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Effect of Aluminium and Cobalt Substituent on Structural and Magnetic Behaviour of Lithium Ceramics

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Abstract

A Lithium hexaferrite samples with chemical formula $Li_{0.5}Fe_{0.5+x}al_{12-2x}co_xo_{19}$ (x =2,3,4,5 & 6) were synthesized using proper stoichiometric proportions by solid state reaction at1200^0c for 120 hrs. The chemical phase analysis of all compounds has been carried out by X-ray powder diffraction (XRD) method, which confirms the formation of the ferrite structure. It shows hexagonal magnetoplumbite (M) type structure having unit cell dimension a and c varies between 5.6950 - 5.8590 A.U. and 21.2623– 22.3230 A.U. Coercivity (H_c), Saturation magnetization (M_s) and Retentivity (M_r) measurements were carried out on a vibrating sample magnetometer with an applied field up to 10 Koe.

Keywords: Lithium ferrite, X-ray diffraction, Magnetization, Coercivity, Retentivity etc.

Introduction

The hexagonal ferrite to be one of the most important materials that has attracted a considerable attention in the field of technological applications by low cost, easy manufacturing and interesting electric and magnetic properties.The Cobalt –Aluminium substituted barium, stroncium and calcium hexaferrite samples of isostructural magnetoplumbite ferrites are widely used in permanent magnet market and wide availability of raw materials. Permanent magnets are characterized by high remanance, coericivity etc. [1]. Another advantage is the great chemical stability of these oxides, which makes in such a context a 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 device application, radio frequency coil, high density recording media, computer memory chip, transformer coil, etc. [2- 4]. The Aluminium – Cobalt substituted lithium ferrite ceramics with chemical composition $Li_{0.5}Fe_{0.5+x}Al_{12-2X}Co_XO_{19}$where(x=2,3,4,5&6) having magnetoplumbite structures were synthesized using perfect stoichiometric mixtures of oxide by standard ceramic method. XRD results show a single phase formation of Lithium hexaferrite. The lattice parameters *a*, c and (h k l) values confirms the formation of hexagonal unit cell. The magnetic properties of polycrystalline sample by the external applied magnetic field are studied, which shows the moderate values of coercivity, remenace and saturation magnetization. The saturation magnetization (M_s), remenace (M_r) and coercivity (H_c) found to decrease with increase in the value of substitution which is attributed to occupation of sublattice spin-up and spin-down sites by Al^{+3} ions and magnetocrystalline anisotropy. The variation in magnetic parameters gives rise to the possibility of controlling magnetic properties by varying the degree of substitution. The magnetic behaviour of lithium hexagonal ferrites depends on the intrinsic magnetic properties of the M-type phase. The M-type ferrite crystallizes 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 $4f_1$ and $4f_2$ which are coupled by superexchange interactions through the O_2 ions [5 - 6]. To understand the lattice behaviour of M- type ferrite, in the present investigation, a significant improvement of the intrinsic magnetic properties of compounds can be obtained by the partial substitution of Al and Co. It has been recently shown that La-Co substitutes $SrFe_{12}O_{19}$ ferrite have improved magnetic properties [2- 4] and [7-8]. This improvement is largely associated with the increase of coercivity H_c 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 this investigatation, the structural analysis of M-type lithium ferrite with composition of Al and Co in $Li_{0.5}\,Me_{(2x+0.5)}Fe_{12-2x}\,O_{19}$ prepared and observed the variation in the magnetic properties.

Materials and Methods

The powdered samples of $Li_{0.5}Fe_{0.5+x}Al_{12-2X}\,Co_xO_{19}$ (x = 2, 3, 4, 5 and 6) have been synthesized by using standard solid state reaction technique. The stoichiometric proportions of weighted oxides were mixed thoroughly in acetone medium for 5 hr and pre sintered at 500^0C for 10 hr to homogenize & calcinations, then calcinated powder were pressed into pellet and sintered at 1200^0 C in air atmosphere for about 120 hrs and cooled slowly to room temperature at the rate of 5^0C/min using a micro- processor controlled furnace. The X-ray diffractograms were obtained using Cu-Kα 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 $P6_3/mmc$ (No.194).

The X- ray powder diffraction pattern of the $Li_{0.5}Fe_{0.5+x}Al_{12-2X}\,Co_xO_{19}$ (x = 2, 3, 4, 5 & 6) is shown in fig.1 and X-ray diffraction data are enumerated in table -1. 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 KG 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.

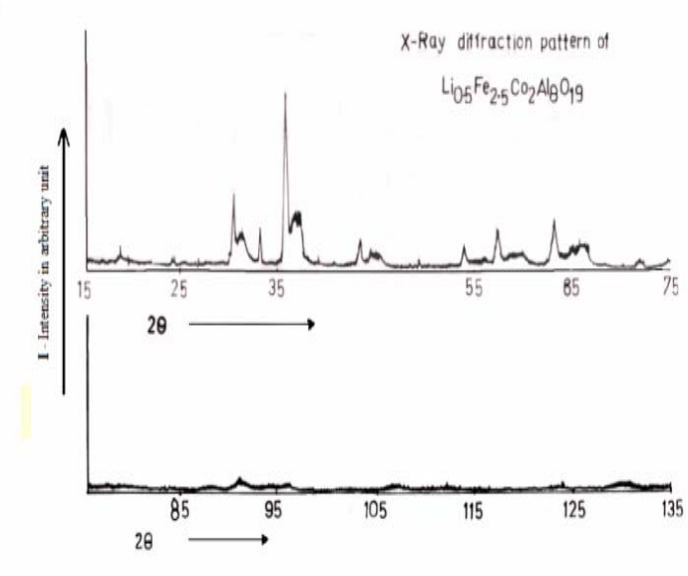

Fig-1: XRD of sample $Li_{0.5}Fe_{2.5}Co_2Al_8O_{19}$

Table. 1: Comparative d - values of samples of $Li_{0.5}Fe_{2.5}Al_8Co_2O_{19}$ and $Li_{0.5}Fe_{5.5}Al_2Co_8O$

X- Ray diffraction of $Li_{0.5}Fe_{2.5}Al_8Co_2O_{19}$

d_{obs} (A.U.)	d_{cal} (A.U.)	I_{obs}	h	k	l
4.802	4.944	16.4	1	0	1
2.941	2.930	40.3	1	1	0
2.816	2.883	13.7	1	1	2
2.700	2.700	30.5	1	0	7
2.513	2.537	100.0	2	0	0
2.464	2.464	27.9	2	2	0
2.455	2.450	29.2	1	1	5
2.444	2.445	34.5	1	0	8
2.402	2.401	29.3	2	0	3
2.007	2.020	13.3	1	1	8
1.843	1.857	09.3	2	1	3
1.691	1.695	14.2	3	0	0
1.606	1.618	13.7	3	0	4
1.590	1.585	24.3	2	0	11
1.580	1.580	10.2	2	1	8
1.470	1.484	32.3	3	0	7
1.466	1.464	31.2	2	2	1
1.449	1.447	10.1	3	0	8
1.436	1.437	10.7	2	2	3
1.427	1.428	10.2	3	0	15
1.403	1.404	16.0	3	1	1
1.400	1.398	10.7	3	0	0

Lattice parameters *a* = 5.8590 A.U
c = 22.3230 A.U

X- Ray diffraction of $Li_{0.5}Fe_{5.5}Al_2Co_8O_{19}$

d_{obs} (A.U.)	d_{cal} (A.U.)	I_{obs}	h	k	l
4.825	4.889	10.0	1	0	1
4.796	4.572	11.5	1	0	2
2.943	4.943	29.1	1	0	6
2.920	2.898	17.7	1	1	0
2.875	2.872	11.2	1	1	1
2.508	2.508	100.0	2	0	0
2.448	2.447	16.8	2	0	2
2.075	2.065	19.2	2	0	6
1.694	1.682	8.5	2	1	6
1.600	1.599	16.6	3	0	4
1.565	1.562	5.88	3	0	5
1.478	1.474	8.2	3	0	7
1.472	1.472	26.8.	2	0	12
1.468	1.448	27.6	2	2	0
1.271	1.270	7.6	3	1	7
1.268	1.255	8.5	4	0	0
1.078	1.079	4.4	3	2	7

Lattice parameters *a* = 5.6950 A.U
c = 21.2623A.U

Results and Discussion:

The X-ray diffraction pattern of all the samples shows that all these lines belong to hexagonal structure. The reflection from the planes appearance proved that the samples are M-type ferrite depicted in table -1. The interplaner distance d (A.U.) were calculated using Bragg's law and the value of lattice constant *a* (A.U) were determined. The observed and calculated values of the interplaner distances for the sample $Li_{0.5}Fe_{0.5+x}Al_{12-2X}Co_XO_{19}$ (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 Fe^{3+} ions (0.64 A.U.) by larger ionic radii of the combinations of aluminium and cobalt ions in $Li_{0.5}Fe_{0.5+x}$ Al_{12-2X} Co_XO_{19} (x = 2, 3, 4, 5 and 6) system. The X-ray density is given in the Table-2, the variation of X-ray density with the concentration of Co^{+3} and Al^{+3}, with Fe^{+3}, which may be due to the ionic difference between Al^{+3} (0.50 A.U.) and Co^{+3} (0.64 A.U.) as reported in the literature [7-8]. 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 ^{0}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 $Li_{0.5}Fe_{0.5+x}Al_{12-2X}Co_XO_{19}$ (x = 2,3,4,5& 6)

Compounds	*a* (A.U.)	c (A.U.)	Mol. Wt in gm	X-ray density (gm/cm3)
$Li_{0.5}Fe_{2.5}Al_8Co_2O_{19}$	5.8594	22.3234	780.89	3.9065
$Li_{0.5}Fe_{3.5}Al_6Co_3O_{19}$	5.8181	21.8796	841.79	4.3578
$Li_{0.5}Fe_{4.5}Al_4Co_4O_{19}$	5.8076	21.8411	902.66	4.6992
$Li_{0.5}Fe_{5.5}Al_2Co_5O_{19}$	5.7948	21.8077	963.54	5.0473
$Li_{0.5}Fe_{6.5}Co_6O_{19}$	5.6953	21.2626	1024.42	5.6963

In table-3, we have summarized the crystallographic characteristics of five different sub lattice together with the spin alignments corresponding to the collinear magnetic structure proposed [9]. The value of saturation magnetization as per formula unit in Bohr magnetron at 300 KG for all the samples obtained from field dependence.

The results for compounds $Li_{0.5}Fe_{0.5+x}Al_{12-2X}Co_XO_{19}$ (x = 2, 3 ,4, 5 and 6) are compared with $Ca_{0.5}Sr_{0.5}(CoAl)_{0.5}Fe_{11}O_{19}$ and $Ca_{0.5}Sr_{0.5}(CoTi)_{0.5}Fe_{11}O_{19}$,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 behaviour is in good agreements to that observe by [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.

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

Sub lattice	Type Point symmetry	Ions	Spin(5η)	Block
12k	Octahedral	m 6	UP ↑	S – R
$4f_1$	Tetrahedral	3m2	Down ↓	S
$4f_2$	Octahedral	3m2	Down ↓	R
2a	Octahedral	□3m 1	UP ↑	S
2b	Five Fold	□6m1	UP ↑	R

Table-4: Magnetic parameters of $Li_{0.5}Fe_{0.5+x}Al_{12-2X}Co_XO_{19}$ (x = 2, 3, 4, 5 and 6)

Compounds	Magnetization $M_s(10^3 emu/g)$	Retentivity $M_r(10^3 emu/g)$	Coercivity H_c	Magnetic Moment(μ)	Magnetic susceptibility 10^{-6} emu/Oe
$Li_{0.5}Fe_{2.5}Al_8Co_2O_{19}$	10.918	1.369	1.116	12	1091
$Li_{0.5}Fe_{3.5}Al_6Co_3O_{19}$	25.476	5.094	1.652	16	2547
$Li_{0.5}Fe_{4.5}Al_4Co_4O_{19}$	38.219	12.734	1.938	30	3821
$Li_{0.5}Fe_{5.5}Al_2Co_5O_{19}$	50.515	15.048	2.223	63	5015
$Li_{0.5}Fe_{6.5}Co_6O_{19}$	57.036	17.813	2.753	94	5703

It is observed that saturation magnetization decreases when Fe is substituted by Al with increasing concentration. In compound $Li_{0.5}Fe_{0.5+x}Al_{12-2X}Co_XO_{19}$ (x = 2, 3, 4, 5 and 6)the magnetic moment from the 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. Which in case of compound $Li_{0.5}Fe_{0.5+x}Al_{12-2X}Co_XO_{19}$ (x = 2, 3, 4, 5 and 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 carried out at room temperature. The observed results are explained on the basis of site distribution. The saturation magnetization, coerecivity, magnetic moment and retentivity decreased with Al substitution. It is evident from the fact that Al ions is weak magnetic in nature. In this compound the magnetic moment from octahedraly surrounded ferric ions in the spinal 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 Ms and Hc 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 in 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 table 5. 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 ordering temperature has variation amongst the compounds, as the magnetic moment of Co^{+3} and Fe^{+3} ions are different ferromagnetic 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 BaM- ferrites [19] shows that the Ti^{+4} ions are mainly distributed with $4f_2$ and12k 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 weaking of superexchange interaction between magnetic ions results in a fairly inclined ferrimagnetisms [23-25].

Conclusion:

In this present work of lithium hard ferrites is to check the formation of ferrite containing Al^{+3} and Co^{+3} ions along with Fe^{+3} ions. X-ray spectra shows a hexagonal peaks. The values of lattice parameters *a* and c confirms the formation of hexagonal unit cell. 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 in the compound. In this series of $Li_{0.5}Fe_{6.5}Co_6O_{19}$ to $Li_{0.5}Fe_{2.5}Al_8Co_2O_{19}$ the Coerecivity, Retentivity, Saturation magnetization, magnetic moment decreased with Al substitution.

It is evident from the fact that Al ions is weak magnetic in nature. Lithium hard ferrites shows magnetic properties which are more useful in the field of information storage recording media.

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