Structural Properties of Antimony Substituted Lithium Ferrites Sintered At High Temperature

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Abstract— Antimony substituted lithium ferrites with compositional formula \([\text{Li}_{0.5+x}\text{Sb}_x\text{Fe}_{2.5+2x}\text{O}_4]\) (where \(x = 0.0\) to \(0.5\) in steps of \(0.1\)) were prepared under standard ceramic method. The bulk and theoretical densities were determined. Bulk density is decreasing up to \(x=0.3\) then increases with gradual increasing the concentration. Similarly theoretical density \((d_t)\) decreasing up to \(x=0.3\) and then increases. From X-ray studies the spinel structure and belonging \(Fd3\) m space group is confirmed. The lattice parameter was found to be decreases up to \(x=0.3\) then it increases with increase in antimony substituent concentration. The other parameters like Oxygen positional parameters, tetrahedral and Octahedral bond lengths, tetrahedral edge, shared and unshared octahedral edge lengths were calculated and found to be increase with substituent concentration except for \(x=0.3\) samples.

Key words: Antimony, Lithium Ferrites, Soft Ferrites

I. INTRODUCTION

Lithium ferrites belongs to the category of soft ferrites. It has more advantages than other ferrites due to highest Curie temperature, excellent rectangular loop characteristics, high resistivity, low eddy current losses, low dielectric loss and high Neel temperatures, superior temperature stability of saturation magnetization, low intrinsic line width and low magnetic losses. Dielectric properties resemble with those of microwave ferrites. Properties rapidly changes with variation in composition [1-3]. They have excellent flat profile of permeability at high frequencies along with high dielectric constant. In addition to the ease of fabrication and low cost they offer better performance over other ferrites.

Owing to their physical properties lithium ferrites have high potential applications in electrical, magnetic, and microwave components such as circulators, Phase shifters, isolators, filters, oscillators, gyrators and micro wave latching devices. They also have applications as core materials of inductors, transformers, as memory devices in computers, cathode material in rechargeable lithium batteries etc. [4-5].

The structure of lithium ferrites is very interesting. \([\text{Li}_{0.5}\text{Fe}_{2.5}]\text{O}_4\) is an inverse spinel with the \(\text{Li}^{1+}\) and three – fifths of the \(\text{Fe}^{3+}\) ions occupying the octahedral \(B\) sites of the cubic spinel structure of the general formula \(\text{AB}_2\text{O}_4\) [6]. Since the number of ferric ions on \(A\) and \(B\) sites is unequal the magnetization of the sample is given by the difference in the magnetic moments of ions on \(A\) and \(B\) sites. Consequently, lithium ferrite possesses a higher Curie temperature than other spinel ferrites [7] and other advantages suitable for applications.

The present paper discusses the variation of lattice constants, density, porosity, grain diameter and other structural parameters with substituent concentration. The lattice constant values give the information on the bond lengths which determine the exchange interactions and chemical interactions.

II. EXPERIMENTAL DETAILS

The ferrite samples with compositional formula \([\text{Li}_{0.5+x}\text{Sb}_x\text{Fe}_{2.5+2x}\text{O}_4]\) (where \(x = 0.0, 0.1, 0.2, 0.3, 0.4\) and \(0.5\)) were prepared by conventional standard ceramic method. The appropriate proportions of \(\text{Li}_2\text{CO}_3\), \(\text{Fe}_2\text{O}_3\) and \(\text{Sb}_2\text{O}_3\) were taken and thoroughly mixed in an agate mortar in the presence of methanol. The dried mixture was pre-sintered at 625°C for 4 hrs. The related powder was ground again and granulated using a small amount of PVA binder. Finally granulated powder was compressed uniaxial under pressure of 5 tones/cm² in a stainless steel die to make pellets and the samples were sintered at 1200°C for 4hrs for good densification. The samples were cooled in the furnace in air atmosphere at the rate of 3°C/min.
III. RESULTS AND DISCUSSION

The bulk density \((d_b)\) is found to decrease up to \(x=0.3\) then it increases with increasing concentration. The observed bulk density of 4.692 gm/cm\(^3\) for the basic (\(x=0.0\)) ferrite is in close agreement with the reported value [13]. When the molecular weight increases with increasing concentration of antimony, the density decreases and this can be explained on the basis of decreasing intermolecular forces. This can be understood in terms of sintering. If the sintering temperature is below 1200 °C the densification decreases as the value of ‘\(x\)’ increases at high concentration the samples are rendered powder into powder form. From the above-mentioned formula 1.1, lattice constant is inversely proportional to the density. This can be attributed to the densification of the material and depends on the sintering, rate of cooling and heating, furnace atmosphere etc.. The X-ray density is found to exhibit higher value when compared with its bulk density for all samples.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Substituent Concentration</th>
<th>Lattice Parameter ((a))</th>
<th>Bulk Density ((d_b))</th>
<th>X-ray Density ((d_X))</th>
<th>Porosity</th>
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<tbody>
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<td>4.6924</td>
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<td>4.5749</td>
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</table>

Table 1: Variation of lattice parameter \((a)\), X-ray density \((d_X)\), experimental density \((d_b)\) along with porosity of the ferrites as a function of antimony \((x)\).

The value of theoretical density \((d_X)\) is 4.7560 gm/cm\(^3\) is in good agreement with reported value of 4.7829 gm/cm\(^3\) [14]. The X-ray density decreases at \(x=0.1\) then increase upto \(x=0.3\) and further increases with continuous increasing concentration of antimony. The variation between these can be related to the porosity differences in materials. Bulk and theoretical/X-ray densities are listed in Table 1.

It is observed porosity ranges varied from 1.3% to 9.4%. Porosity increases from \(x=0.0\) to \(x = 0.3\) then decreases. Lower porosity is required for good quality ferrites material since larger porosity affects physical properties of the material. High valancy cations create cation vacancies, microvoids and bulk diffusion of cations contribute to the increase in percentage of porosity. Generally percentage of porosity is approximately 10 [15]. Since the charge balance is affected by the creation of vacancies, the porosity is found to be more for these ferrites which have high valancy cations as substituents.

From X-ray diffractometer, the lattice parameter was calculated and is in good agreement for \(x=0.0\) with standard JCPDS data card number 72-1911.

Some of the typical spectra are shown in the Fig. 1. The patterns of all the samples exhibited lines corresponding to single phase spinel structure for Sb\(^+\) substituted lithium ferrites. The important peaks of planes \((111), (311), (222), (400), (422), (511), (440)\) and \((531)\) confirm the presence of single phase with face-centered cubic structure [16].

![Fig. 1: X-ray diffraction patterns of [(Li\(_{0.5-x}\)Sb\(_x\)Fe\(_{2.5-2x}\)]2O\(_4\) ferrites, where ‘\(x\)’ varies from 0.00 to 0.5 (X-ray diffraction pattern was corresponding to \(x=0.3\) and was recorded using a different X-ray diffractometer). Due to sintering at 1200°C lithium volatility occurs as a result Fe\(^{2+}\) ions exists [8]. Some of the properties are more attractive sintering at 1200°C than sintered at 1000°C [9-11].

Theoretical density \((d_t)\) of the samples were calculated by using formula

\[
(d_t) = \frac{8M}{N\alpha^3} \text{ gm/cm}^3 \quad (1.1)
\]

Where

\(\alpha = \text{Lattice Parameter}\)

\(S = \text{Number of molecules in a unit cell of a spinel lattice}\)

\(M = \text{molecular weight in gram mole of the spinel}\)

\(N = \text{Avogadro number (6.0225x10}\(^{23}\)\text{atom/mole)}.\)

The bulk density \((d_b)\) of the samples was measured through the Archimedes principle. The lattice parameter ‘\(\alpha\)’ of the samples was determined using PHILIPS (X’pert: Japan) diffractometer in the range between 15° to 80° at room temperature. The Cu-K\(\alpha\) radiation was used and scanning rate was 3°/ minute.
The obtained lattice constant (8.3313 Å) is in good agreement with the reported values (8.316 Å) \([14,17-18]\) of basic ferrite. The values of lattice constant \((a)\) are computed using the standard extrapolation method (Nelson-Riley function) \([19]\) with error error ± 0.0019 Å.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Substituent</th>
<th>Oxygen</th>
<th>Tetrahedral</th>
<th>Octahedral</th>
<th>Tet. edge</th>
<th>Oct. edge</th>
<th>Unshared edge</th>
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<tbody>
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<td>(Å)</td>
<td>(Å)</td>
<td>(Å)</td>
<td>(Å)</td>
<td>(Å)</td>
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Table 2: Oxygen positional parameters, tetrahedral, octahedral bond lengths, tetrahedral edge, shared and unshared octahedral edge lengths of Li-Sb ferrites as a function of substituent concentration.

The lattice parameter \((a)\) values of the basic and substituted ferrites are given in the table 1. It shows that the compositional variation of lattice constant is increasing with increasing of antimony concentrations. The ionic radius of \(\text{Sb}^{3+}\) (0.62 Å) is smaller than the \(\text{Fe}^{3+}\) (0.64 Å) which it replaces at A site. The \(\text{Sb}^{3+}\) ions seems to replace the \(\text{Fe}^{3+}\) at B site. When \(\text{Li}^{+}\) is added, the \(\text{Fe}^{3+}\) moves from A site to B site. Therefore, lattice constant increases. The similar behavior with \(\text{Sb}^{3+}\) was observed earlier \([20-21]\).

Further this can be explained as, lithium ferrites exist in two different crystallographic forms \([22]\). The phase with FCC inverse spinel structure and space group P4\(3\)\(m\) in which all \(\text{Li}^{+}\) ions and \(3/5\) of all \(\text{Fe}^{3+}\) ions occupy the octahedral \(B\)–sites in an ordered fashion whereas the remaining \(\text{Fe}^{3+}\) ions occupy the tetrahedral \(A\)–sites. The \(B\)-phase is a similar structure except that \(\text{Li}^{+}\) and \(\text{Fe}^{3+}\) ions are randomly distributed in the octahedral interstices and space group \(\text{Fd}3\text{m}\). Therefore, it is supports the above observations of increasing lattice constant as \(\text{Li}^{+}\) replaces \(\text{Fe}^{3+}\).

Using the lattice constant \(a\), we can calculate some other structural parameters also i.e. inter ionic distances, tetrahedral and octahedral bond lengths etc. have been computed and presented in the Table 2 with the following formulae \([21,23-24]\):

\[
d_{\text{AL}} = \alpha \left( u - \frac{1}{3} \right) \]

\[
d_{\text{BL}} = \alpha \left( 3u^2 - \frac{11}{4}u + \frac{43}{64} \right)^{\frac{1}{2}} \]

\[
d_{\text{AE}} = \alpha \left( 2u^2 - \frac{1}{2} \right) \]

\[
d_{\text{BE}} = \alpha \left( 1 - 2u \right)^{\frac{1}{2}} \]

\[
d_{\text{BEU}} = \alpha \left( 4u^2 - 3u + \frac{11}{16} \right)^{1/2} \]

Where ‘\(u\)’ is the oxygen positional parameter values are calculated \([25-26]\) and listed in the Table 2. \(d_{\text{AL}}\) and \(d_{\text{BE}}\) represent the tetrahedral and octahedral bond lengths, \(d_{\text{AE}}, d_{\text{BE}}\) and \(d_{\text{BEU}}\) are the tetrahedral edge, shared and unshared octahedral edge lengths. From the table 2 the oxygen parameters ‘\(u\)’ of antimony substituted lithium ferrites increases. All the \(d_{\text{AL}}, d_{\text{AE}}, d_{\text{BE}}\) and \(d_{\text{BEU}}\) values are increased except at \(x=0.3\) where they decreased and then increased. This is attributed to the fact that at \(x=0.3\) lattice parameter is decreases.

IV. Conclusion

The bulk and X-ray densities were calculated and the differences between them were discussed. The bulk density is expected to decrease up to \(x=0.3\) and then increases. The X-ray densities were calculated and found to decrease up to \(x=0.1\) and then it increases up to \(x=0.3\) from where it increases with continuous increasing of antimony concentration. The changes in density with substituent concentration are attributed to the changes in sintering. The differences between the bulk density and theoretical densities are attributed to porosity. Porosity of the samples was calculated and found to be increasing from 1.3 to 9.4%. X-ray diffraction pattern of all the samples confirm single phase spinel structure without any evidence of unreacted ingredients. X-ray diffraction pattern of lithium ferrites confirm the \(\beta\)-phase with space group \(\text{Fd}3\text{m}\). The lattice constant is found to increase with increasing \(\text{Sb}\) substituent concentration except \(x=0.3\) where it decreases. Oxygen positional parameters, tetrahedral and octahedral bond lengths, tetrahedral edge, shared and unshared octahedral edge lengths been evaluated and these are found to be increasing except \(x=0.3\) sample where they decrease slightly.

REFERENCES


