



Synthesis and Electrical Conduction of Al and Co Doped Lithium Ceramic

Suresh. S. Darokar

Science College Congress Nagar, Nagpur, Maharashtra, India

ABSTRACT

A new compound of Lithium hexaferrites with general chemical formula $\text{Li}_{0.5}\text{Fe}_{0.5+x}\text{Al}_{12-2x}\text{Co}_x\text{O}_{19}$ where $x = 2, 3, 4, 5$ and 6, were synthesized by standard ceramic technique using stoichiometric proportion. The lattice parameters of the multicrystalline materials have been determined and characterized by X-ray diffraction technique. XRD data shows the formation of samples of a single phase hexagonal M-type ferrites with a space group P63/mmc(194). The electrical conduction was carried out over the temperature range from 270C- 8000 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.

Keywords: Magnetoplumbite, Hexaferrites, electrical conductivity, Seebeck coefficient etc.

I. INTRODUCTION

Among 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, in computer system etc. The application need particularly magnetic and electrical specification with the view, many attempts have been improved the properties of hexagonal ferrites using different tract of additives. The Calcium hexaferrites [1-9] have magnetic properties comparable to BaM and SrM. In calcium ferrites many attempts have 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 [10-12] 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 [13] In the present study a series of five samples with chemical formula $\text{Li}_{0.5}\text{Fe}_{0.5+x}\text{Al}_{12-2x}\text{Co}_x\text{O}_{19}$

where $x = 2, 3, 4, 5$ 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 like compound with a space group P63/mmc (194) can be described as superposition of two structure blocks namely R-block with composition $\text{BaFe}_6\text{O}_{11}$ and S-block with composition Fe_6O_8 [14] in the stoichiometric ratio.

II. MATERIALS AND METHODS

All the multicrystalline powder samples were synthesized by high temperature solid state reaction using A.R grade oxides of stoichiometric ratio Li_2O_3 , Fe_2O_3 , Al_2O_3 and Co_2O_3 mixture. Li_2O_3 oxide was carefully dehydrated before the mixing procedure. After grinding the mixture under acetone acid for six hours, 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 pellets slowly heated in the furnace at 600 °C for 5-6 hours to remove binder [15]. Then it was fired at 1200 °C for 120 hours continuously, after that the furnace was cooled at the rate of 20 °C per hour up to 1000 °C and then 50 °C per hour and then cooled in natural way the phase of final sample were verified by Philips X-ray

diffraction using Ni-filter copper radiation. The mean grain size of multicrystalline samples was in the range 150-200 Å. All the samples show single phase formation with a space group P63/mmc (194).

The d.c. electrical conductivity was measured by the methods using LCR meter. 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.

III. RESULT AND DISCUSSION

In the present work cobalt and aluminium substituted lithium hexaferrites were introduced with general formula $\text{Li}_{0.5}\text{Fe}_{0.5+x}\text{Al}_{12-2x}\text{Co}_x\text{O}_{19}$ where $x = 2, 3, 4, 5$ and 6. The ions in Ba-M compounds can 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 [16]. In all the specimens substituted ions would be chosen to keep electrical neutrality and to have similar ionic radii in these ferrites. The cobalt and aluminium play an important role in the property variation. The XRD technique is used to confirm the formation of hexagonal magnetoplumbite structure of compounds belonging to a space group P63 / mmc (194), X-ray diffraction pattern of the compound $\text{Li}_{0.5}\text{Fe}_{2.5}\text{Al}_8\text{Co}_2\text{O}_{19}$ is shown in Figure 1.

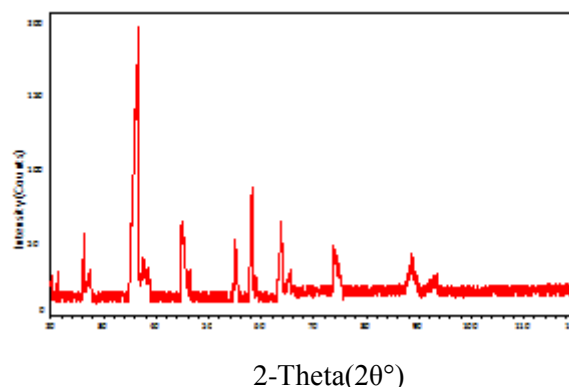


Figure 1. XRD of compound $\text{Li}_{0.5}\text{Fe}_{2.5}\text{Al}_8\text{Co}_2\text{O}_{19}$

Due to the resemblance of ionic radii of Fe^{+3} with Co^{+3} and Al^{+3} ions, the ferrite ions will be replaced by cobalt and aluminium. It is seen that former ions are very easily replaced at any substituted variation in all specimens. The hexagonal lattice parameters 'a' and 'c' decrease linearly with the substitution variation Co^{+3} and Fe^{+3} concentration in all specimens. Lattice parameters decrease due to close packing of lattices in the materials [17]. The decrease in lattice parameter and cell volume agree with results for Ba and Sr ferrite [18], the numerical values of compositional data such as lattice constant, cell volume and X-ray density are tabulated in table 1. The observed value of electrical conductivity and activation energy for specimens are also tabulated in table 2.

Table 1. Consolidated structural data of lithium ferrites

| Compounds | Lattice parameters | | Cell Volume (Å^3) | Mol. Wt gm | X-Ray Density gm/cc |
|---|--------------------|--------|------------------------------|------------|---------------------|
| | a (Å) | c (Å) | | | |
| $\text{Li}_{0.5}\text{Fe}_{2.5}\text{Al}_8\text{Co}_2\text{O}_{19}$ | 5.859 | 22.323 | 663.81 | 780.89 | 3.9065 |
| $\text{Li}_{0.5}\text{Fe}_{3.5}\text{Al}_6\text{Co}_3\text{O}_{19}$ | 5.818 | 21.879 | 641.48 | 841.79 | 4.3578 |
| $\text{Li}_{0.5}\text{Fe}_{4.5}\text{Al}_4\text{Co}_4\text{O}_{19}$ | 5.807 | 21.841 | 637.90 | 902.66 | 4.6992 |
| $\text{Li}_{0.5}\text{Fe}_{5.5}\text{Al}_2\text{Co}_5\text{O}_{19}$ | 5.794 | 21.807 | 633.96 | 913.96 | 5.0473 |
| $\text{Li}_{0.5}\text{Fe}_{6.5}\text{Co}_6\text{O}_{19}$ | 5.695 | 21.262 | 597.22 | 1024.42 | 5.6963 |

Table 2. Electrical conductivity of lithium ferrites

| Compounds | Electrical Resistivity (e) at room temp. ($\Omega\text{ cm}$) | Activation energy E in (eV) | Electrical Conductivity (σ) at room temp. ($\Omega\text{ cm}$) ⁻¹ |
|---|---|-----------------------------|---|
| $\text{Li}_{0.5}\text{Fe}_{2.5}\text{Al}_8\text{Co}_2\text{O}_{19}$ | 4.559×10^{11} | 0.77 | 2.193×10^{-12} |
| $\text{Li}_{0.5}\text{Fe}_{3.5}\text{Al}_6\text{Co}_3\text{O}_{19}$ | 3.21×10^9 | 0.63 | 3.11×10^{-10} |
| $\text{Li}_{0.5}\text{Fe}_{4.5}\text{Al}_4\text{Co}_4\text{O}_{19}$ | 4.65×10^7 | 0.52 | 2.148×10^{-8} |
| $\text{Li}_{0.5}\text{Fe}_{5.5}\text{Al}_2\text{Co}_5\text{O}_{19}$ | 6.84×10^6 | 0.48 | 1.46×10^{-7} |
| $\text{Li}_{0.5}\text{Fe}_{6.5}\text{Co}_6\text{O}_{19}$ | 1.72×10^5 | 0.39 | 5.78×10^{-6} |

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 $2.193 \times 10^{-12} (\Omega \text{ cm})^{-1}$ to $5.78 \times 10^{-6} (\Omega \text{ cm})^{-1}$ of these ferrites [20], the electrical conductivity values obtained by Reddy et al 1981 is $2.3 \times 10^{-6} (\Omega \text{ cm})^{-1}$ cm. and $2 \times 10^{-2} (\Omega \text{ cm})^{-1}$ Rezlescu et al 1974 for lithium ferrite.

In the present work the electrical conductivity value obtained for the compounds are $2.193 \times 10^{-12} (\Omega \text{ cm})^{-1}$ to $5.78 \times 10^{-6} (\Omega \text{ cm})^{-1}$. 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 parameters x - may be explain on the basis of Verway model [21] 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 ($\text{Fe}^{+2}-\text{Fe}^{+3}+e^-$) [23-24], However these transition take place for a very small interval of time and are not detectable by the ordinary method. This valence exchange mechanism of Verway may be considered for these ferrites as general applicable to M-type ferrites.

IV. CONCLUSION

In this present work, the formation of lithium hard ferrites containing Al^{+3} and Co^{+3} ions along with Fe^{+3} ions were checked. 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 electrical conductivity of $\text{Li}_{0.5} \text{Fe}_{0.5+x} \text{Al}_{1-2x} \text{Co}_x \text{O}_{19}$ at different concentrations has been explained on the basis of the hopping mechanism of holes (Co^{2+} and Co^{3+}) and electrons (Fe^{2+} and Fe^{3+}). As evident from the change in slope of the Arrhenius plot at temperature. The temperature variation in the dc electrical conductivity of pure $\text{Li}_{0.5} \text{Fe}_{6.5} \text{Co}_6 \text{O}_{19}$ and mixed $\text{Li}_{0.5} \text{Fe}_{2.5} \text{Al}_8 \text{Co}_2 \text{O}_{19}$ shows a definite kink, which corresponds to ferromagnetic to paramagnetic transitions. The activation energy in the paramagnetic region is higher than the ferromagnetic region. Ferrite with the presence of Co leads to a decrease in activation energy and a decrease in conductivity because there is a

significant decrease in crystallite shape area. The presence of Co in ferrites leads to disorder and hence to localization of electrons, leading to the metal-insulator transition-like properties of the Anderson model. The lattice disorder plays a significant role in determining dc conductivity behavior of such ferrites.

V. 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 Kulkarni and J.M.Khobragade to guide and given a facility to do the work in laboratory.

VI. REFERENCES

- [1]. Beretea J. and Brown T.B, Austral. J.Chem, 1971,24,273.
- [2]. Lipka V. J, .Gruskova A, Orlicky O, Sitek J, Miglierini M, Grone R, Hucl M and Toth.I, Hyperfine Interaction ,1990,59, 381
- [3]. Albanese G., Deriu A, Lucchini E and Slokar G., Appli Phys,1981, 26A,45
- [4]. Haneda K, Kojima H, J. Appl. Phys,1973, 14 B. 3760
- [5]. Adelskod V, Avkir Kemi, Miner Geo, 1938, 12 A 1, 29
- [6]. Gu B.X,ZangH.Y.ZhaiH.R,B.G.SlenB.G,LuM,Zhang S.Y&MaoiY.Z,Phys Status Solidi,1992,133, K83.
- [7]. Renson J.G, Schullces J.A. and Van.Wlering J.S., J.Phys Collog.,1971,32,C1;924
- [8]. Darokar S.S,Rewatkar K.G,Chowkase M.S & Kulkarni D.K, Indian J.Phys,2000,74A (2),155-157
- [9]. Rezlescu N,Condurachi D,Petrarju P and LuccaE, J.Am.Ceream Soc,1974, 57, 40
- [10]. Ghare D.B, Sinha A.P.B, J. Phys Chem Solids, 1968 ,29, 885
- [11]. Kulkarni .D.K and Prakash C.S., Bull Mater Sci, 1994, 17, 35
- [12]. Hanmawalt, International table for X-ray diffraction photograph,1936
- [13]. Kanke K,Takayamamuromachi E,Uchida,Y, Kato K. &Takikawa,S, J.Solid state Chem, 1991, 95,438
- [14]. Prakash C.S and Kulkarni D.K. Ind J. Appl.Phys,1994, 32,361

- [15]. Rewatkar K.G, Prakash CS and .Kulkarni D.K, Mater Sci. Lett 1996, 28, 36
- [16]. Albense G, Carbulichhio M and Deriu A J.Phys Solid State, 1974, A 23,351
- [17]. Haneda K, Kojima H., J. Phys State Solid, 1971, A 6,256.
- [18]. Rodrigue Z,ObradorsX, Labrata A,Tejeja.J.,Pernet M. Solid Paul M and Tholente J,J.Phys Collog ,1988,149,119
- [19]. Versteegen J.M, D.T.J.Solid State Chem ,1973,1, 468
- [20]. Rezlescu N,Condurache D.Petrarju P and Luca E.,J.Am.CereamSoc,1974 ,57,40
- [21]. VerwayE.J J. De-BarJ.H., Pec.Trar.Chem Pay Bull ,1936 ,55 ,531
- [22]. Fang T T, Hwang J B and Shign F S, J.Mater sci Lett, 1992, 11,1217
- [23]. Asti.G,Carbuccocchio.M,Deriu A,Lucchini E and.Slokar G,J.Magn.Magn Mater, 1980, 20, 44
- [24]. Darokar S.S,Rewatkar K.G.and.Kulkarni D.K.,Mater Chem.Phys.,1998,56,84-85.