PROCESSING OF LI-MN FERRITE AND ITS CHARACTERISATION

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ABSTRACT

The ferrite material design in terms of their morphologies has gained much attention for various advantages. The morphology depends on the processing method. The recent advance in the processing of ferrimagnetic oxides or ferrites is being reviewed. Attention is paid to the processing of $Li_{0.45}Fe_{2.45}Mn_{0.1}O_4$ ferrite powder by citrate precursor method. The synthesized sample was given sintering at 1080°C, one sample without a pre-sintering process and another with a pre-sintering at a temperature of 540°C. XRD was used to confirm the spinel phase. From the analysis crystallite size was calculated and was found to be in the nanometer range. The electrical studies such as dc resistivity and dielectric constant were also investigated at room temperature. Resistivity increases while dielectric constant decreases with effect of double sintering. The magnetic study such as Curie temperature was measured. Possible reason for all the above observation is being discussed.

Keywords: Ferrite, Nanomaterials, XRD, Dielectric Constant, Curie temperature, Dc Resistivity

I. INTRODUCTION

Lithium and substituted lithium ferrite are a large class of oxides with remarkable properties. Due to its technical application in various field ferrites have been investigated and applied during the last decades. Their application ranges to many aspect like power handling capacity, simple permanent magnets, and magnetic recording [1-3]. These applications are based upon the basic properties of ferrites which include a significant saturation magnetization, a high electrical resistivity, low electrical losses, a very good chemical stability, a high Curie temperature, a rectangular hysteresis loop and a high dielectric constant etc [4-7]. The said material can be obtained by many methods, and the feasibility to prepare is unlimited. As such there are conventional ceramic methods as well as wet chemical method [8-10]. The conventional ceramic method involves high-temperatures sintering which often results in a low quality material; the volatility of lithium above 1000 °C affects the magnetic properties and the resistivity.

1.1 Ceramic Method: In this method manual mixing is done using agate mortar and pestle. Mostly agate made of porcelain is used as it is hard and unlikely to contaminate the mixture. Sufficient amount of a volatile organic liquid like acetone or alcohol which gradually volatilizes after 10 to 15 minutes of grinding and mixing is added for homogenization. After mixing the powder mixture is calcined at an elevated temperature like 1000°

C to coreact the individual oxides. Reaction to give final product usually requires hours or even days depending on reaction temperature. It is than given final sintering [11-12]. In order to overcome such difficulties, a number of wet chemical methods have been developed to prepare lithium and substituted lithium ferrites at low temperatures yielding material at nanoscale. They include the solvothermal method, sol–gel method, the microemulsion method, the citrate precursor's method etc.

1.2 Solvothermal Method: In order to prepared cobalt ferrite analytical grade chemicals of cobalt chloride and ferric chloride was used. They were separately dissolved in ethylene glycol and after complete dissolution it was mixed together. The resulting mixture was poured In a Teflon vessel and placed in a microwave pressurized reactor and heated at an ambient temperature about 200°C for few minutes. After cooling at room temperature a black product was obtained which was wash with demineralised water and ethanol several times. Finally it was heated at a higher temperature and is the required ferrite [13]. The possibility of preparing ferrites in the form of nanoparticles has open a new and exciting research field, with revolutionary applications in field such as electronic technology, biotechnology etc.

In this paper emphasis on processing of lithium manganese ferrite by citrate precursor method and its characterisation is being discussed.

II. EXPERIMENT

Ferrites with the formula $Li_{0.45}Fe_{2.45}Mn_{0.1}O_4$ was prepared using the citrate precursor method [14-15]. The starting chemicals used in this study were lithium nitrate, manganese acetate, iron nitrate and citric acid. Stoichiometric amount of lithium nitrate, zinc nitrate, manganese acetate, iron nitrate and citric acid were mixed to make a solution. The ratio of metal cations to citric acid is 1:1. The solution was mixed homogenously with the help of a magnetic stirrer using a magnetic agitator. The value of pH was controlled at 7 by adding ammonia solution drop by drop. After controlling pH at 7 it was refluxed at 40°C with continuous stirring for about half an hour. The solution was then put in an oven at 100°C. The dried gel then ignited, undergoing a strong auto combustion process with evolution of large amount of gases, giving rise to the ash-synthesized product. The product so obtained is the typical spinel structured lithium ferrite powder with nanocrystallite size. The synthesized powder was mixed with polyvinyl alcohol as binder and pressed into pellets with 50 kilo Newton pressure. The synthesized sample was given sintering at 1080°C, one sample without a pre-sintering process and another with a pre-sintering at a temperature of 540°C and furnace cooled. XRD was used to identify the spinel phase using X-ray diffractometer (Phillips) with CuKα (λ=1.5405 Aº) radiation. From an XRD analysis crystallite size was calculated and was found to be in the nanometer range. The crystallite size is calculated using the angle θ in the Debye Scherrer equation [16] given by,

$$D_{hkl} = \frac{0.89\lambda}{\beta \cos\theta}$$

The electrical studies such as dc resistivity and dielectric constant were also investigated at room temperature. The d.c resistivity was calculated using the four probe method and the dielectric constant was measured using Agilent HP 4284A LCR meter using the relation $C_p = \frac{\varepsilon_O \varepsilon' A}{d} = \frac{\varepsilon A}{d}$

Where A is the area and d the thickness of the sample, ε_O is the permittivity of free space and ε the dielectric constant of the ferrites sample. Resistivity increases while dielectric constant decreases with effect of double sintering. The magnetic study such as Curie temperature was measured using the Soohoo's method [17]. Possible reason for all the above observation has been discussed.

III.RESULTS AND DISCUSSION

Spinel phase structure of the prepared ferrite samples was confirmed from XRD pattern (Figure1). All peaks could be indexed to the standard pattern reported by the Joint Committee on Powder Diffraction Standards (JCPDS). No extra peak due to impurities is observed. The typical XRD pattern for the ash-synthesized powder (AS) is shown in Figure 1.

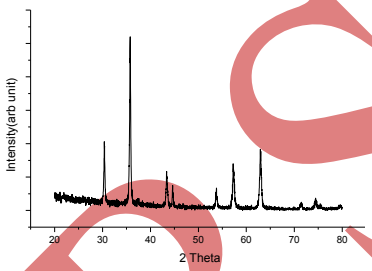

Fig.1 XRD Pattern of Ash Synthesized Ferrite Powder

From an XRD analysis crystallite size was calculated and was found to be in the nanometer range (Table 1). The room temperature dc resistivity decrease while dielectric constant increase with double step sintering (Table 1).

TABLE 1

Sample Name	Crystallite size(nm)	DC resistivity (ohm-cm)	Dielectric constant	T_C (^oC)
SS	68	$1.822x10^8$	51.038	653
DS	75	$1.963x10^8$	50.652	629

The dielectric properties such as dielectric constant have been investigated. The variation in dielectric constant can be explained on the basis of space charge polarization and Koop's two layer model, where the ferrite is assumed to be made up of well conducting grains separated by poor conducting layers or grain boundaries [18]. The electrical conduction in ferrite is explained by the Verwey mechanism of electron hopping where conduction takes place by hopping of electrons between Fe^{2+} and Fe^{3+} ions at B sites. The electrons reach the grain boundary through hopping and due to its higher resistivity, the electrons pile up, thereby producing space charge polarization. In the present case a decrease in dielectric constant with double sintering temperature is observed. In general if the sintering temperature is more there is possibility of formation of Fe^{2+} ion due to volatilization. In the present case there seems to be almost no loss of lithium with increase in sintering. It is learnt from various reports that there is a decrease of charge mobility carrier with the increase of sintering

temperature due to oxidation of Fe^{2+} to Fe^{3+} ion during sintering [18-19]. The space charge polarization therefore decreases, leading to a decrease in dielectric constant. The Curie temperature is observed to decrease with increasing sintering temperature as given in table 1. This may be due to the weakening of the AB superexchange interaction as there is a decrease in the number of active $Fe_A^{3+} - O^{2-} - Fe_B^{3+}$ linkages with increase in sintering temperature. Hence the thermal energy required to offset the spin alignment decreases, leading to the observed decrease in Curie temperature.

IV. CONCLUSIONS

$Li_{0.45}Fe_{2.45}Mn_{0.1}O_4$ nanoparticles have been prepared at considerably low temperature by citrate precursor method. The crystallite size and room temperature dc resistivity increase with double sintering while room temperature dielectric constant decreases with double sintering. The Curie temperature is observed to decrease with double sintering. Thus controlling the sintering temperature material can be processed to get desired properties for specific application.

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