

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 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 $a = 5.807 \text{ \AA}$ to 5.906 \AA and $c = 22.507 \text{ \AA}$ to 22.585 \AA 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 magntoplumbite M-type hexagonal structure like $\text{BaFe}_{12}\text{O}_{19}$ and $\text{SrFe}_{12}\text{O}_{19}$ 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 $\text{CaFe}_{12}\text{O}_{19}$ (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 studies magnetically, electrically and structurally [12].

In the present study of aluminum substituted lithium ferrites with the chemical formula $\text{Li}_{0.5}\text{Fe}_{2.5+x}\text{Al}_{12-x}\text{O}_{19}$ are reported. In calcium ferrites[13] forming solid solution of the end members considering a barium ferrites $\text{BaFe}_{12}\text{O}_{19}$, the unit cell contain 38 oxygen ion, 24 ferrite ions and two barium ions. Oxygen ions occupy five different crystallographic sites viz, 2a,2b,4f₁, 4f₂ and 12k of these 2a, 4f₂ and 12k are octahedral, 4f₁ is tetrahedral site and 2b the tetragonal bipyramide site. The unit cell contains two spinal blocks, in which aside from slight different in the

lattice parameters, the ionic position are identical with those in the spinal structure with the c axis of the hexagonal unit cell oriented along the (111) axis of the spinal structure.[14].With a view to understand the structural properties of the compound with the chemical formula $\text{Li}_{0.5}\text{Fe}_{2.5+x}\text{Al}_{12-x}\text{O}_{19}$ ($x = 2$ 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 $\text{Li}_{0.5}\text{Fe}_{2.5+x}\text{Al}_{12-x}\text{O}_{19}$ ($x = 2$ to 6) were found to be in the range of $\text{CaAl}_{12}\text{O}_{19}$ and $\text{CaFe}_{12}\text{O}_{19}$ [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_2O , Al_2O_3 : Fe_2O_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 $200^\circ\text{C}/\text{Hrs}$. 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-K_α radiation with the wavelength 1.542 \AA . 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 $\text{P6}_3/\text{mmc}$ or D_{6h}^4 [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 nature at room temperature. The variations of inverse molar susceptibility ($1/\chi_m$) versus absolute temperature $T^\circ\text{K}$ 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 $\text{Li}_{0.5}\text{Fe}_{2.5+x}\text{Al}_{12-x}\text{O}_{19}$ ($x = 2$ to 6). The ions in BaM compounds can be replace partly by Al^{3+} or completely by Li^{1+} 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 $\text{P6}_3/\text{mmc}$ (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 $1/\chi_m$ versus temperature $T^\circ(\text{K})$ 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.

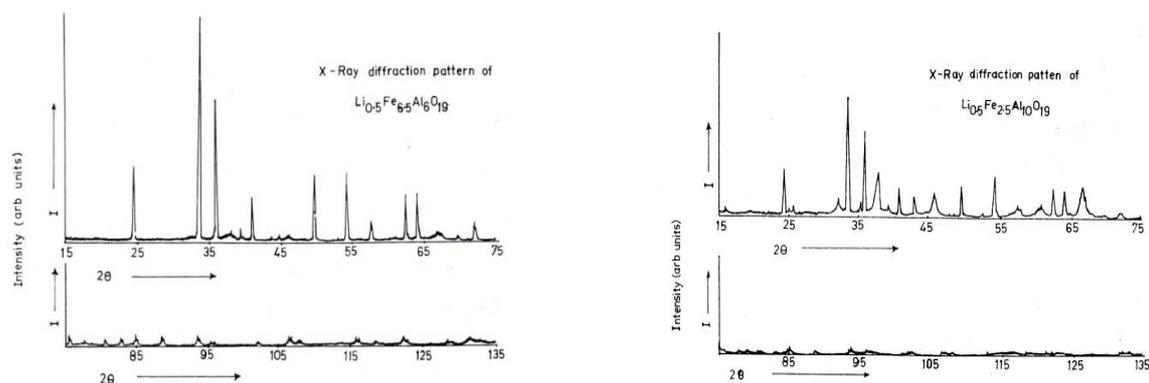


Fig-1: X-ray diffraction pattern of $\text{Li}_{0.5}\text{Fe}_{6.5}\text{Al}_6\text{O}_{19}$ and $\text{Li}_{0.5}\text{Fe}_{2.5}\text{Al}_{10}\text{O}_{19}$

Table -1: X-Ray data of $\text{Li}_{0.5}\text{Fe}_{6.5}\text{Al}_6\text{O}_{19}$ and $\text{Li}_{0.5}\text{Fe}_{2.5}\text{Al}_{10}\text{O}_{19}$ (d_{obs} , d_{cal} , I_{obs} and hkl Plane)

$\text{Li}_{0.5}\text{Fe}_{6.5}\text{Al}_6\text{O}_{19}$						$\text{Li}_{0.5}\text{Fe}_{2.5}\text{Al}_{10}\text{O}_{19}$					
d_{obs} (Å)	d_{cal} (Å)	I_{obs}	h	k	l	d_{obs} (Å)	d_{cal} (Å)	I_{obs}	h	k	l
3.676	3.676	32.3	0	0	6	5.646	5.646	10.3	0	0	4
2.696	2.670	100.0	1	0	7	3.674	3.674	36.4	0	0	6
2.514	2.514	66.6	2	0	0	2.979	2.822	15.8	0	0	8
2.290	2.290	5.4	1	1	6	2.695	2.726	100.0	1	0	7
2.204	2.203	16.9	1	0	9	2.557	2.557	15.1	2	0	0
2.077	2.076	2.3	2	0	6	2.551	2.542	13.2	2	0	1
1.981	1.996	3.5	1	1	8	2.507	2.509	62.5	0	0	9
1.840	1.840	31.5	2	1	3	2.458	2.471	8.8	1	1	5
1.835	1.835	14.5	2	0	8	2.433	2.422	12.5	2	0	3
1.694	1.696	23.5	0	0	13	2.341	2.429	12.8	2	0	4
1.690	1.689	20.3	2	1	6	2.203	2.225	19.5	2	0	5
1.599	1.604	9.5	3	0	4	2.089	2.069	12.2	0	1	0
1.486	1.484	23.2	3	0	7	1.986	1.934	18.4	2	1	0
1.458	1.465	21.9	1	1	13	1.837	1.829	29.4	2	1	4
1.450	1.451	11.4	2	2	0	1.695	1.700	20.9	3	0	1
1.402	1.404	4.2	2	2	4	1.692	1.692	30.9	2	0	10
1.311	1.311	8.3	2	2	7	1.687	1.686	20.9	3	0	2
1.259	1.257	5.1	4	0	0	1.522	1.536	14.7	2	1	9
1.101	1.101	4.3	3	2	5	1.508	1.508	7.3	3	0	7
1.039	1.038	1.7	4	1	7	1.479	1.478	19.9	2	2	0
0.908	0.909	4.3	4	2	7	1.451	1.458	22.8	2	2	2
-	-	-	-	-	-	1.404	1.404	21.7	2	2	5
-	-	-	-	-	-	1.394	1.394	20.1	3	1	4

Table-2: Consolidated data of $\text{Li}_{0.5}\text{Fe}_{2.5+x}\text{Al}_{12-x}\text{O}_{19}$

Compound	Lattice Parameters		Cell Volume (Å) ³	Mol .Wt . in gm	X-ray Density gm/cc
	a (Å)	c (Å)			
$\text{Li}_{0.5}\text{Fe}_{6.5}\text{Al}_6\text{O}_{19}$	5.807	22.507	644.26	832.35	4.2903
$\text{Li}_{0.5}\text{Fe}_{5.5}\text{Al}_7\text{O}_{19}$	5.811	22.081	645.86	803.48	4.1313
$\text{Li}_{0.5}\text{Fe}_{4.5}\text{Al}_8\text{O}_{19}$	5.827	22.208	653.03	774.62	3.9390
$\text{Li}_{0.5}\text{Fe}_{3.5}\text{Al}_9\text{O}_{19}$	5.852	22.452	665.92	745.75	3.7189
$\text{Li}_{0.5}\text{Fe}_{2.5}\text{Al}_{10}\text{O}_{19}$	5.906	22.585	682.23	716.89	3.4895

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 Fe⁺³ ions in the 12k sub lattice are substituted by the non-magnetic Al⁺³ 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.

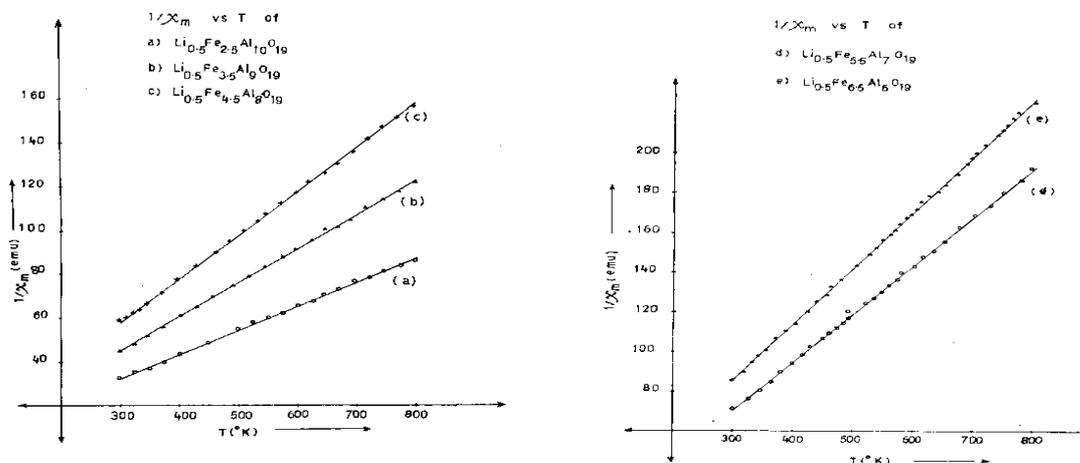


Fig – 2 : Inverse molar susceptibility($1/\chi_m$) vs. Temperature $T^\circ \text{K}$

Table -3

Sr.No	Compounds	Curie molar constant C_M (expected)	Curie molar constant C_M (Observed)
1	$\text{Li}_{0.5}\text{Fe}_{6.5}\text{Al}_6\text{O}_{19}$	28.43	28.00
2	$\text{Li}_{0.5}\text{Fe}_{5.5}\text{Al}_7\text{O}_{19}$	24.06	23.85
3	$\text{Li}_{0.5}\text{Fe}_{4.5}\text{Al}_8\text{O}_{19}$	19.68	19.30
4	$\text{Li}_{0.5}\text{Fe}_{3.5}\text{Al}_9\text{O}_{19}$	15.31	15.22
5	$\text{Li}_{0.5}\text{Fe}_{2.5}\text{Al}_{10}\text{O}_{19}$	10.93	10.70

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 depends 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 weakened by Al^{3+} substituting in to some Fe^{3+} sites.

Acknowledgement

Author is thankful to UGC New Delhi for providing financial assistance to carry out the work under minor research project scheme. Author is also thankful to D.K. Burghate, D.K Kulkarni, J. M. Khobragade and S.B Khasare to guided and encourage time to time and allowed me to do the work in laboratory.

REFERENCES

- [1] Di Marcello E; Glance B; Joubert J.C. and Mollard P. *J Phys.Cooloq (France)* **1988** , 49 , 933
- [2] Bahadur D and Chakraborty D. *Cryst. Prop. (Switzerland), proceedings ICF-5 Bombay*, **1989**. 189, 27- 30 .
- [3] Twafik A; Bakarar M.M., *J. Mater.Sci .Lett. (UK)* **1988** ,7 ,!098
- [4] Kotnala R K. *Bull Mater.Sci.* **1992** ,15, 149

-
- [5] Prakash C.Sand Kulkarni D.K, *Indian J. Appl.Phys.* 199 , 32, 361
- [6] Prakash C.S.and.Kulkarni D. *Bull.Mater Sci.* **1994**, 17, 35
- [7] Asti G; Carbuccocchino M; Deriu A; Lucchini E and Slokar G. *J. Magn. Magn. Mater*, 1980, 20 , 44
- [8] Haneda K and Kojima . *Jap. J. Appl.Phys.* **1973**, 12 ,355
- [9] Kanke Y; Takayamamurochi E; Uchida Y; Kato K and Takekawa S. *J Solid state Chem.* **1991**, 95, 438.
- [10] Florescu.V;Popescund M and Ghizdeanu C, *Inten. J.Mag.* **1973** , 5 , 257
- [11] Gu B.X;Zhang H.Y;Zhai H R;Shen B.G;Lu.M; Zhng Y.S and Maoi Y.Z. *Phys.States Solidi.***1992**, A 133, K83
- [12] Darokar S.S, Rewatkar K.G and Kulkarni D.K. *Mater Chem.Phys.* **1998** 56, 84-85
- [13] Glasser F.P; Woodhams F.W.D; Meads R.E. and Parker W.G. *J.Solid state Chem .* **1972** , 5 ,255
- [14] Summerguard R.N. and Banks E. *J Phys Chem. Solids* **1957**, 2 ,312
- [15] Wisnyi L.G **1967**. *In Power diffraction file (Philadelphia: Joint Committee on Power Diffraction Standards)*
- [16] Economos G J. *Am.Ceram.Soc* , **1955**, 38 ,241
- [17] Stendley K J **1972**. *In Oxide Magnetic Materials (London: Oxford Uni. Press)*
- [18] Henery N F M, Lipson H and Wooster W A. **1953** ,*The interpretation of X ray diffraction photographs (London Macmillan & Co)*
- [19] Bates I.F.**1939**, *Modern Magnetism (Cambridge: Cambridge Univ. Press)*
- [20] Smit J and Wijn H P. **1959**, *In Ferrites. (Netherlands: PHILIPS Technical Library)*
- [21] Darokar S.Suresh. *Adv. Appl. Sci. Res, Pelagia Research Library.* **2012**, 3(3):1395-1398
- [22] Darokar S.S; Rewatkar K.G;Choukuse M. S and Kulkarni D.K. *Indian J. .Phys.* **2000**, 74 A 155- 157
- [23] Rewatkar K G; Prakesh C S; Kulkarni D K. *Mater. Lett.* **1996**, 28, 365-368
- [24] Bertaut E.F; Deschamps A;Pauthenet R; Pickart S. *J Phys Ct Rad*, **1959**, 20 404
- [25] Rensen J.G, Schulkes J.A. and Van . Wlering J.S. *J.Phys Colloq*, **1971**, 32,C1;924
- [26] Neel L; *Ann. Phys (Paris)*, **1948**, 3, 137
- [27] Aanderson P.W, *Phy Rev.* **1950**, 79, 705
- [28] Shepherd P; Mallick K.K; Green R.J, *J. Magn.Magn, Mater.***2007**, 311, 683-692