X-ray analysis and IR absorption spectra of Li-Ge ferrite

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(Received May 13, 1992; accepted August 12, 1992)

Abstract

X-ray diffraction and IR spectroscopy have been used to study the mixed ferrite $L_{0.5+0.5x}Ge_xFe_{2.5-1.5x}O_4$ (where x=0.0, 0.2-0.5). The X-ray diffraction data established that the prepared samples were homogeneous and that spinel structure was formed. The lattice parameter for each composition was calculated; the lattice parameter of the sample with x=0.0 was 0.832 nm, and that for x=0.2-0.5 had a constant value of ≈ 0.828 nm. IR spectra were recorded in the range 200 to 1200 cm⁻¹. Three main bands were observed. The band at ≈ 600 cm⁻¹ (ν_1) and the band at ≈ 400 cm⁻¹ (ν_2) were assigned to the tetrahedral and the octahedral complexes, respectively. A small band (ν_3) at ≈ 350 cm⁻¹ indicated the presence of octahedral divalent metal-oxygen in the complexes. When Ge content was introduced, a shoulder band appeared at 790 cm⁻¹. This band can be related to the stretching vibrational modes of GeO₄ tetrahedra.

1. Introduction

Lithium ferrites are low-cost materials that have found application in microwave devices and the memory core industry. Modifications in the properties of ferrites due to substitution of various ions, which depend on the nature and amount of the substituted species, have been studied by various workers.

A wide range of spinel compositions has been examined in the infrared region, although no exact calculations have been attempted. Preudhomme and Tarte [1, 2] were able to detect isotropic shifts in their sharp low-frequency bands of only 0.5 cm⁻¹. They documented how the spectra of normal spinels (AB_2O_4) vary along isomorphous series or between isotropic pairs in which either the tetrahedral (A) or octahedral (B) cations are changed. Other researchers (Waldron [3]; De Angelis et al. [4]) have discussed the conditions imposed by symmetry on the vibrations. As a result, these spectra are probably understood as well as possible on a purely quantitative basis. One difficulty in discussing and describing the vibrations of spinel structures arises from the fact that each oxygen is shared between one tetrahedral and three octahedral cations, so that no vibration can be said to be associated solely with oxygen tetrahedra or solely with octahedra. It is, however, meaningful to ask whether vibration is controlled by the A-O or B-O force constant, and whether

the A and B cations are moving relative to each other.

It is known that there is a correlation between the ionic radius and the lattice constant [5]. Pascard *et al.* [6] have found that the distance between the magnetic ions on the tetrahedral site (i.e., the lattice constant) increases with the introduction of larger ions. It is important to study the distance between the magnetic ions, as it gives insight into the fundamental properties of materials, such as the Curie temperature (to be published).

The purpose of the present investigation, which is part of our work on electrical (d.c. and a.c.) and magnetic properties (Mössbauer) of Li–Ge ferrite (to be published elsewhere), was to obtain information about the effect of Ge ion addition to $Li_{0.5}Fe_{2.5}O_4$ on the structure of the compound.

2. Experimental

The mixed ferrites $Li_{0.5+0.5x}Ge_xFe_{2.5-1.5x}O_4$ (where x=0.0, 0.2, 0.3, 0.4 and 0.5) were prepared according to standard ceramic technique. Details of the preparation have been given for different ferrites in many previous works.

X-ray diffraction patterns were recorded for the finest powder samples. A Philips recording diffractometer (model PW 1024/00) was used and a Co K α radiation source was applied with an iron filter to obtain the spectrum.

The infrared (IR) measurements were carried out (using KBr disks) using a Perkin-Elmer 783 spectro-photometer.

3. Results and discussion

3.1. X-ray analysis

Figure 1 shows the X-ray diffraction patterns for the above-mentioned samples of Li-Ge ferrite. The main reflection planes of the spinel structure of ferrites are shown in the X-ray patterns; these planes are (111), (211), (220), (311), (400), (422), (511) and (440). The diffraction data showed that the $Li_{0.5+0.5x}Ge_xFe_{2.5-1.5x}O_4$ (x=0.0-0.5) samples formed in the cubic spinel structure. It was observed that the (111) plane disappears at high Ge concentration (x = 0.4 and 0.5), while the (211) plane completely disappears in all samples except that where x = 0.0. According to Ohnishi and Teranishi [7], and as in previous work by Mazen et al. [8], the intensity ratio I(hkl)/I(400) is considered to be sensitive to the cation distribution, which depends on the parameter x. It was found that the intensity ratios I(311)/I(400), I(220)/I(400) and I(440)/I(400) were most sensitive to the parameter x. These ratios are plotted against the composition in Fig. 2. We notice that the relation is linear for the (220) and (440) planes, i.e., for the two parallel planes, and parabolic for the (311) plane. The ratio I(hkl)/I(400) increases with increasing Ge (or Li) content. In general the diffraction data proved that the prepared samples have been formed in the cubic spinel structure.

The values of the d-spacing for the recorded peaks are calculated according to Bragg's law. The precise values of the lattice parameters were calculated using the extrapolation function [9]

$$F(\theta) = \frac{1}{2} \left[\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta_r} \right]$$

where θ is the Bragg angle. The lattice parameters a_{exp} as a function of composition are shown in Fig. 3. It was expected that the lattice parameter would decrease with increasing Ge content, because the ionic radius of Ge⁴⁺ (0.044 nm) is smaller than that of Fe³⁺ (0.064 nm) [10]. It was found that the experimental lattice parameter (a_{exp}) of the sample with x=0.0 is about 0.832 nm. This value is in good agreement with the value of the ASTM card (0.8337 nm) and also with the literature values (0.831–0.837 nm) [11]. The value of a_{exp} for x=0.0 is slightly larger than that for the samples with x=0.2–0.5, which have a constant value of about 0.828 nm. In fact, the replacement process



Fig. 1. X-ray diffraction pattern of Li_{0.5+0.5x}Ge_xFe_{2.5-1.5x}O₄.

between the ions is not occurring between Fe³⁺ (0.064 nm) and Ge⁴⁺ (0.044 nm) only, but also between Fe³⁺ and Li⁺ ions (0.068 nm) [10]. Thus the ionic replacement process does not affect the size of the lattice in the compositions in which x=0.2-0.5. To obtain more



Fig. 2. Relation between the intensity ratios I(hkl)/I(400) and the parameter x.

Fig. 3. Variation of the theoretical lattice parameter (a_{th}) , experimental lattice parameter (a_{exp}) , tetrahedral ionic radius (r_A) and octahedral ionic radius (r_B) vs. composition x.

information about this behavior, we calculated the theoretical values of the lattice constant.

It is known that there is a correlation between the ionic radius and the lattice constant. The ionic radii of A-site and B-site ions can be determined by the following equations [11]:

$$r_{\rm A} = \left(U - \frac{1}{4}\right)\sqrt{3}a - R_{\rm O} \tag{1}$$

$$r_{\rm B} = \left(\frac{5}{8} - U\right)a - R_{\rm O} \tag{2}$$

where $R_{\rm O}$ = radius of the oxygen ion (0.132 nm), a = lattice constant and U = oxygen parameter (the ideal value = 3/8).

By eliminating U and solving eqn. (1) with (2) we get:

$$a_{\rm th} = \frac{8}{3\sqrt{3}} \left[(r_{\rm A} + R_{\rm O}) + \sqrt{3}(r_{\rm B} + R_{\rm O}) \right]$$
(3)

The theoretical lattice parameter (a_{th}) can be calculated using the values of r_A , r_B and R_O . In order to calculate r_A and r_B , it is necessary to know the cation distribution, which can be represented by the formula

$$(Ge_x^{4+}Fe_{1-x}^{3+})^{A}[Li_{0.5+0.5x}^{+}Fe_{1.5-0.5x}^{3+}]^{B}O_4$$
(4)

where the parentheses () and square brackets [] indicate the A-site and B-site, respectively. The ionic radius for each site is calculated from

$$r_{\rm A} = x r_{\rm Ge^{4+}} + (1 - x) r_{\rm Fe^{3+}} \tag{5}$$

$$r_{\rm B} = \frac{1}{2} [(0.5 + 0.5x)r_{\rm Li^+} + (1.5 - 0.5x)r_{\rm Fe^{3+}}]$$
(6)

According to the formula (4) for cation distribution, all the Ge⁴⁺ ions reside at A-sites, because the Ge⁴⁺ ion has a strong affinity for these sites [12], and Li⁺ ions occupy B-sites. The theoretical values of the lattice parameters (a_{th}) and r_A and r_B [which depend on the assumption of the cation distribution (eqn. (4))] have been calculated and are plotted versus the composition in Fig. 3. It is seen that a_{th} is smaller than a_{exp} , and the reason can be discussed as follows.

The calculated values of the lattice constant depend mainly on the ideal formula (4) of cation distribution. But, in fact, there is a deviation from the ideal formula. This deviation is related to the presence of some divalent iron ions, Fe^{2+} (this will be seen later in the IR spectra). The increase in the value of x is associated with the replacement of 2 Fe^{3+} ions by Fe^{2+} ion and Ge^{4+} ion or the replacement of Fc^{3+} ion by Fc^{2+} ion and Li^+ ion, i.e.

$$2Fe^{3+} \longrightarrow Fe^{2+} + Ge^{4+}$$
or
$$Fe^{3+} \longrightarrow Fe^{2+} + Li^{+}$$
(7)

It is well known that the ionic radius of Fc^{2+} (0.074 nm) [10] is larger than that of Fe^{3+} . For this reason, the experimental values (a_{exp}) are larger than the theoretical values (a_{th}) ; also, a_{exp} depends on the amount of formation of Fe^{2+} ions.

3.2. IR analysis

The IR spectra of the above-mentioned samples were recorded in the range 200-1200 cm^{-1} and are shown in Fig. 4. The absorption band frequency values are given in Table 1. The IR spectra of Li-Ge ferrite show the presence of two broad absorption bands along with some side bands in the $\approx 400-800$ cm⁻¹ region. Waldron [3] and Hafner [13] have attributed the band at around $600 \text{ cm}^{-1}(\nu_1^*)$ to the stretching vibrations of tetrahedral complexes and that at around 400 cm⁻¹ (ν_2^*) to that of octahedral complexes (the asterisk means primary band). The IR spectrum of $Li_{0.5}Fe_{2.5}O_4$ is given in Fig. 4(a). This spectrum indicates splitting in the absorption bands, i.e., the first of the primary band (v_1) consists of two shoulders at 710 and 670 cm⁻¹ and another band at 550 cm⁻¹. It has been shown by Potakova *et* al. [14] that the presence of Fe^{2+} ions in ferrites can produce splitting of or shoulders on absorption bands. This is attributed to the Jahn-Teller distortion produced by the Fe^{2+} ions, which cause local deformations in the lattice owing to the noncubic component of the crystal field potential, and hence lead to the splitting of the band ν_1 . Also, the band that appeared at 335



Fig. 4. The IR absorption spectra of Li_{0.5+0.5x}Ge_xFe_{2.5-1.5x}O₄.

cm⁻¹ in pure lithium ferrite and the small band at 350 cm⁻¹ in other samples indicate the presence of a small amount of Fe²⁺ ions in the above-mentioned samples. Thus this band is assigned to ν_3 and can be attributed to Fe²⁺-O²⁻ octahedral complexes. In other words, this band can be assigned to the divalent metal ion-oxygen complexes on octahedral sites. The band at 470 cm⁻¹ and the weak band (shoulder) at 440 cm⁻¹ can be attributed to Li-O vibrations. Tarte [15] investigated a series of solid inorganic compounds of lithium containing either LiO₄ tetrahedra or LiO₆ octahedra, and the actual results can be summarized as follows.

(i) The fundamental frequencies of LiO_6 octahedra should lie below 300 cm⁻¹.

(ii) A few bands in the 400–500 cm⁻¹ region are displaced by 20–30 cm⁻¹; this is always related to the occurrence of LiO_4 tetrahedra. In the spectra of Fig. 4, no such bands are observed for LiO_6 , but are observed for LiO_4 . These bands completely disappeared upon addition of Ge content.

In the IR spectra of Li–Ge ferrite (samples of x=0.2-0.5), some bands change and shift upon introduction of the Ge ions. For the octahedral site (Bsite), three bands (at 470, 440 (sh) and 375 cm⁻¹) disappear completely; the primary band at 400 cm⁻¹ shifts to lower frequency (390 cm⁻¹), while the third band ν_3 for divalent ion at 335 cm⁻¹ is shifted to higher frequency (350 cm⁻¹). For the tetrahedral site (A-site), the small bands at 550, 710 and 670 cm⁻¹ are transformed into shoulders at 540, 730 and 670 cm⁻¹, respectively. With the increase in Ge content, there is the possibility for Ge⁴⁺ ions to migrate to octahedral sites. Thus the disappearance of IR bands may be attributed to this migration.

It is noticed that the primary band of the tetrahedral site ν_1^* decreases with increasing Ge⁴⁺ ion concentration. Fig. 5 shows the behaviour of the primary bands of the octahedral site ν_2^* and tetrahedral site ν_1^* with increasing Ge content. The same behaviour was seen in previous work involving Cu-Cd ferrite [16]. A difference in the band position of ν_1^* (in the range 575–590 cm⁻¹) and ν_2^* (which has a constant value) is expected because of the difference in Fe³⁺-O²⁻ distance for the tetrahedral and octahedral complexes. It was found that the Fe-O distance of the A-site (0.189 nm) is smaller than that of the B-site (0.199 nm) [17]. This has been interpreted as due to the more covalent bonding of Fe³⁺ ions at the A-site. Since the frequency is proportional to the force constant, the band shift ν_1^* of the Fe-O vibration to lower frequency with increasing Ge content indicates that the force constant of the Fe-O bond decreases in Li-Ge ferrite. The calculated values of the force constant are given in Table 2.

x	Tetrahedral site (A-site)					Octahedral site (B-site)				
	Ge–O	Fe–O(Fe ³⁺)				Li–O(LiO₄)		FeO(Fe ³⁺)		Divalent Fe ²⁺
	$\nu_1(2)$	$\nu_1'''(1)$	$\nu_1''(1)$	$\nu_1^{*}(1)$	$\nu_1'(1)$	$\nu_2(2)$	$\nu_{2}'(2)$	$\nu_2^{*}(1)$	$\nu_{2}'(1)$	$\nu_{3}(1)$
0.0	_	710	670	590	550	470	440(sh)	400	375	335
0.2	790(sh)	730(w, sh)	670(w)	585	540(sh)	_	-	390	_	350(w)
0.3	790(sh)	730(w, sh)	670(w)	580	540(sh)		_	390	-	350(w)
0.4	790(sh)	730(w, sh)	670(w)	580	540(sh)	_	_	390	-	350(w)
0.5	790(sh)	730(w, sh)	670(w)	575	_ ``	-	_	390	-	350(w)

TABLE 1. The IR absorption bands of $Li_{0.5+0.5x}Ge_xFe_{2.5-1.5x}O_4$

*Denotes the primary band; w: weak, sh: shoulder.



Fig. 5. The change in the frequency of the primary bands ν_1^* and ν_2^* with the composition x.

TABLE 2. The force constant F versus the composition x^a

x	$F(\nu_1^*)$ (dyne cm ⁻¹)	$F(v_2^*)$ (dyne cm ⁻¹)			
0.0	2.554×10^{5}	1.174×10^{5}			
0.2	2.511×10^{5}	1.116×10^{5}			
0.3	2.468×10^{5}	1.116×10^{5}			
0.4	2.468×10^{5}	1.116×10^{5}			
0.5	2.426×10^{5}	1.116×10^{5}			

 ${}^{a}F = 4\pi^{2} c^{2}\gamma^{2}\mu$; c: velocity of light, γ : frequency, μ : reduced mass.

Also, upon introduction of the Ge^{4+} ions, a new shoulder band appears at 790 cm⁻¹. This band can be related to the stretching vibrational modes of GeO_4 tetrahedra. Thus the appearance of absorption at 790 cm⁻¹, when Ge substitutes for Fe³⁺ in lithium ferrite, is considered to be good evidence for the entry of Ge into tetrahedral sites, as was supposed in the X-ray analysis.

From the IR spectra of Li–Ge ferrite, we notice that, as the Ge content increases, there is an increase in the broadening of the spectra and a decrease in the intensity of the absorptions. It is well known that the absorbance of an IR band is proportional to its intensity at constant half band width. The intensity of the IR absorption band is a function of the concentration and the thickness of the samples in solid solutions [8]. The change in the dipole moment with the internuclear distance during vibration $(d\mu/dr)$ depends on the estimated intensity according to the following equation [19]:

$$A = 10^{-3} \frac{N}{3mc^2} \left(\frac{\mathrm{d}\mu}{\mathrm{d}r}\right)^2 \tag{8}$$

where N is the Avogadro constant, m is the reduced mass and c is the velocity of light. It is clear that the

intensity values give an indication of the value of $d\mu/dr$ dr and this latter value represents the contribution of the ionic character of the Fe–O bond in the lattice. So, from the previous discussion, one can conclude that the IR spectra can give information about changes in the molecular structure of the ferrite due to the perturbation occurring in the Fe–O bond upon introduction of the Ge⁴⁺ ion. On the other hand, the electronic distribution of the Fe–O bond is greatly affected when the Ge ion, with $4s^2ep^2$ orbitals, is introduced as its neighbour, which consequently affects the value of $d\mu/dr$ of the Fe–O bond, as measured by the absorbances of the IR bands.

4. Conclusion

From the results obtained and the discussion of $Li_{0.5+0.5x}Ge_xFe_{2.5-1.5x}O_4$, the following conclusions can be drawn.

(1) The X-ray diffraction data established the homogeneity of the prepared samples, i.e., there is one single phase, and the spinel structure in the cubic system is formed. Deviations in the value of the measured experimental lattice parameter (a_{exp}) are related to the presence of divalent iron ions Fe²⁺, as shown by the IR spectra.

(2) The IR spectra also confirmed the formation of the spinel structure and gave information about the distribution of ions between the two sites (A and B sites). Also, we can conclude that the IR spectra can give information about changes in the molecular structure of the ferrite due to the perturbation occurring in the Fe–O bond upon introduction of the Ge⁴⁺ ion.

References

- 1 J. Preudhomme and P. Tarte, *Acta Crystallogr., Sect. A, 27* (1971) 961, 845 and 1817.
- 2 J. Preudhomme and P. Tarte, Spectrochim. Acta, Part A, 28 (1972) 69.
- 3 R. D. Waldron, Phys. Rev., 99 (1955) 1727.
- 4 B. A. De Angelis, V. G. Kermidas and W. B. White, J. Solid State Chem., 3 (1971) 358.
- 5 F. H. S. Vemaas and E. R. Schmidt, Beitr. Mineral. Petrogr., 6 (1959) 219.
- 6 H. Pascard, A. Globus and V. Cabon, J. Phys. (Paris), Colloq., 38 (1977) C1-163.
- 7 H. Ohnishi and T. Teranishi, J. Phys. Soc. Jpn., 16 (1961) 36.
- 8 S. A. Mazen, A. E. Abd-El-Rahiem and B. A. Sabrah, J. Mater. Sci., 23 (1988) 2917.
- 9 B. D. Cullty, *Elements of X-ray Diffraction*, Addison-Wesley, Reading, MA, 1959, pp. 329-330.
- 10 G. Busch and H. Schade, Lectures on Solid State Physics, Pergamon, New York, 1976.
- 11 K. J. Standley, Oxide Magnetic Materials. Clarendon, Oxford, 1972, pp. 26–27.

- 12 A. Watanabe, H. Yamasura, Y. Moriyoschi and S. Shirasaki, Ferrites: Proc. Int. Conf., Sept.-Oct. 1980, 1981, p. 170.
- 13 S. T. Hafner, Z. Kristallogr., 115 (1961) 331.
- 14 V. A. Potakova, N. D. Zverv and V. P. Rommanonv, Phys. Status Solidi (a), 12 (1972) 623.
- 15 P. Tarte, Acta Crystallogr., 16 (1963) 228.

- 16 S. A. Mazen, N. A. Hakeem and B. A. Sabrah, Phys. Status Solidi (b), KI (1984) 123.
- 17 B. J. Evans and S. Hafner, J. Phys. Chem. Solids, 29 (1968) 1573.
- 18 E. B. Wilson and A. J. Wells, J. Chem. Phys., 14 (1946) 578.
 19 J. C. Dwcius, O. G. Maln and A. W. Thomson, Proc. R. Soc. London, Ser. A, 275 (1963) 295.