



## Synthesis, structural and magnetic studies of cobalt and aluminium mixed lithium ceramics

Suresh S. Darokar

Shivaji Science College, Nagpur, Maharashtra, India

### ABSTRACT

In the present investigation, the series of aluminium and cobalt substituted lithium hexaferrites with chemical compositional formula  $Li_{0.5}Fe_{0.5+x}Al_{12-2x}Co_xO_{19}$  (where  $x=2,3,4,5$  and  $6$ ) was synthesized using perfect stoichiometric mixtures of oxide by standard ceramic solid state reaction method at  $1200^\circ C$  for 120 hrs. The chemical phase analysis of all compounds has been checked by X-ray powder diffraction (XRD) which confirmed the formation of the ferrite structure. It shows all are hexagonal magnetoplumbite (M -type) structure without traces of uncertainly ambiguous reflection having unit cell dimension 'a' in the range from 5.6953 A.U to 5.8594 A.U and 'c' varies between 21.2626 A.U to 22.3234 A.U 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 magnetic properties of polycrystalline sample are studied by using the external applied magnetic field up to 10 KOe and it shows the moderate values of coercivity ( $H_c$ ), saturation magnetization ( $M_s$ ) and retentivity ( $M_r$ ). This measurements were carried out on a vibrating sample magnetometer (VSM).

**Keywords:** Lithium hexaferrites, coercivity, saturation magnetization and retentivity etc.

### INTRODUCTION

In the family of ferrites or ferrimagnetisms, the hexagonal ferrite be the most important materials, that has been attracted a considerable attention in the field of technological applications by low cost, easy manufacturing and interesting electric and magnetic properties. The aluminium and cobalt substituted barium, strontium and calcium hexaferrite are widely used in permanent magnet market and wide availability of raw materials. Permanent magnets are characterized by high remanance, coercivity etc.[1]. Another advantage is the great chemical stability of these oxides, which make in such a context of little improvement of their magnetic properties of great importance. Ferrite are technologically important materials because of their interesting physical and chemical properties that have attractive microwave devices, radio frequency coil, high density recording media, computer memory chip, transformer coil etc. [2-4]. In my present work the aluminium and cobalt substituted lithium ferrite with chemical composition  $Li_{0.5}Fe_{0.5+x}Al_{12-2x}Co_xO_{19}$  where ( $x=2,3,4,5$  and  $6$ ) having magnetoplumbite structures were synthesized using perfect stoichiometric mixtures of oxide by standard ceramic method. From XRD results, all shows a single phase formation of lithium hexaferrite magnetoplumbite structure pertaining to the space group  $P6_3/mmc$  (No.194). The lattice parameters  $a$ ,  $c$  and  $(h k l)$  values confirms the formation of hexagonal unit cell. The magnetic properties of polycrystalline compounds by the external applied magnetic field up to 10 KOe are studied, which shows the moderate values of saturation magnetization ( $M_s$ ), remenace or retentivity ( $M_r$ ) and coercivity ( $H_c$ ). By the experimental result it is found to decrease with increase in the value of substitution  $Al^{+3}$  ions, which attributed to occupation of sublattice spin-up and spin-down sites by  $Al^{+3}$  ions and magneto crystalline anisotropy. The variation in magnetic parameters gives rise to the possibility of controlling magnetic properties by varying the degree of substitution. The magnetic behavior of lithium hexagonal ferrites depends on the intrinsic magnetic properties of the M-type phase. The M-type ferrite crystallized in a hexagonal structure with 64 ions per unit cell on 11 different symmetry sites. The 24  $Fe^{+3}$  atoms are distributed over five distinct sites, three octahedral sites ( $12k$ ,  $2a$  and  $4f_2$ ), one tetrahedral ( $4f_1$ ) site and one bipyramidal site ( $2b$ ). The magnetic structure given by the Gorter model

in the ferrimagnetic with five different sub-lattices, three parallel (12k, 2a and 2b) and two antiparallel 4f<sub>1</sub> and 4f<sub>2</sub> which are coupled by superexchange interactions through the O<sub>2</sub> ions [5-6]. In the present investigation initially to understand the lattice behaviour of M- type ferrite. A significant improvement of the intrinsic magnetic properties of compounds can be obtained by the partial substitution of Co and Al ions. It has been recently shown that La and Co substitutes SrFe<sub>12</sub>O<sub>19</sub> ferrite have improved magnetic properties [2- 4] and [7- 8]. This improvement is largely associated with the increase of coercivity (H<sub>c</sub>) and underlying magneto crystalline anisotropy. On the other hand, the complete substitution of Sr by La induces an increase of the anisotropy field [2]. In this way, a rare earth ion may contribute to a change of new magnetic interactions, thus improving the magnetic properties. In the present investigation, the structural analysis of M-type lithium ferrite with composition of Al and Co in Li<sub>0.5</sub>Fe<sub>(0.5+x)</sub>Me<sub>12-2x</sub>O<sub>19</sub> (where Me = Al - Co) prepared and observed the variation in the magnetic properties.

### MATERIALS AND METHODS

All the multicrystalline powdered samples Li<sub>0.5</sub>Fe<sub>0.5+x</sub>Al<sub>12-2x</sub>Co<sub>x</sub>O<sub>19</sub> ( where x = 2, 3, 4, 5 and 6) were synthesized by using high temperature standard solid state reaction technique. The stoichiometric ratio of weighted A.R grade oxides Li<sub>2</sub>O, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and Co<sub>2</sub>O<sub>3</sub> were mixed thoroughly in acetone medium for 5 hr and pre sintered at 500<sup>0</sup>C for 10 hr for homogenization & calcinations. Calcinated powder were pressed into pellet, sintered at 1200<sup>0</sup> C for 120 hrs continuously and then cooled slowly to room temperature at the rate of 5<sup>0</sup>C/min using a microprocessor-controlled furnace. The X-ray diffractograms were obtained using Cu- K<sub>α</sub> radiation on a Philips X-ray diffractometer. The XRD pattern shows a single crystalline phase without traces of impurities. The patterns were indexed to hexagonal magnetoplumbite structure pertaining to the space group P6<sub>3</sub>/mmc (No.194). The X-ray powder diffraction pattern of sample Li<sub>0.5</sub>Fe<sub>0.5+x</sub>Al<sub>12-2x</sub>Co<sub>x</sub>O<sub>19</sub> (x = 2) is shown in Fig.1 and X-ray diffraction data are enumerated in Table-1.

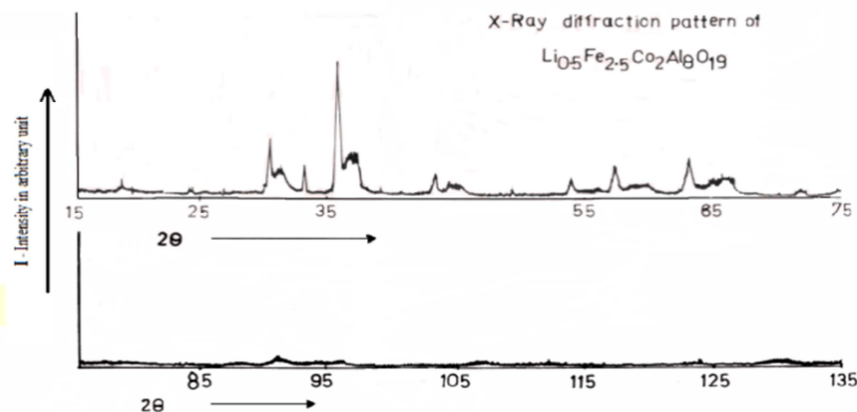


Fig.-1. XRD Diffraction of compound Li<sub>0.5</sub>Fe<sub>2.5</sub>Al<sub>8</sub>Co<sub>2</sub>O<sub>19</sub>

Table-1: Comparative 'd' values of compounds Li<sub>0.5</sub>Fe<sub>2.5</sub>Al<sub>8</sub>Co<sub>2</sub>O<sub>19</sub> and Li<sub>0.5</sub>Fe<sub>5.5</sub>Al<sub>2</sub>Co<sub>8</sub>O<sub>19</sub>

d <sub>obs</sub> (A.U)	d <sub>cal</sub> (A.U.)	I <sub>obs</sub>	h	k	l	d <sub>obs</sub> (A.U.)	d <sub>cal</sub> (A.U.)	I <sub>obs</sub>	h	k	l
4.802	4.944	16.4	1	0	1	4.825	4.889	10	1	0	1
2.941	2.93	40.3	1	1	0	4.796	4.572	11.5	1	0	2
2.816	2.883	13.7	1	1	2	2.943	4.943	29.1	1	0	6
2.7	2.7	30.5	1	0	7	2.92	2.898	17.7	1	1	0
2.513	2.537	100	2	0	0	2.875	2.872	11.2	1	1	1
2.464	2.464	27.9	2	2	0	2.508	2.508	100	2	0	0
2.455	2.45	29.2	1	1	5	2.448	2.447	16.8	2	0	2
2.444	2.445	34.5	1	0	8	2.075	2.065	19.2	2	0	6
2.402	2.401	29.3	2	0	3	1.694	1.682	8.5	2	1	6
2.007	2.02	13.3	1	1	8	1.6	1.599	16.6	3	0	4
1.843	1.857	9.3	2	1	3	1.565	1.562	5.88	3	0	5
1.691	1.695	14.2	3	0	0	1.478	1.474	8.2	3	0	7
1.606	1.618	13.7	3	0	4	1.472	1.472	26.8	2	0	12
1.59	1.585	24.3	2	0	11	1.468	1.448	27.6	2	2	0
1.58	1.58	10.2	2	1	8	1.271	1.27	7.6	3	1	7
1.47	1.484	32.3	3	0	7	1.268	1.255	8.5	4	0	0
1.466	1.464	31.2	2	2	1	1.078	1.079	4.4	3	2	7

X- Ray diffraction Result of Li<sub>0.5</sub>Fe<sub>2.5</sub>Al<sub>8</sub>Co<sub>2</sub>O<sub>19</sub>  
a = 5.8594 A.U and c = 22.3234 A.U

X-Ray diffraction Result of Li<sub>0.5</sub>Fe<sub>5.5</sub>Al<sub>2</sub>Co<sub>8</sub>O<sub>19</sub>  
a = 5.6953 A.U and c = 21.2626 A.U

The lattice parameters, X-ray density and molecular weight were calculated for each sample. The magnetic properties of polycrystalline sample have been measured by using a vibrating sample magnetometer in the applied field upto 10 KOe at room temperature. In order to avoid rotation of the powder grain, pressed samples were used. The transition temperature ( $T_c$ ) has been measure by using a Gouy's balance.

## RESULTS AND DISCUSSION

The X-ray diffraction pattern of all the samples shows that all these are belongs to hexagonal structure. The reflection from the planes appearance proved that the samples are M-type ferrite. The interplaner distance 'd' (A.U.) was calculated using Bragg's law and the value of lattice constant 'a' was determined. The observed and calculated d-values of the interplaner distances for the sample  $\text{Li}_{0.5}\text{Fe}_{0.5+x}\text{Al}_{12-2x}\text{Co}_x\text{O}_{19}$  ( $x = 2, 3, 4, 5$  and  $6$ ) are depicted in Table-1. Thus obeying the Regard's law which may be attributed to the replacement of smaller  $\text{Fe}^{3+}$  ions (0.64 A.U.) by larger ionic radii of the combinations of cobalt and aluminium ions in  $\text{Li}_{0.5}\text{Fe}_{0.5+x}\text{Al}_{12-2x}\text{Co}_x\text{O}_{19}$  (where  $x = 2, 3, 4, 5$  &  $6$ ) system. The X-ray density is given in the Table-2, the variation of X-ray density with the concentration of  $\text{Co}^{+3}$  and  $\text{Al}^{+3}$  with  $\text{Fe}^{+3}$  which may be due to the ionic difference between  $\text{Al}^{+3}$  (0.50 A.U.) and  $\text{Co}^{+3}$  (0.64 A.U.) as reported in the literature [7]. The bulk density is determined and value as a function of concentration is observed that the bulk density increases with concentration Co and Al. At sintering temperature of  $1200^\circ\text{C}$ , the number of pores is reduced, as a result of which individual grains come closer to each other and the effective area of grain to grain contact increases as also described [8]. The sample comprises hexagonal particles indicating improved homogeneity and grain size reduction of the starting powders.

Table- 2. Consolidated X-Ray diffraction analysis data of  $\text{Li}_{0.5}\text{Fe}_{0.5+x}\text{Al}_{12-2x}\text{Co}_x\text{O}_{19}$  ( $X= 2,3,4,5$  &  $6$ )

Compound	a (A.U.)	c (A.U.)	Mol. Wt in gm	X-ray density ( $\text{gm}/\text{cm}^3$ )
$\text{Li}_{0.5}\text{Fe}_{2.5}\text{Al}_8\text{Co}_2\text{O}_{19}$	5.8594	22.3234	780.89	3.9065
$\text{Li}_{0.5}\text{Fe}_{3.5}\text{Al}_6\text{Co}_3\text{O}_{19}$	5.8181	21.8796	841.79	4.3578
$\text{Li}_{0.5}\text{Fe}_{4.5}\text{Al}_4\text{Co}_4\text{O}_{19}$	5.8076	21.8411	902.66	4.6992
$\text{Li}_{0.5}\text{Fe}_{5.5}\text{Al}_2\text{Co}_5\text{O}_{19}$	5.7948	21.8077	963.54	5.0473
$\text{Li}_{0.5}\text{Fe}_{6.5}\text{Co}_6\text{O}_{19}$	5.6953	21.2626	1024.42	5.6963

Table-3 is to summarize the crystallographic characteristics of five different sublattice together with the spin alignments corresponding to the collinear magnetic structure. The value of saturation magnetization as per formula unit in Bohr magneton at 300 KG for all the samples obtained from field dependence [9].

Table 3: Five iron lattice sites, their spin direction, point symmetry, number of Fe ions per formula, and block situation in M-type ferrite

Sublattice	Type Point symmetry	Ions	Spin( $5\eta$ )	Block
12k	Octahedral	m 6	UP $\uparrow$	S – R
4f <sub>1</sub>	Tetrahedral	3m2	Down $\downarrow$	S
4f <sub>2</sub>	Octahedral	3m2	Down $\downarrow$	R
2a	Octahedral	$\bar{3}m$ 1	UP $\uparrow$	S
2b	Five Fold	$\bar{6}m$ 1	UP $\uparrow$	R

Table-4: Magnetic parameters of  $\text{Li}_{0.5}\text{Fe}_{0.5+x}\text{Al}_{12-2x}\text{Co}_x\text{O}_{19}$  ( $x = 2, 3, 4, 5$  and  $6$ )

Compounds	Magnetization $M_s$ ( $10^3\text{emu/g}$ )	Retentivity $M_r$ ( $10^3\text{emu/g}$ )	Coercivity $H_c$	Magnetic Moment ( $\mu$ )	Magnetic susceptibility $10^{-6}\text{emu/Oe}$
$\text{Li}_{0.5}\text{Fe}_{2.5}\text{Al}_8\text{Co}_2\text{O}_{19}$	10.918	1.369	1.116	12	1091
$\text{Li}_{0.5}\text{Fe}_{3.5}\text{Al}_6\text{Co}_3\text{O}_{19}$	25.476	5.094	1.652	16	2547
$\text{Li}_{0.5}\text{Fe}_{4.5}\text{Al}_4\text{Co}_4\text{O}_{19}$	38.219	12.734	1.938	30	3821
$\text{Li}_{0.5}\text{Fe}_{5.5}\text{Al}_2\text{Co}_5\text{O}_{19}$	50.515	15.048	2.223	63	5015
$\text{Li}_{0.5}\text{Fe}_{6.5}\text{Co}_6\text{O}_{19}$	57.036	17.813	2.753	94	5703

The magnetic result of the compounds  $\text{Li}_{0.5}\text{Fe}_{0.5+x}\text{Al}_{12-2x}\text{Co}_x\text{O}_{19}$  ( $x = 2,3,4,5$  &  $6$ ) are given in table- 4 compared with  $\text{Ca}_{0.5}\text{Sr}_{0.5}(\text{Co-Al})_{0.5}\text{Fe}_{11}\text{O}_{19}$  and  $\text{Ca}_{0.5}\text{Sr}_{0.5}(\text{Co-Ti})_{0.5}\text{Fe}_{11}\text{O}_{19}$ , found that the saturation magnetization, magnetic moment and retentivity, coercivity values are larger. This is due to the increase of Fe and decrease of Al content, the contribution towards saturation magnetization due to Fe-O-Fe exchange interaction gets reduced. The behavior is in good agreements to that observe by Bertant E.F, Deschamps A, [10-12] etc, when Fe is substituted by Al, Ga and Cr in M-ferrites affect the lattice dimensions, site distribution, Curie temperature and saturation magnetization. It is observed that saturation magnetization decreases when  $\text{Fe}^{+3}$  ion is substituted by  $\text{Al}^{+3}$  with increasing concentration. In compound  $\text{Li}_{0.5}\text{Fe}_{0.5+x}\text{Al}_{12-2x}\text{Co}_x\text{O}_{19}$  ( $x = 2, 3, 4, 5$  &  $6$ ) the magnetic moment from the octahedral surrounded ferric  $\text{Fe}^{+3}$  ions in the spinel blocks and those in the trigonal bipyramidal sites are opposed by a minority of ferric ions in tetrahedral sites of the spinel block along with octahedral sites. Which in case of compound  $\text{Li}_{0.5}\text{Fe}_{0.5+x}\text{Al}_{12-2x}\text{Co}_x\text{O}_{19}$  ( $x=2, 3, 4, 5$  &  $6$ ) larger value of saturation magnetization is observed, which is obvious as substitution of

ferrimagnetic ions such as Co in spinel blocks of the M- structure occupying the octahedral sites (12k), the interaction energy increase so high, which in turn increases the saturation magnetization [13]. The B-H curve measurements were also carried out at room temperature. The observed results are explained on the basis of site distribution. The saturation magnetization  $M_s$ , coercivity  $H_c$ , magnetic moment and retentivity  $M_r$  decreased with Al substitution. It is evident from the fact that  $Al^{+3}$  ions is weaken the magnetic in nature. In this compound the magnetic moment from octahedral surrounded ferric ions in the spinel blocks and those in the trigonal bipyramidal sites are opposed by a minority of ferric ions in tetrahedral sites of the spinel block along with octahedral sites. The large value of  $M_s$  and  $H_c$  are attributed to the fact that the interaction energy is so high, which in turn increases the saturation magnetization [14] have shown that the interaction 2a-12k is of immense importance and determines the magnetic behaviour of the compounds. The  $Fe^{+3}$  ions have high magnitude of superexchange and interactions, particularly when all the 24 sites 2a, 2b,  $4f_1$ ,  $4f_2$  and 12k are filled by magnets and ferromagnetic ions alone Fe (12k) sublattice making the link along octahedral R-S structural blocks is subjected to very strong competitive exchange interaction in Table 4. A plot of inverse molar magnetic susceptibility versus temperature (T) is linear for the samples containing Co and Al ions, resembles ferromagnetic behaviour. The variation in magnetic moment of  $Co^{+3}$  and  $Fe^{+3}$  ions are different ferromagnetic are formed. The high value of  $T_c$  demonstrates that some inter substitute exchange interaction between two close sites, are decisive for strong magnetic characters.[15-17]; while the low value of  $T_c$  means that the cations of the additive substitute for the  $Fe^{+3}$  of the 2b or the 12 k sites will weaken the total distance or angle due to the superexchange interaction Fe-O-Fe [18]. The interaction between close site such as 2a -2k, 2a -  $4f_1$ , and  $4f_1$ -12k are decisive for strong magnetic character. Whenever magnets ions are present in these sites, strengthening of superexchange interaction produces an increase in the magnetic characteristics such as Curie temperature, magnetization etc. In case of M-structure, the orientations of the magnetic moments of the ferric ions in the crystals are generally aligned along the c-axis in antiparallel with each other. The neutron diffraction and NMR studies in Ba M- ferrites [19] shows that the  $Ti^{+4}$  ions are mainly distributed with  $4f_2$  and 12k sites  $Co^{+2}$  ions occupy mainly  $4f_1$  and 12 k sites [20], because of  $4f_1$  and  $4f_2$  with down spin have larger value of magnetic moment can be obtained according the cationic distribution deduced from the neutron & NMR studies using the Gorter collinear spin model. A mean field analysis of the exchange interaction in M-type hexaferrite has been carried out by [21-22]. The result shows that the Fe (12k) sublattice making link among R-S structural blocks is subject to very strong competitive exchange interaction. So when  $Fe^{+3}$  ions in the 12k sublattice are subjected to non magnets viz.  $Al^{+3}$  ions weakening of superexchange interaction between magnetic ions results in a fairly inclined ferrimagnetisms [23-25].

## CONCLUSION

In the present work, the samples were checked to formation of hexagonal ferrite containing  $Al^{+3}$  and  $Co^{+3}$  ions along with  $Fe^{+3}$  ions of lithium ferrites ceramic. All these compounds have M-structure through the site distribution changes. No changes occur in the charge distribution but the site distribution is change due to strichiometric changes. The intensity of magnetisation of the cobalt content compounds decreases linearly by increasing concentration of  $Al^{+3}$  ions as well as decreasing the magnetic moment. From Hysteresis tracing, all compounds at room temperature indicative a ferrimagnetic in nature. The coeresivity, retentivity and saturation magnetization of cobalt content samples are decreases with increasing the substitution of  $Al^{+3}$  ions preferentially performed on spin up Fe site and made a magnetic dilution. Non-magnetic collinear Fe-O-Fe superexchange interaction may be weakening by  $Al^{+3}$  substitutions in the compounds.

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