N/m) $\times 10^2$	k (N/m) $\times 10^2$
0.0	0.8341	4.58	52.693	83.312	603.4	436.0	1.462	0.841	1.152
0.2	0.8310	4.50	48.989	81.243	569.5	426.5	1.211	0.785	0.998
0.4	0.8281	4.41	45.285	79.174	588.5	443.1	1.195	0.825	1.010
0.6	0.8264	4.30	41.581	77.105	590.1	451.8	1.103	0.836	0.969
0.8	0.8237	4.21	39.769	73.144	602.3	460.2	1.099	0.823	0.961
1.0	0.8213	4.10	37.957	69.183	616.3	471.2	1.099	0.816	0.956

The IR spectra were used to obtain band positions in order to calculate force constants (Table 1)

3. Results and discussion

The room temperature (300 K) infrared spectra for $MgAl_xFe_{2-x}O_4$ system with $x = 0.0$, 0.4, 0.6 and 1.0 are shown in Fig. 1. The IR spectra exhibit two main absorption bands, $\upsilon_1 \sim 600\ cm^{-1}$and $\upsilon_2 \sim 450\ cm^{-1}$ which may be attributed to the A- and B-sites in the spinel lattice. The high frequency band is in the range 569–616 cm^{-1} and the lower frequency band is in the range 426–471 cm^{-1}. The absorption band υ_1 is caused by the stretching vibration of the tetrahedral metal-oxygen bond, and the absorption band υ_2 is caused by the metal–oxygen vibrations in octahedral sites. The band positions for all the compositions are given in Table 1. The detailed infrared spectral analysis is given elsewhere [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 constants, for tetrahedral site (k_t) and octahedral site (k_o) were calculated employing the method suggested by Waldron [7]. According to Waldron the force constants, k_t and k_o, for respective sites are given by,

$$k_t = 7.62 M_1 \upsilon_1^2 \times 10^{-7}$$

$$k_o = 10.62 \times \frac{M_2}{2} \times \upsilon_2^2 \times 10^{-7}$$

where M_1 and M_2 are the molecular weights of cations on A- and B-sites respectively, calculated from cation distribution determined through X-ray intensity calculations [5].

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 [7] $C_{11} \approx C_{12}$ therefore, B simply given by C_{11}. Further force constant (k) is a product of lattice constant (a) and stiffness constant [1]. The values of lattice constant and average force constant ($k = (k_t + k_o)/2$) have been used for the determination of B and are presented in Table 2. We have determined the value of longitudinal elastic wave velocity (V_l) using the formula suggested by Waldron [7]: $V_l = (C_{11}/\rho)^{1/2}$ and the transverse elastic wave velocity (V_s) by general approximation $V_l = \sqrt{3}V_s$ [8–10]. The values of V_l and V_s are in the same order obtained from IR spectral analysis [2,3,7] and ultrasonic pulse transmission technique [8–10], and are summarized in Table 2.

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

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

$$\text{Poisson's ratio } (\upsilon) = \frac{3B - 2G}{6B + 2G}$$

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

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

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

The calculated values of G, υ, E and V_m for all the compositions (Table 2) are in good agreement to those obtained from UPT technique. This validates the present method of elastic moduli determination.

It can be seen from the Table 2 that, E, G and B decrease continuously with increasing Al-content (x). The Poisson's ratio, however, remains constant as a function of compositions. The value of υ is found 0.35 for all the compositions. This value lies in the range from -1 to 0.5, which is in conformity with theory of isotropic elasticity. Following

Table 2
Elastic wave velocity (V), bulk modulus (B), Young's modulus (E), rigidity modulus (G), Poisson's ratio (υ) and Debye temperature (θ) for $MgAl_xFe_{2-x}O_4$ system

Content (x)	V_l (m/s)	V_s (m/s)	V_m	B	E (GPa)	G	υ	θ (K) (IR)	θ (K) (MMMR)
0.0	5491.20	3170.35	3519.84	138.10	124.28	46.03	0.35	480.87	446.66
0.2	5166.10	2982.65	3311.31	120.10	108.08	40.03	0.35	454.16	443.87
0.4	5259.04	3036.31	3370.79	121.97	109.70	40.66	0.35	463.57	441.07
0.6	5222.94	3015.47	3347.74	117.30	105.57	39.10	0.35	461.57	438.27
0.8	5264.95	3039.72	3374.66	116.70	105.03	38.90	0.35	467.00	435.47
1.0	5328.30	3076.30	3415.28	116.40	104.76	38.80	0.35	473.66	432.66

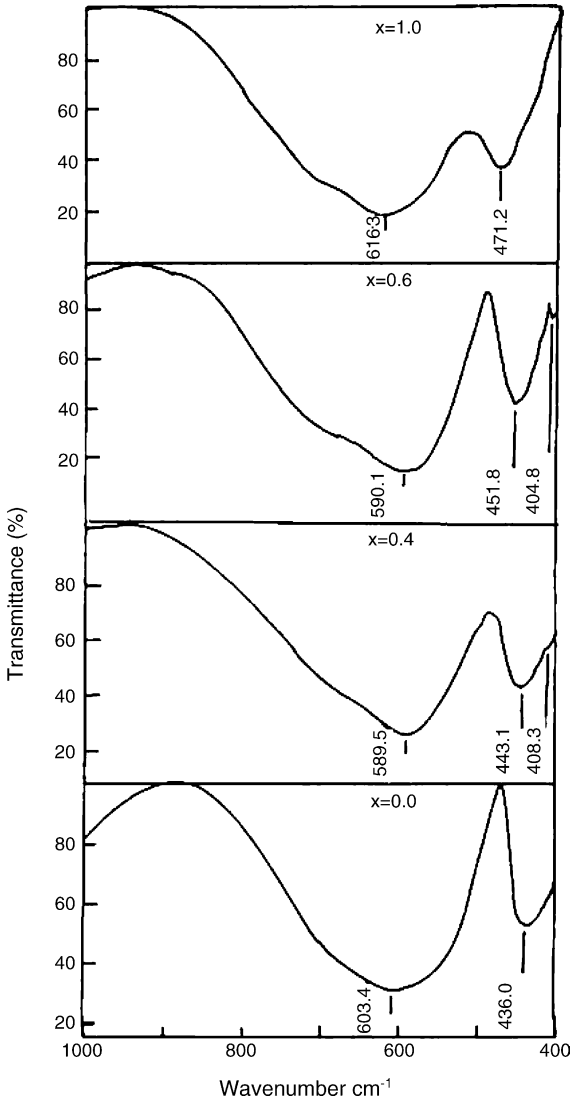

Fig. 1. Infrared spectra of Mg–Al–Fe–O system with $x = 0.0$, 0.4, 0.6 and 1.0 compositions.

Wooster's work [11], the variation of E, G and B with increasing Al-concentration may be interpreted in terms of interatomic bonding. Thus, it can be inferred from the decrease of elastic moduli with concentration (x) that the interatomic bonding between various atoms is getting weakened continuously.

In the present system weakening of strength of interatomic bonding on aluminium (Al^{3+}) substitution for Fe^{3+} ions can be explained as follows: The Fe^{3+} ions with $3d^5$ outer most orbital configuration are replaced by Al^{3+} ions with $2p^6$ configuration, that form bond with $2p^6$ orbit of oxygen ion (O^{2-}). It is well known that completely filled orbit is more stable as compared to half filled orbit. In the present case Fe^{3+} ions with half filled outermost orbit ($3d^5$) are replaced by cations Al^{3+} having completely filled outermost orbit ($2p^6$), which do not contribute to the bond formation. Thus, on increasing aluminium substitution strength of bonding is expected to be weakened.

The Debye temperature (θ) value of all the ferrites have been calculated using the Anderson's formula [12]:

$$\theta = \frac{h}{k}\left[\frac{3N_A}{4\pi V_A}\right]^{1/3} V_m$$

where V_A and N_A are mean atomic volume and Avogadro's number. The value of θ for each composition is presented in Table 2. It is seen that θ show random variation with Al-content (x). The magnitude of Debye temperature in the present work is consistent with those obtained for various ferrite system [8,9] through ultrasonic pulse transmission technique.

Recently, we have developed and reported a simple but absolutely novel method of estimation of elastic moduli for various types of polycrystalline materials [4]. According to this model "the elastic constant and Debye temperature value of polycrystalline oxide material (K^*_{pm}) is equal to the average stochiomatric compositional addition of elastic constant and Debye temperature values of metallic elements present in the material (Modi's heterogeneous-metal-mixture rule, MMMR). The applicability of the model has been tested for the present system.

The elastic constant and Debye temperature value to be estimated, for a given spinel ferrite system can be given as:

$$K^*_{pm} = \frac{1}{n}\sum_{\substack{i>0 \\ n=1}}^{\infty} C_{in}K_n$$

where, K^*_{pm} is either bulk modulus (B), Young's modulus (E), rigidity modulus (G) and Debye temperature of the polycrystalline system to be estimated, n is the total concentration of metallic cations involved in the chemical formula of the polycrystalline material, C_{in}, concentration of the nth cation in the formula unit while K_n is the corresponding elastic modulus and Debye temperature of metallic element [13–15]. Here it should be noted that for any spinel ferrite system $n = 3[A_1{}^{2+}B_2{}^{3+}O_4]$.

On the same line, attempt has been made to estimate Debye temperature for all the compositions and compared with those obtained from IR spectral analysis. The Debye temperature is the temperature at which maximum lattice vibrations take place. 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

Table 3
Bulk modulus (B^*), Young's modulus (E^*) and rigidity modulus (G^*) for $MgAl_xFe_{2-x}O_4$ obtain from mixture rule

Content (x)	B^* (GPa)	E^*	G^*
0.0	128.10	155.67	60.33
0.2	121.81	146.2	56.53
0.4	115.53	136.73	52.73
0.6	109.24	127.27	48.93
0.8	102.95	117.8	45.13
1.0	95.56	108.33	41.33

parameters such as mean square atomic displacement, elastic constants, are known to depend upon the Debye temperature obtained through different physical properties or experimental techniques will not in general be equal [16].

The values of bulk modulus (B^*), Young's modulus (E^*) and rigidity modulus (G^*) and Debye temperature values for all the compositions obtained from metal-mixture rule are summarized in Tables 2 and 3. It is seen that there is reasonable agreement between the two (Tables 2 and 3).

4. Conclusions

The summing up of elastic moduli and Debye temperature determination through (i) Infrared spectral analysis and (ii) heterogeneous metal-mixture rule are found valid, more informative and easier for spinel ferrite system. The observed decrease in elastic constants with aluminium substitution for Fe^{3+} in the system suggest weakening of interatomic bonding and that is due to replacement of Fe^{3+} ions with half filled outermost 3d-orbit by Al^{3+} ions of completely filled $2p^6$ orbit, which do not contribute in the bond formation.

Acknowledgement

One of the authors (K.B.M.) is thankful to All India Council of Technical Education, New Delhi for providing financial support in the form of career award for young teachers (2004).

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