

Influence of Cobalt and Aluminium ions on Structural and Electrical Behavior Mixed Lithium Ceramics

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Abstract: A series of cobalt ions and aluminium ions substituted lithium ferrite (M-type) samples with the general chemical formula $\text{Li}_{0.5}\text{Fe}_{0.5+x}\text{Al}_{12-2x}\text{Co}_x\text{O}_{19}$ were synthesized using reacting oxides 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 uncertainty ambiguous reflection. From XRD pattern lattice parameter has been recorded with increasing doped aluminium 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 densities of the ferrites were found to vary linearly and depend upon the mass and volume of the sample. The X-Ray density depends upon the lattice constant and molecular weight of the compounds. The average particle size was also estimated. The electrical conduction was carried out over the temperature range from 27°C - 800°C . The electrical conduction in the ferrites was explained on the basis of Verwey models. A Seebeck study reveals that all samples are N-type semiconductors. The compounds were studied magnetically by using Guoy's method in the temperature range 300 to 550 K. The result shows that the compounds are paramagnetic in nature. The Curie molar constant was determined.

Keywords: Magnetoplumbite, electrical conductivity, activation energy etc.

1. Introduction

A series of lithium hexaferrites $\text{Li}_{0.5}\text{Fe}_{12.5}\text{O}_{19}$ magnetoplumbite (M-Type) has been a great technological interest in many electromagnetic devices from a long time. High electrical resistivity, low eddy current losses, low magnetic losses, and very good thermal and chemical stability. Lithium ferrite material has a great importance for microwave applications. In the family of hexagonal ferrites, the Magnetoplumbite hexaferrites (M-Type) created much attention due to wide range of application in industries and created potential to interest in technological and scientific research due to their application importance such as high density magnetic recording, microwave device materials, hard disc in computer system. The application need particularly magnetic and electrical specification with the view, many attempt have been improved the properties of hexagonal ferrites using different tract of additives. The calcium hexferrites [1-6] have magnetic properties comparable to BaM and Sr M. In Calcium ferrites many attempt has been made to replace Fe^{+3} ions with Al^{+3} , Cr^{+3} and Co^{+3} etc. A compound with the combination of bivalent-tetravalent cation was also used to replace Fe^{+3} ion such as Cu-Ti, Co-Ti, Co-Sn, Zn-Sn etc [7, 8] without any appreciable change in BaM structure. When Fe^{+3} ions are replaced by non magnetic ions like Ti^{+4} and Sn^{+4} etc. In the same way Lithium ferrites substituted with Al and Co has been studied structurally, electrically and magnetically [9]. In the present study of series of compounds with chemical formula $\text{Li}_{0.5}\text{Fe}_{0.5+x}\text{Al}_{12-2x}\text{Co}_x\text{O}_{19}$ ($x = 2, 3, 4, 5$ and 6) were prepared. Lithium ferrites have attracted considerable attention because of the squareness of hysteresis loop coupled with superior temperature performance the crystal structure of M-type compound with a space group $P6_3/mmc$ (194) can be described as superposition of two structure block namely R-block with

composition $\text{BaFe}_6\text{O}_{11}$ and S-block with composition Fe_6O_8 [10] in the stoichiometric ratio.

2. Material and Methods

All the polycrystalline powder sample were synthesized by high temperature solid state reaction using AR grade oxides with stoichiometric ratio Li_2O , Fe_2O_3 , Al_2O_3 and Co_2O_3 mixture. Li_2O oxide was carefully dehydrated before the mixing procedure and then grinding the mixture under acetone upto six hours. During the preparation of pellets of thoroughly grounded mixture in the proper molar ratio with 5% of PVA as a binder are prepared by applying 10 tone pressure per square inch. These pallets slowly heated in the furnace at 600°C for 5 - 6 hours to remove binder. Then it was fired at 1200°C for 120 hours continuously, after that the furnace were cooled at the rate of 20°C per hours up to 1000°C and then 50°C per hours and then cooled in natural way the phase of final sample were verified by Philips X-ray diffractometer using N-filter copper radiation. The mean grain size of multicrystalline samples was in the range 150 - 200 A° . All the samples show single phase formation with a space group $P6_3/mmc$ (194). X-ray pattern of the samples is shown in fig.1.1(a). Also the variation of lattice parameters a and c with Al and Co concentration in the composition of ferrites as shown in fig 1.1 (b and c)

The electrical resistivity was measured by the method using LCR meter/Q meter.[11]. The end faces of pellets were coated with thin layer of conducting silver paste and measurement were made from room temperature to 800 K. Thermoelectric power measurement were carried out after sandwiching the thick pellet between two copper rod from room temperature to 550°C

3. Result and discussion

In this present investigation, the Cobalt and Aluminium substituted Lithium hexaferrites were introduced with general formula $\text{Li}_{0.5}\text{Fe}_{0.5+x}\text{Al}_{12-2x}\text{Co}_x\text{O}_{19}$ ($x = 2, 3, 4, 5$ and 6). The ions in Ba-M compounds may be replaced partly by Co^{+3} or completely Li^{+1} and combination of Fe^{+3} and Al^{+3} ions without changing the crystal lattice symmetry [12]. In all the specimens substituted ions would be chosen to keep electrical neutrality and to have a similar ionic radii in these ferrites. The Cobalt and Aluminium play an important role in the property variation. XRD technique is used to confirm the formation of hexagonal M structure of compounds belonging to a space group $P6_3/mmc$ (194) Homawalt 1956.

Table1 (a): Consolidated X-ray diffraction analysis data of

x	Lattice Parameters		Cell Volume (AU) ³ (AU) ³	Mol. Wt (gm)	X-ray Density gm/cm ³
	a (A.U)	c (A.U)			
2	5.8594	22.324	663.81	780.89	3.9065
3	5.8181	21.876	641.48	841.79	4.3578
4	5.8076	21.841	637.90	902.66	4.6992
5	5.7948	21.807	633.96	963.54	5.0473
6	5.6953	21.266	597.22	1024.4	5.6963

Table 1(b): Consolidated X-ray diffraction analysis data of

X	Lattice Parameters		Cell Volume (AU) ³ (AU) ³	Mol.Wt gm	X-ray Density gm/cm ³
	a (A.U)	c (A.U)			
2	5.906	22.585	682.23	716.89	3.4895
3	5.852	22.452	665.92	745.75	3.7189
4	5.827	22.208	653.03	774.62	3.9390
5	5.811	22.081	645.86	803.48	4.1313
6	5.807	22.507	644.26	832.35	4.2903

Due to the resemblance of ionic radii of Fe^{+3} with Co^{+3} and Al^{+3} ions [13, 14], the ferrite ions are replaced by cobalt and aluminium. It is seen that former ions are very easily replaced at any substituted variation in all specimens [15]. The hexagonal lattice parameters 'a' and 'c' decreases linearly with the substitutional variation Co^{+3} and Fe^{+3} concentration in all specimens. The decrease in lattice parameters due to close packing of lattice in the materials [16-18]. The decrease in lattice parameter and cell volume agrees with result for Ba / Sr ferrite [19-20]. The numerical values of compositional data such as lattice constant, cell volume and X- ray density are tabulated in table -1(a) and 1(b). Lattice parameters 'a' and 'c' changes with composition of Al & Co ions in lithium ferrites as given in table- 1(c)

Table 1 (c)

Sub lattices	Type Point symmetry	Ions	Spin (5η)	Block
12k	Octahedral	m 6	UP \uparrow	S – R
4f ₁	Tetrahedral	3m2	Down \downarrow	S
4f ₂	Octahedral	3m2	Down \downarrow	R
2a	Octahedral	3m1	UP \uparrow	S
2b	Five Fold	-6m1	UP \uparrow	R

X-ray diffraction pattern of the sample

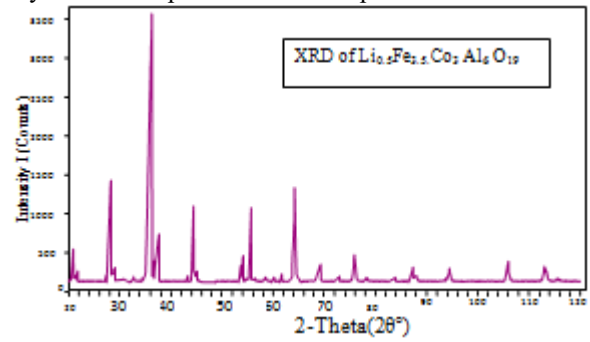


Figure 1(a): X-ray diffraction pattern of $\text{Li}_{0.5}\text{Fe}_{3.5}\text{Co}_3\text{Al}_6\text{O}_{19}$

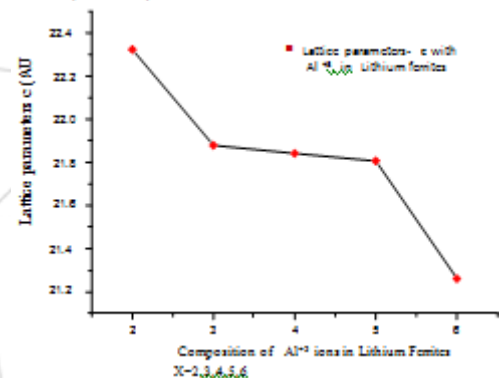
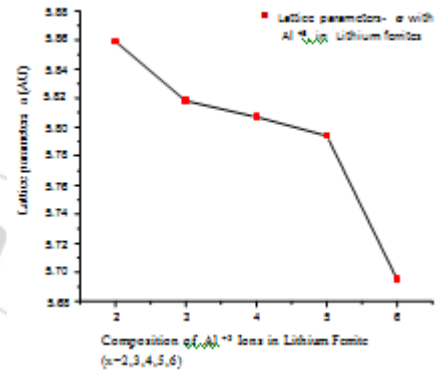


Figure 1(b): Lattice parameters- a and c with Al^{+3} in Lithium Ferrites

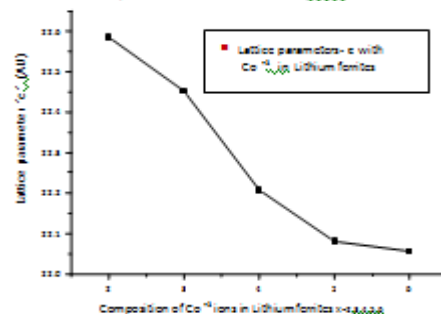
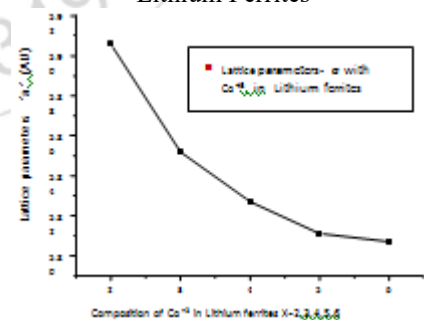


Figure 1(c): Lattice parameters a and c with Co^{+3} in Lithium ferrites

The plot of $\ln(\sigma)$ vs $(1/T) \times 10^{-3}$ K for the entire sample was almost linear. The electrical conductivity of these ferrites increases with increasing ferrite ion concentration. The electrical conductivity of sintered specimens varies from $2.193 \times 10^{12} \Omega^{-1} \text{cm}$ to $5.78 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ of these ferrites. The other workers have obtained a conductivity value of $2 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ for Li-ferrite that obtained is $2.3 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ [21]

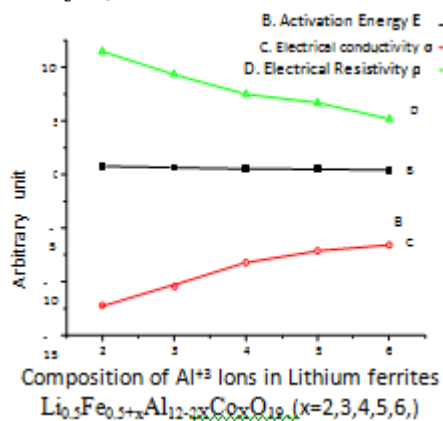


Figure 2

In this present work the electrical conductivity value obtained for the compounds are 2.193×10^{-12} to $5.78 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$. The value of the conductivity may be partly attributed to the low evaporation of lithium from the sample prepared different from these of Rozlescu et al 1974 and Venugopal Reddy 1981. The variation of activation energy with the substitutional variable parameter x may be explain on the basis of Verway model [22-24], a small number of ferrous ions (Fe^{+2}) are generally developed during sintering process which lead the conductivity in ferrites suggesting the hopping mechanism according ($\text{Fe}^{+2} = \text{Fe}^{+3} + e^-$) [25-28]. However these transitions take place for a very small interval of time and are not detectable by the ordinary method. This valence exchange mechanism of Verwey may be considered for these ferrites as general applicable to M-type ferrite.

4. Conclusion

In this present work, the lithium hardferrites were checked for the formation of ferrite containing Al^{+3} and Co^{+3} ions along with Fe^{+3} ions. 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 stochiometric changes. The electrical conductivity value obtained and may be partly attributed to the low evaporation of lithium from the sample. The activation energy varies with the substitution variable parameter such as Al and Co ions.

5. Acknowledgement

Author is thankful to UGC New Delhi for providing financial assistance to carry out this work under minor research project scheme File No 47-1345/10(WRO). Author also thankful to D. K. Burghate, N.S. Bhawe, D.K.Kulkarni, S.B.Khasare and J.M.Khobragade to guiding and allow me for laboratory facility to study the series of lithium hexaferrite.

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