EFFECT OF STOICHIOMETRIC AND NON-STOICHIOMETRIC ON CHENICAL AND PHYSICAL PROPERTIES OF FERRITE MATERIALS: AN ANALYTICAL STUDY

M.V.K.MEHAR
Dept. of Physics, GDC, Alamuru, A.P State

K.VENKATESWARA RAO
Dept. of Physics, P.R.G.College (A), Kakinada, A.P State

V.SOMASHEKARA RAO
Dept. of Chemistry, GDC, Alamuru, A.P State

D.RAMARAO
Dept. of Chemistry, P.R.G. College(A), Kakinada, A.P State

Abstract

Different types of ferrites were prepared with compositional formulae $[Li_{0.5+x}\ Sb_x\ {}_{Fe2.5-2x}]0_4$, $2[Li_{(1+3y)/2}\ Mo_y\ Fe_{2.5-3y/2)}]O_4$, $[Li_{0.5+x}Nb_xFe_{2.5-2x}]O_4$, $[Mg_{0.9}Mn_{0.1+x}\ Ti_x\ Fe_{2.-2x}]O_4$, $[Mg_{0.9}Mn_{0.1+x}Zr_x\ Fe_{2-2x}]O4$ *etc. were prepared under solid state reaction method sintered at different temperatures (1000°C – 1300°C). All are showed different properties at different sintering temperatures due to evaporation of some dopent elements like lithium, Niobedium, Zirconium ect.at high temperatures due to reduction of* Fe^{3+} *to* Fe^{2+}*. At high temperature all are showed at high density and high coercivity. Saturation magnetization were measured and showed good values at lesser temperatures (~1100°C) but Curie Temperatures showed maximum at High Temperature especially Lithium ferrites. Mechanical properties of all materials were good at high Temperatures. Conduction mechanism showed different due to different temperatures take place between* Fe^{2+} *and* Fe^{3+}*.*

Keywords: *Ferrite Materials, Sintering Temperatures, Properties, Stoichiometry*

INTRODUCTION

Field of ferrites has attracted the attention of scientists and technologists for a long time since a wide variety of applications such as electrical and magnetic devices used over wide range of frequencies require their high resistivity and low loss behavior [1] as one of the significant properties. Resistivity of the ferrites is very high compared to resistivity of individual metal oxides. The high resistivity of ferrites facilated to reduce the eddy current losses so as to be useful in industrial applications. The combination of magnetic and electrical characteristics in addition to desirable properties over appreciable range of temperatures lead to many industrial applications of ferrites. The technological importance of ferrites increases continuously as many applications require the use of magnetic materials such as permanent magnets. Spinel ferrites with chemical formula MFe_2O_4, where M stands for divalent metal, such as nickel, magnesium, copper Zinc or cadmium.

Cation distribution is one of the important said parameters which depend on stoichiometry as well as temperature, atmosphere, pressure etc. which Control the cation distribution and oxygen parameter also provides a means of developing the desired physical properties of their proper use in industry [2]. All the above applications based on different categories Viz Mn-Zn, Ni-Zn, copper, Mg-Mn, Li, Mg and other Microwave mixed ferrites.

EXPERIMENTAL TECHNIQUES

All the samples of different ferrites were prepared under solid state reaction method with chemical formulae $[Li_{0.5+x}Sb_{x}Fe_{2.5-2x}]0_{4}$: with x=0.0 to 1.0 insteps of 0.05, $2[Li_{1+3y/2}Mo_{y}Fe_{2.5-3y/2}]O_{4}$: with x =0.05 to 0.5 insteps of 0.1, $[Li_{0.5+x}Nb_{x}Fe_{2.5-2x}]O_{4}$ and $[Li_{0.5+x}V_{x}Fe_{2.5-2x}]O_{4}$: with x=0.0 to 0.5 insteps of 0.1,$[Mg_{0.9}Mn_{0.1+2x}Sb_{x}Fe_{2-3x}]O_{4}$ and $[Mg_{0.9}Mn_{0.1+3x}Mo_{x}Fe_{2-4x}]O_{4}$: with x=0.0 to 0.40 insteps of 0.05, $[Mg_{0.9}Mn_{0.1+x}Ti_{x}Fe_{2-2x}]O_{4}$ and $[Mg_{0.9}Mn_{0.1+x}Zr_{x}Fe_{2-2x}]O_{4}$: with x= 0.0 to 0.4 insteps of 0.1 [3-5]. After stiochometry satisfied the raw materials were taken into aggate mortar then added methanol and again ground for two hours thereafter the mixed powdered was calcinated at different temperatures Viz for Li-Sb, Li-Mo were calcinated at 625 ^{o}C for 4 hours with raw marerials Li_2Co_3,Sb_2O_5,Fe_2O_3,MOo_3, for Li- Nb and Li-V with chemicals Nb_2O_5,V_2O_5,Li_2Co_3,Fe_2O_3 were calcinated at 625^{0}C for 4 hours, for Mg-Mn with dopant element Sb and Mo with raw materials the chemicals MgO,MnO,Sb_2O_5,& MOo_3 were calcinated 950 ^{o}C for 2 hours, Mg-Mn with Zr and Mg-Mn with Ti and chemicals MgO, MnO_2,ZrO_2,& TiO_2 were calcinated at 1000^{o}C for 4 hours. All the chemicals were with AR grade used. The Calcinated mixed powder were grinded for 2 hours then after added PVA and finally groung for 2 hours. The mixed powder was made as pellets and toroids then taken into furnace at different temperatures Viz Li-Sb and Li-Mo samples were sintered at 1200^{o}C for 4 hours,Li-Nb,Li-V were sintered at 1050 ^{o}C for 4 hours similarly Mg-Mn with dopent elements Mo and Sb sintere at 1200^{o}C for 2 hours and Mg-Mn with dopent elements Zr and Ti were sintered at 1300^{o}C for two hours.

RESULTS AND DISCUSSION

Density of the samples were measured according to Archimediies principle and X-ray densities were calculated using the formula given below from XRD studies and also confirms the single phase.

$$d_X = \frac{ZM}{NV} \text{ gm/cm}^3 \qquad (1)$$

Where, Z = Number of molecules per unit cell (8 for spinel structure), M = Molecular weight of the sample, N= Avogadro's Number (6.023 X1023), V = Theoretical volume of the unit cell, V = a^3; a is the unit cell dimension). In lithium ferrites with Sb and Mo dopent elements the theoretical densities were almost decreases with increasing concentrations. Due to sintering at high temperature loss of lithium takes place thereby Oxygen dissociation and lithium volatility occurs resulting non-stoichiometric compostion formed. The reduction of Fe^{3+} to Fe^{2+} takes place due to loss of lithium which is confirmed by photo chemical Redox titration method. The percentage of Fe^{2+} increases with concentration. In case of Nb and V dopents the X-ray density decreases with increasing concentration. Due to sintering at less Temperature it is showed no loss of lithium thereby resulting in stoichiometry ferrites. The theoretical densities of Mg-Mn ferrites with Sb and Mo are increases with increasing substituent composition. The percentage of Fe^{2+} is increases with concentration for Mo^{6+} substitution element. The percentage of Fe^{2+} is initially increases then decreases with continuous increases of

Sb^{5+} substitution element. The X –ray densities of Mg-Mn ferrites with Zr is increases and Ti were decreases with continuous increasing dopant.

The Magnetic measurements of various ferrites of Li-Sb, Li-Mo, Li-Nb, Li-V, Mg-Mn with Sb,Mo,Zr,Ti substituent composition at x = 00

Table.1

S.No	Ferrites Type	Stoichimetry type	Curie Temperature (^oC)	Saturation Magnetization
1	$[Li_{0.5+x}Sb_{x}Fe_{2.5-2x}]0_{4}$	Non Stoichiometry	720	61.7 emu/gm
2	$2[Li_{1+3y/2}Mo_{y}Fe_{2.5-3y/2}]O_4$:	Non Stoichiometry	720	61.7 emu/gm
3	$[Li_{0.5+x}Nb_{x}Fe_{2.5-2x}]O_4$	Stoichiometry	640	304 gauss
4	$[Li_{0.5+x}V_{x}Fe_{2.5-2x}]O_4$	Stoichiometry	640	304 gauss
5	$Mg_{0.9}Mn_{0.1+x}Ti_xFe_{2-2x}O_4$	Stoichiometry	490	144 gauss
6	$O_{4\,0.9}Mn_{0.1+x}Zr_xFe_{2-2x}O_4$	Stoichiometry	490	144 gauss
7	$Mg_{0.9}Mn_{0.1+2x}Sb_{x}Fe_{2-3x}O_4$	Non Stoichiometry	480	10.9 emu/gm
8	$Mg_{0.9}Mn_{0.1+3x}Mo_{x}Fe_{2-4x}O_4$	Non Stoichiometry	480	10.9 emu/gm

From the above table, It is observed that the Curie Temperature is high at Non stoichimetric ferrites and low at stoichimetric ferrites. This is due to the reason of oxygen dislocation thereby reduction of Fe^{3+} to Fe^{2+}. The saturation magnetization is high at stoichiometric ferrites due to fact that the site Mechanism (between A site and B site). The Dielectric constant also studied at high frequencies and showing good at Mega frequency region where its dielectric constant is in lies between 10-20 and dielectric loss is very small.

CONCLUSIONS

All the ferrites were prepared under solid state reaction method. After systematical study the sintering effect leads to stoichiometric and non-stoichimetric ferrites. The increasing and decreasing in theoretical densities are due to porosity effect. The high sintering Temperature causes the Non-stoichimetric ferrites due fact that reduction of Fe^{3+} to Fe^{2+}. The saturation magnetization increases in stoichimetric ferrites may be the fact that site mechanism between A ans B site i.e interaction between A and B sites. The dielectric constant at frequencies shows flat profile and its values is lies in between 10-20 and dielectric loss is very small.

REFERENCES

[1] S. C. Watawe, U. A. Bamme , S. P. Gonbare, Mater. Chem.Phys., 103 (2007) 323.

[2] K. B. Modi, J. D. Gajera, M. C. Chhantbar, K. G. Sailaja, G. J.Baldha, H. H. Joshi, Mater. Lett., 57 (2003) 4049.
[3] V.V.HaiBabu, Thesis submitted, Dept. of Phys., A. U, Vizag, India (1998).
[4] P.Sridevi, Thesis submitted, Dept. of Phys., A. U, Vizag, India (2001).
[5] D.Vijayalakshmi, Thesis submitted, Dept. of Phys., A. U, Vizag, India (2003).