

# REVIEW ON THE EFFECT OF SUBSTITUTION IN BASIC LITHIUM FERRITES

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## ABSTRACT

*Lithium ferrite has emerged in recent years as a material that shows significant technological application, the properties being dependent on substitution to a large extent. This review article provides a summary of fundamental theoretical aspects of lithium ferrite and the effect of substitution.*

**Keywords:** *Lithium Ferrites, Dielectric constant, DC resistivity, Curie temperature, Saturation-magnetization, Initial permeability*

## I. INTRODUCTION

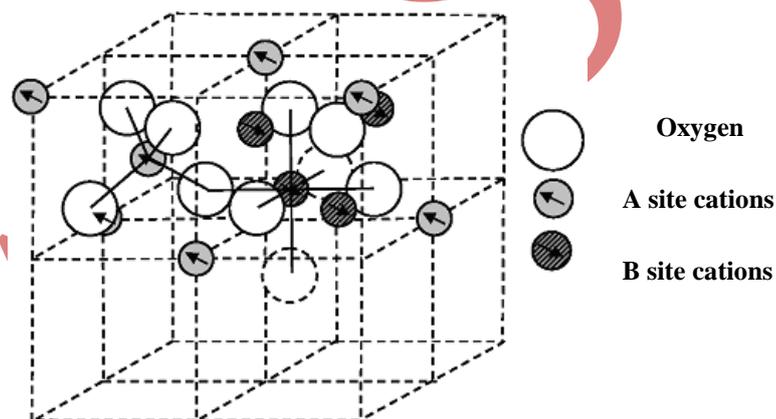
In order to meet the high performance demands of ferrites for fast emerging technologies, processing of ferrites has gained tremendous importance.  $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$  which possesses a spinel structure is a material of extensive study both in its pure and in its substituted form. They are found to be used in certain applications like magnetic components, microwave devices such as isolators, circulators, gyrators and phase shifters, memory core, power transformers in electronics, antennae, etc.[1-6]. There are various factors which play the role in tailoring the properties of basic ferrite material. Substitution type and amount, processing methods, finishing etc are few which can be mentioned. As far as substitution is concern the metal ions can be distributed over the tetrahedral A and octahedral B sites. Consequently there arise changes in ionic radii of metal ions, the electronic configuration, the electrostatic energy of the spinel structures etc. and hence the properties of the material. There are a number of substitution which may be divalent ( $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mg}^{2+}$  etc.), trivalent ( $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$  etc.), tetravalent ( $\text{Si}^{4+}$ ,  $\text{Sb}^{4+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Ge}^{4+}$  etc.) that had been used to tailored the properties of ferrite materials for specific applications [7-16]. In this paper, the effect of few substitutions on the basic lithium ferrite was reviewed.

## II. THEORETICAL BACKGROUND

The spinel structure ferrites have the general formula  $\text{MFe}_2\text{O}_4$ , where M represents a divalent metal ion. The divalent metal ion can be one of the divalent ions of the transition elements or a combination of these ions or a combination of ions having average valency of two, like  $0.5\text{Li}^{1+}+0.5\text{Fe}^{3+}$  as in  $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ . The trivalent ion and tetravalent ion may completely or partly replaces the  $\text{Fe}^{3+}$  ions in  $\text{MFe}_2\text{O}_4$ . Gorter, Hafner, and Blasse have extensively studied the crystal chemistry of the compound crystallizing in the spinel structure although Bragg

and Nishikawa first determined it [17-20]. The spinel crystal structure depends on the oxygen ion lattice, the radii of the oxygen ions ( $\sim 1.32\text{\AA}$ ) being several times larger than the radii of the metallic ions ( $0.6\text{\AA}$  &  $1.0\text{\AA}$ ). The crystal structure was thought to be made up of the closest possible packing of oxygen ions, i.e. it forms an f.c.c. lattice leaving the tetrahedral or the A-site and the octahedral or the B-site as shown in Fig.1 (E. W. Gorter, 1954). In the unit cell of a spinel lattice there are eight molecules of  $M\text{Fe}_2\text{O}_4$  consisting of 32 oxygen ions. It forms a cubic close packed structure, 8 divalent ions and 16 trivalent ions. The 32 oxygen ions leave 64 tetrahedral interstices (A) site and 32 octahedral interstices (B) site. Of these only 8 A sites and 16 B sites are occupied by the metal ions.

Spinel ferrites can be classified into three categories, viz. normal, inverse and mixed ferrites based on site occupancy by divalent and trivalent metal ions. In normal ferrites all the tetrahedral sites are occupied by the eight divalent cations and the octahedral sites by the sixteen trivalent metal ions, in inverse ferrite eight out of the sixteen trivalent metal ions occupy tetrahedral sites, and the octahedral sites are occupied by eight divalent metal ions and the remaining eight trivalent cations. Mixed ferrite is a kind of ferrites, which is neither completely normal nor inverse since the A, and B sites are randomly occupied by both divalent and trivalent metal ions [11].



**Fig 1. Structure of Spinel ferrite.**

### **III. SUBSTITUTION EFFECT**

Various substitutions are being studied by large number of researchers. The present study is concern with few substitutions such as chromium, aluminium, silicon, zirconium and antimony.

#### **3.1 CHROMIUM SUBSTITUTION**

The increase in the substitution of trivalent  $\text{Cr}^{3+}$  increases the ac resistivity ascribed to a hopping mechanism between  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  ions and the availability of ferrous ions on octahedral sites. Navdeep Gill et al [21] studied lithium ferrite substituted with  $\text{Cr}^{3+}$  and found that the substitution of  $\text{Cr}^{3+}$  ion reduces the internal magnetic field at A site as well as B sites. It produces ferromagnetic relaxation for higher contents of  $\text{Cr}^{3+}$  ions and was explain based on super transferred hyperfine field and domain wall displacement. Kutznetsov et al [12] studied  $\text{Cr}^{3+}$  substituted lithium ferrite prepared by self-propagating high combustion synthesis and observed

super-paramagnetic behaviour. Radhapiyari et al [22] investigated the effect of simultaneous substitution of  $\text{Cr}^{3+}$  and  $\text{Sb}^{5+}$  in lithium ferrites and observed that dc resistivity increased whereas saturation magnetization decreases.

### 3.2 ALUMINIUM SUBSTITUTION

AA Sattar [23] studied the effect of Al content on lattice parameter, powder density, crystallite size, Curie temperature, and magnetic properties. Experimental results revealed that the lattice constant, powder density, and crystallite size decrease linearly with the increasing Al content in  $\text{Li}_{0.5}\text{Fe}_{2.5}\text{Al}_x\text{O}_4$  samples. The saturation magnetization, remanent magnetization, Curie temperature, and coercive force decrease significantly with the increasing of Al content [24].

### 3.3 SILICON SUBSTITUTION

The substitution of Si increases the electrical resistivity and was explained as due to accumulation of silica on grain boundaries. There is a continuous decrease in Curie temperature with increase in silicon content and was explained due to the dilution of strength of the A–B interaction induced by silicon substitution [25]. The studies revealed that the grain size and  $M_s$  both increases up to silicon concentration and then decrease with further increase in concentration showing that the silicon substituted lithium ferrite samples exhibit a good potential, electromagnetic wave absorber material because of its low dielectric constant in the frequency range 1–16MHz in spite of its better magnetic properties compared to other substituted Li-ferrite material [6].

### 3.4 ZIRCONIUM SUBSTITUTION

The substitution of nonmagnetic  $\text{Zr}^{4+}$  ions in mixed Li-Zn ferrite leads to an increase in the saturation magnetization ( $M_s$ ) to a maximum value at concentration  $x=0.02$ , the behavior was explained using the cation distribution between (A) and [B] sites. The initial permeability ( $\mu_i$ ) at room temperature attains maximum value at Zr-concentration  $x=0.01$  whose behaviour was explained using Globus [26]. The values of coercivity ( $H_c$ ) and remanence ratio ( $B_r/B_s$ ) for the investigated samples reached a minimum at  $x=0.01$ . This change was explained using Brown's relation. It is found that increase of concentration of  $\text{Zr}^{4+}$  up to  $x=0.05$  has negligible effect on values of the lattice parameter and Curie temperatures. The dc electrical resistivity showed a gradual increase by about one order of magnitude.

### 3.5 ANTIMONY SUBSTITUTION

Evans and Swartzendruber studied Mössbauer effect under an external field of 50kG on  $\text{Sb}^{5+}$  substituted lithium ferrite [27]. They found B-site cation disorder not nearly effective as A-site cation disorder. In spite of the large concentration approximately 30% of diamagnetic ions on the B site, it results in collinear antiparallel Neel spin structure of the material. Dehe and Suwatsky [28] studied Mössbauer effect on Li-Sb ferrite at 4.2K with and without longitudinal magnetic field at 6T. The sample was found to have collinear Neel structure. The internal magnetic field at the nuclei of  $\text{Sb}^{5+}$  ion was observed to be high. The sample was then subjected to  $^{121}\text{Sb}$

Mössbauer study. The observed Mössbauer spectra showed unresolved magnetic splitting. This was explained as existence of small supertransferred hyperfine field interpreted in terms of indirect influence of B-site occupancy on the A-O-B transfer. Chongtham et al [14] investigated the dielectric behaviour of  $\text{Sb}^{5+}$  substitution on lithium ferrite and found that the dielectric constant decreases with substitution except for 0.15  $\text{Sb}^{5+}$  concentrations. Dispersion was observed for variation of loss tangent with frequency. The temperature variation showed anomalous peak [14].

#### IV. CONCLUSIONS

The effect on the various electrical and magnetic properties by substituting  $\text{Cr}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Si}^{4+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Sb}^{5+}$  on lithium ferrite based material has been reviewed. There occur changes in properties due to substitution. Hence the materials can be used for desired a specific application, which requires the changes properties.

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