Structural analysis and magnetic characterization of aluminum doped lithium hexaferrites

Suresh S. Darokar

Science College, Congress Nagar, Nagpur, Maharashtra State, India

ABSTRACT

In the present investigation of a series of the compounds with a substitution of aluminum in lithium ferrite (M type) with the general chemical formula $\text{Li}_{0.5}\text{Fe}_{2.5+x}\text{Al}_{12-x}\text{O}_{19}$ were synthesized using reacting oxide by high temperature solid state reaction technique. The structural characterization of compound has been carried out from X-ray diffraction powder pattern. The compounds are in single hexagonal phase without traces of uncertainly ambiguous reflection. From XRD pattern lattice parameters has recorded with increasing doped aluminum element in the range from $a = 5.807$ Å to 5.906 Å and $c = 22.507$ Å to 22.585 Å pertaining the space group P6$3$/mmc (No.194). The mass density of the ferrites were found linearly varies and depends upon the mass and volume of sample. The X-Ray density has depends upon the lattice constant and molecular weight of the compounds. The average particle size was also estimated. The compounds were studies magnetically by using Guoy’s method in the temperature range 300 to 800K; the result shows that the compounds are paramagnetic in nature. The Curie molar constant was work out.

Key words: Lithium hexaferrites, Gouy’s method, Curie molar constant, Magnetic Properties.

INTRODUCTION

In the ferrites belonging to the family of magnetoplumbite M-type hexagonal structure like BaFe$_{12}$O$_{19}$ and SrFe$_{12}$O$_{19}$ have attracted more attention due to wide range of application in industries particularly as permanent magnets, recording media and microwave devices. There has been considerable interest in the past years in the study of ferrites from the point of view of their innumerable applications in science and technology. The polycrystalline ferrites are low cost materials that have attractive microwave device application owing their high resistivity A substituted M-type ferrites with, Ba and Sr are extensively studied, while lithium substitution are not reported so far [1-4]. The calcium hexaferrites Ca Fe$_{12}$O$_{19}$ (5-7) have been less studied and have a magnetic properties comparable to BaM and SrM. Many workers have been made to replace Fe$^{3+}$ ions with Al$^{3+}$, Cr$^{3+}$ and Co$^{3+}$ etc in BaM and SrM ferrites [8-9]. A combination of bivalent and tetravalent cations was also used to replace Fe$^{3+}$ like Ur-Ti, Co-Ti, Co-Sn, Zn-Mn. etc [10-11] without any appreciable changes in BaM / SrM structure, when Fe$^{3+}$ ions are replaced by non magnetic ions like Ti$^{4+}$, Sn$^{4+}$ etc. The reduction in magnetic parameter is observed. Also calcium hexaferrites substituted with Co/Cr/Al has been studied magnetically, electrically and structurally [12].

In the present study of aluminum substituted lithium ferrites with the chemical formula Li$_{0.5}$Fe$_{2.5+x}$Al$_{12-x}$O$_{19}$ are reported. In calcium ferrites [13] forming solid solution of the end members considering a barium ferrites BaFe$_{12}$O$_{19}$, the unit cell contain 38 oxygen ion, 24 ferrite ions and two barium ions. Oxygen ions occupy five different crystallographic sites viz, 2a,2b,4f$_1$, 4f$_2$ and 12k of these 2a, 4f$_2$ and 12k are octahedral, 4f$_1$ is tetrahedral site and 2b the tetragonal bipyramid site. The unit cell contains two spinal blocks, in which aside from slight different in the
The crystallographic analysis data of aluminium substituted lithium ferrite with general chemical formula Li_{1-x}Fe_{2.5x}Al_{12-x}O_{19} (x = 2 to 6) were prepared by classical ceramic method with the proper molar ratio and characterized by X-ray diffraction (XRD). The XRD pattern should a single phase with hexagonal structure of M-type ferrites. Interestingly as expected value of the lattice parameter of Li_{1-x}Fe_{2.5x}Al_{12-x}O_{19} (x = 2 to 6) were found to be in the range of CaAl_{2}O_{19} and CaFe_{2}O_{19} [15] and hence may be consider as a solid solution of the end members in the appropriate properties. Further characterization was carried out for other properties such as electric and magnetic properties.

MATERIALS AND METHODS

Preparation method:
All samples were prepared by classical standard ceramic technique with AR grade oxides were mixed in the molar ratio 1: 2: 4 of Li_{2}O, Al_{2}O_{3}; Fe_{2}O_{3} and grinding using AR grade acetone in agate mortar [16]. Then the power was heated in air at 1200°C for 120 Hrs in an electric furnace, which was then cooled at the rate of 200°C/Hrs. up to 500°C and then cooled naturally to room temperature. The hard sample thus formed and then grinded for about one hours [17] for experimental investigations.

X-ray Diffraction (XRD): The sample was analyzed using a Philips X-ray diffractometer and Cu-kα radiation with the wavelength 1.542 Å. The X-ray pattern showed a single crystalline phase without impurity and un-reacted oxide reflection. The XRD patterns were indexed as a hexagonal magnetoplumbite structure with a space group P6_{3}mm or D_{6h}[18-19].

Magnetic properties: The magnetic properties such as magnetic susceptibility of powered samples were studied by Gouy’s method [20]. The sample were paramagnetic at room temperature. The variations of inverse molar susceptibility (1/χm) versus absolute temperature T°K were measure as shown in figure (2). From the paramagnetic behavior of the sample the curie molar constant C_M was calculated and match with theoretically expected value of C_M with spin (Fe^{3+}). Also, the electrical conductivity of the sample were measured by two terminal method reported in earlier paper [21].

RESULTS AND DISCUSSION

The crystallographic analysis data of aluminium substituted lithium ferrite with general chemical formula Li_{1-x}Fe_{2.5x}Al_{12-x}O_{19} (x = 2 to 6). The ions in BaM compounds can be replace partly by Al^{3+} or completely by Li^{3+} and combination of Fe^{3+} and Al^{3+} ions without changing the crystal lattice symmetry. In all the specimens, the substituted ions would be chosen to keep electrically neutral and to have similar ionic radii. In these ferrites the aluminium plays an important role in the properties variation [22]. Formations of samples were confirmed by XRD technique which has hexagonal M type structure belongs to a space group P6_{3}mm (194), as shown in fig.-1. The replacement of Fe^{3+} ions by Al^{3+} ions has been investigated because of resemblance of the ionic radii. It is seen that the former ions are very easily replaced at any substitution ratio without changing the crystal geometry. The lattice parameter ‘a’ and ‘c’ decreases linearly with substitution ratio in all the compounds. The decrease in lattice parameters ‘a’ and ‘c’ may occurs due to closed packing of lattices in the materials. The numerical values of compositional data such as observed and calculated d-values, observed intensities with the reflection indices are indicated in Table -1. Also, the lattice constant, cell volume and X-ray density are reported in Table-2 and has reported as same nature as in Sr / Ba-M ferrites [23].

The temperature dependence of magnetic susceptibility measurement was made upto temperature 800°C. The curve for variation of 1/χm versus temperature T°K were shown in figure (2). The compounds are paramagnetic in nature in the studied temperature range. The determined Curie molar constant C_M are tabulated in Table-3. The theoretically predicted values of C_M are in good agreement with experimentally observed value. The fair agreement in the value of C_M implies that there is no change in valence distribution, as the lattice contains both magnetic and non-magnetic ions with different site preferences. It is possible to guess the site distribution from Mössbauer experiment and hypothesized that the Al^{3+} ions enter the 2a and 12k sites in lattices in referring to the X-ray investigation, they came to the conclusion that Al^{3+} first occupy 2a sites then 12k sites. There assumptions are theoretically support by Mössbauer studies [24-25]. The presence of magnetic ion in the site 2a and 12k shown strong magnetic behavior.
In M type compounds, the orientations of the magnetic moments of the ferric ions in the crystal are generally aligned along the c-axis in antiparallel with each other [26-28]. First considered from theoretically point of view, that these alignments of magnetic ions can be realized by super-exchange interaction through oxygen ion, which has also been proved from experimental facts. These exchange interaction are responsible for spin alignment. In magnetoplumbite the interaction between two close sites, such as 2a-12k, 2a-4f₁ and 4f₁-12k are decisive for strong magnetic character. So, when Fe³⁺ ions in the12k sub lattice are substituted by the non-magnetic Al³⁺ ions, weakening of the super-exchange interaction between magnetic ions, results in a fairly inclined paramagnetic nature.
The presence of Al$^{3+}$ ions in 2a and 12k sites in the lattice imply the decrease in interaction energy and thereby decrease in Curie temperature has been seen in the compound.

![Graph showing inverse molar susceptibility vs. temperature]

**Fig - 2 : Inverse molar susceptibility(1/\(\chi_m\)) vs. Temperature T° K**

### Table -3

<table>
<thead>
<tr>
<th>Sr.No</th>
<th>Compounds</th>
<th>Curie molar constant (C_M) (expected)</th>
<th>Curie molar constant (C_M) (Observed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Li$<em>2$Fe$</em>{6/3}$Al$<em>{1/3}$O$</em>{19}$</td>
<td>28.43</td>
<td>28.00</td>
</tr>
<tr>
<td>2</td>
<td>Li$<em>2$Fe$</em>{5/3}$Al$<em>{1/3}$O$</em>{19}$</td>
<td>24.06</td>
<td>23.85</td>
</tr>
<tr>
<td>3</td>
<td>Li$<em>2$Fe$</em>{6/3}$Al$<em>{1/3}$O$</em>{19}$</td>
<td>19.68</td>
<td>19.30</td>
</tr>
<tr>
<td>4</td>
<td>Li$<em>2$Fe$</em>{6/3}$Al$<em>{1/3}$O$</em>{19}$</td>
<td>15.31</td>
<td>15.22</td>
</tr>
<tr>
<td>5</td>
<td>Li$<em>2$Fe$</em>{6/3}$Al$<em>{1/3}$O$</em>{19}$</td>
<td>10.93</td>
<td>10.70</td>
</tr>
</tbody>
</table>

**CONCLUSION**

In the present work, the aluminium substituted lithium ferrites was synthesized by standard ceramic method. The X-ray diffraction studies confirm the formation of samples containing Al$^{3+}$ions along with Fe$^{3+}$ions. All these compounds have M-structure through the site distribution changes. No changes occurs in the charge distribution but the site distribution is change due to strichiometric changes and the value of ‘a’ and ‘c’ of the sample supported the conformation. The structural studies have conformed the space group of samples to be P63/mmc (No. 194). The mass density of ferrites have been found linearly varies and depends upon samples mass and volume. The X-ray density dependents upon the lattice constant ‘a’ and ‘c’ and molecular weight of samples.

The magnetic susceptibility and saturation magnetization decreases with the substitution of Al$^{3+}$ ions. Thus the substitution of Al$^{3+}$ ions in lithium hexaferrites changes the magnetic character of the sample. The decrease in magnetization is therefore attributed to Al$^{3+}$ ions occupying on the spin up Fe sites and magnetic dilution or non collinear structure Fe$^{3+}$-O-Fe$^{3+}$ superexchange interaction may be weaken by Al$^{3+}$ substituting in to some Fe $^{3+}$sites.

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