



# Effect of Phases of $TiO_2$ and Li as Substituents on $Bafe_{12}O_{19}$ – a Comparative Study

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#### Abstract

The significant differences in the activity of iron oxide and titanium oxide make the investigations of the reactivity of Fe-Ti-O mixed oxides interesting and significant insight could be obtained by studying the interplay of different parameters like doping, iron content, phase compositions on the reactivity of these mixed oxides. A hexaferrite system in which Li and Ti are substituted in such a manner so as to have barium enriched and barium deficient and yet charge balanced hexaferrites, has been successfully synthesized and electrically and magnetically characterized. The synthesis is carried out by taking both allotropes of TiO<sub>2</sub> namely anatase and rutile to see the effect of edge sharing nature of the rutile and vertices sharing of anatase on the physical properties of the samples. Samples of hexaferrites  $Ba_{0.844}Ti_{3.378}Fe_{7.2}Li_{1.266}O_{19}$  and  $Ba_{1.266}Ti_{2.956}Fe_{7.6}Li_{0.844}$  $O_{19}$  are synthesized by mixing  $BaCO_3$ ,  $Fe_2O_3$ ,  $Li_2CO_3$  and anatase/ rutile TiO<sub>2</sub> in such a manner to maintain the charge balance. For reference pure samples  $BaFe_{12}O_{19}$  were also synthesized under similar step sintering conditions. The variation of different structural, electrical and magnetic parameters of the hexaferrite samples with variation in Li/Ti/Ba contents respectively is discussed in the paper.

Keywords: Hexaferrites, Curie temperature, Magnetoplumbic

#### Introduction

Barium ferrite particles media is considered a promising material for high density magnetic recording [1] and a lot of work has been done to tailor their magnetic characteristics by substitution of  $Fe^{+3}$  cations with other diamagnetic and paramagnetic cations. Significant variations in magnetic properties have been reported in Bi, Zn doped BaFe<sub>12</sub>O<sub>19</sub> [2,3]. Co-Ti substituted BaFe<sub>12</sub>O<sub>19</sub> particles have led to archivally stable media for magnetic recording [4]. The magnetic behavior of the hexaferrites has been explained in the light of interactions among the ions occupying their five crystallographic sites [5]. The role of Lithium in Lithium ferrite has led to attractive electric and magnetic properties for microwave and memory core applications [6]. The coupled substitution of Ti<sup>4+</sup> and Li<sup>+</sup> for Fe<sup>3+</sup> is reported in pseudobrookites [7] and spinels [8]. The bulk properties of anatase and rutile allotropes of TiO<sub>2</sub> are quite different due to vertex and edge sharing in the respective phase. Variations in the structural and electrical properties have been reported in mixed oxide systems using anatase and rutile TiO<sub>2</sub> [9]. A study of phase equilibria in the BaO:Fe<sub>2</sub>O<sub>3</sub>:TiO<sub>2</sub> system has revealed the existence of number of ternary compound that form between high dielectric constant polytitanates and magnetic barium hexaferrite having properties in





wide variety electronic applications [10]. The above mentioned considerations have prompted us to study the influence of the substitution of titanium and lithium on the properties of barium ferrite.

#### Materials and methods

The hexaferrites were prepared by usual high-temperature solid-state technique by mixing homogeneously AR grade powders of BaCO<sub>3</sub> Fe<sub>2</sub>O<sub>3</sub> Li<sub>2</sub>CO<sub>3</sub> and anatase / rutile TiO<sub>2</sub> and using step sintering for 6 hours each at 600 °C, 800 °C and 1000 °C and final sintering at 1150 °C for 24 hrs to ensure decomposition of carbonates and a homogeneous reaction.  $BaFe_{12}O_{19}$  was also synthesized in the same manner to facilitate comparison. The hexaferrites  $Ba_{0.844}Ti_{3.378}Fe_{7.2}Li_{1.266}O_{19}$  and  $Ba_{1,266}Ti_{2,956}Fe_{7,6}Li_{0,844}$   $O_{19}$  maintain the charge balance and therefore are cation deficient. The XRD patterns for the samples were obtained using a highly sophisticated microprocessor based JEOL-JDX 8030 diffractometer using a copper target. The IR spectra of the compounds were recorded on the Nicollet Instrument corporation, USA MAGNA 550 Spectro Photometer at room temperature, in the range of 50 to 4000 cm<sup>-1</sup>. Fine coat ion sputter JFC-1100 and JSM-840 Jeol Scanning Microscope were used to obtain the SEMs. For dielectric measurements, the samples were polished to obtain flat, smooth and parallel surfaces. The two surfaces were electrode with high purity ultra fine silver paste by firing at 500° C for 5 minutes. The dielectric properties were studied in the temperature range 300-650 K at 100Hz and 1 kHz using Aplab4910 auto compute LCR-Q meter. The variation in capacitance(C) and loss factor (tan delta) with the frequency range 10 kHz to 1000 kHz was also recorded at room temperature using a HP 4277 ALCZ LCR meter. The dc resistivity at room temperature and the ac resistivity (1kHz) in the temperature range 300-838 K were determined by two-probe method using the same electrode system that was used in dielectric studies. Magnetic properties were obtained using Hysteresis loop tracer and susceptibility apparatus.

#### **Results and discussion**

Pure barium ferrite sample exhibits magnetoplumbic structure with space group P63/mmc [11]. The SEM of barium ferrite indicates low crystallanity which is also reflected in the XRD pattern. The synthesized Barium ferrite sample is a hard ferrite with single domain features. Its Curie point is close to the reported value of 750 K. The saturation magnetization Ms our polycrystalline sample is equal to 35 emu/g which is lower than some of the reported values of 55 emu/g and 72 emu/g. The variation in the values is observed since orientation, surface and inhomogeneity of particle and preparation method affect Ms, Mr/Ms and Hc [12,13]. ]. The FTIR spectrum corresponding to BFO shows two sharp bands around 587cm<sup>-1</sup> and 436 cm<sup>-1</sup> agreeing well with reported values of 582 and 432 respectively . These bands correspond to the lattice vibration of the oxide ions against the cations .

Table 1: Variation in coefficient of correlation with respect to content of Li/Fe/Ti for various parameters





	Coefficient of correlation ( $\gamma$ ) with variation in		
Parameter	Li content	Ti content	Fe content
Particle size	0.80	0.97	- 0.73
Grain size	0.96	0.87	- 0.78
Density	- 0.88	- 0.79	0.70
Resistivity	- 0.89	- 0.77	0.67
Нс	0.97	0.99	0.98
Mr	- 0.99	0.97	0.92
Ms	- 0.99	- 0.97	0.92
Mr / Ms	- 0.89	- 0.78	0.68
Curie temperature	- 0.94	- 0.99	0.98



Figure 1: Variation of particle size with change in(a) Li content(b) Ti content(c) Fe content











All the substituted ferrites also exhibit magnetoplumbic structure, a magnetic ordering & have single domain grains[14,15]. They exhibit the properties of soft ferrites. There magnetic properties viz. Ms, Mr, Hc, the hysteresis loop area as well as Curie temperature Tc decrease with increasing Li & Ti [16] and decreasing Fe substitution. Unlike soft ferrites such as spinels, magnetic susceptibility decreases slowly with increase in temperature after transition.











Figure 7: Variation of saturation magnetization Mswith change in :(a) Li content(b) Ti content(c) Fe content











A peak is noticed at the magnetic transition for all the samples. This peak indicates single domain state [14]. Grain size ( $< 1\mu$ m) of all the samples also support single domains [15]. The values of Ms, Mr and Hc are slightly more for the rutile allotrope based sample as compared to their anatase counterparts for the same stiochiometry. The magnetic transition Trends are seen very clearly in which the difference between the two band frequencies decreases more rapidly as Fe content decreases is also sharper at Curie temperature for the rutile based allotropes as compared to the anatase based samples. FTIR spectra corresponding to all the substituted samples show two bands around 587cm<sup>-1</sup> and 436 cm<sup>-1</sup> positions of which agree well with those observed for BFO. These bands correspond to the lattice vibration of the oxides ions against the cations . The bands in the substituted samples are broadened because of the random distribution of (Ba<sup>2+</sup>, Li<sup>1+</sup>, Ti<sup>4+</sup>) ions. As the Fe content decreases, the two bands come closer for both anatase and rutile samples implying a strong coupling which may be responsible for the significant growth in the grain / particle size .

The relaxation spectra of all the samples indicate that the spectra are of Maxwell –Wagner type implying presence of space charge. Heating and cooling cycles in the dielectric constant vs. temperature curves form a distinct loop for all the hexaferrites. The value of K' at room temperature is slightly more and space charge component and grain size are slightly less for rutile samples. The gain in K' for anatase samples is insignificant however tanð decreases considerably. The increase in relative intensities of the planes in the samples when compared with the most intense (114) plane with decreasing Fe content may be attributed to the fact that (114) plane is either occupied by Li or is vacant in the substituted samples. This is more significant in anatase based samples. The increase in the grain size & conductivity in anatase based samples. It is interesting to note that semiconducting behaviour commences at lower temperatures for the rutile allotrope based samples i.e. they have a smaller PTCR region. Activation energies seem to depend on site preference by Li and Ti & their distribution. Figures 1 to 9 shows the variation of different parameters of the hexaferrite samples with variation in Li/Ti/Ba contents respectively. The coefficient of correlation calculated for the various curves is recorded in Table 1.

#### Conclusion

Better values of coefficient of correlation ( $\gamma$ ) with variation in Lithium content suggests that lithium plays an equally important role in deciding the structural and electrical properties of the various samples. The magnetic properties are governed by all the cations. The a.c. resistivities and the corresponding dielectric constant at 1 kHz. follow opposite trends implying that space charge plays significant role in the conduction at low frequencies. The d.c. resistivity increases with decreasing grain size of the samples.



Overall the allotropes of  $TiO_2$  i.e. vertice sharing in anatase and edge sharing in rutile phase, site preferences and cation distribution all result in the variation in the properties of the hexaferrites. The strong variation observed in coercivity, saturation magnetization and Curie temperature with substitution and with two phases of  $TiO_2$  gives rise to the possibility of controlling these properties.

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