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Abstract- In order to study the effect of intercalation of LiAl on the cation distribution and properties of Fe_2TiO_5 , the samples are prepared by standard ceramic technique. The single-phase formation of the pseudobrookite is confirmed by XRD technique. The retention of amount and proportion of LiAl in the ceramics is confirmed by ICP technique. The ac and dc resistivity of the ceramic increases considerably whereas the interfacial contribution to the dielectric constant decreases by intercalation of LiAl. The experimental data of relaxation spectra, variation of dielectric constant and resistivity with temperature is analyzed and correlated. The magnetic hysteresis and susceptibility measurement shows that LiAl enhances the long range magnetic ordering. The proposed empirical model determines the cation distribution of the samples using lattice parameters.

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Effect of Intercalation of LiAI on Cation Distribution and Properties of Fe₂Tio₅

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Abstract- In order to study the effect of intercalation of LiAl on the cation distribution and properties of Fe_2TiO_5 , the samples are prepared by standard ceramic technique. The singlephase formation of the pseudobrookite is confirmed by XRD technique. The retention of amount and proportion of LiAl in the ceramics is confirmed by ICP technique. The ac and dc resistivity of the ceramic increases considerably whereas the interfacial contribution to the dielectric constant decreases by intercalation of LiAl. The experimental data of relaxation spectra, variation of dielectric constant and resistivity with temperature is analyzed and correlated. The magnetic hysteresis and susceptibility measurement shows that LiAl enhances the long range magnetic ordering. The proposed empirical model determines the cation distribution of the samples using lattice parameters.

I. INTRODUCTION

magnetic spinel establishes a long range magnetic ordering by linking its octahedral and tetrahedral sites. Lithium Ferrite and substitutions such as AI, Ti, Mn and Ge have been studied extensively for their magnetic structure [1], crystallographic orderdisorder [2, 3], provision of holes for Li⁺ ions [4], oxygen loss [5], curie temperature [6], sensitivity towards CO₂ [7], lithium diffusion coefficient [8] etc. A pseudobrookite (AB_2O_5) consists of two octahedral sites M₁ and M₂. One of them is larger and more distorted and connects the other through edge / corner sharing. The cations occupy 1 M1 and 2 M2 sites and large interstitial sites / voids equal to M1 site are vacant [9]. The crystal structure of Fe₂TiO₅was first determined by Pauling [10] only minor changes in it have since been reported [11,12,13]. The Ti⁴⁺ions prefer fairly regular octahedra [14]. On the other hand four of the six oxygen ions surrounding Fe³⁺ions are disposed almost tetrahedrally. On the basis of the cation distribution between two sites the compound is said to be ordered / disordered. Both the orthorhombic [15] and monoclinic [16] structures have been reported for Fe₂TiO₅. Hence it is thought possible to intercalate Fe₂TiO₅ by Li⁺ to incorporate the long range magnetic ordering.

II. Experimental

The samples are prepared by the standard ceramic technique and sintered at 1250°C for 24 hours.

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The single-phase formation of the pseudobrookite is confirmed by XRD technique. The mixture of Fe₂TiO₅ and $\text{LiAlH}_{\scriptscriptstyle\!\!A}$ powders is thoroughly mixed for 24 hours by magnetic stirring in the dry Benzene to avoid the contact of LiAlH₄ with moisture in the air. The samples Fe₂TiO₅, $Fe_2TiO_5 + (0.5)$ LiAl, $Fe_2TiO_5 + (1.0)$ LiAl are abbreviated as [FTR], [FTL₁R] and [FTL₂R] respectively. That Li⁺ do not vaporize during the heat treatment is confirmed by Inductively Coupled Plasma (ICP) technique. The samples are studied by X-ray diffractometry, Infrared spectroscopy, electric, dielectric and magnetic measurements.

III. Results and Discussion

a) Determination of Cation Distribution

The cation distribution in Fe₂TiO₅ and related compounds has been reportedly determined by using Reitveld Refinement technique [17-20]. It is observed that lattice parameters of these compounds depend on the cation distribution as also in other cases [9]. However, the magnitudes of the lattice parameters depend on the heat treatment, fineness and purity of the powder, etc. Therefore it is proposed to have a new model, which is dependent on the relative values of lattice parameters of the reported samples. As larger cation Li⁺enters M1 site and excess Li enters interstitial sites there is an expansion along 'c' and a contraction along 'a' and 'b'parameters [20] for the space group Bbmm. Hence a parameter (c/ab) is chosen to obtain the relationship between lattice parameters and cation distribution. Table 1 gives the values of parameter (c/ab) obtained from the reported data and the ratio q1/q2 of cationic charge distributions g1 and g2 on M_1 and M_2 sites respectively. The nonlinear relationship is observed between (c/ab) and (q_1/q_2) as shown in Figure 1. Cation distributions of the reported samples are shown in Table 1.

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Sample	Cation distribution	(c/ab)	q ₁ /q ₂	
R 1[17]	[Fe ₀ Ti _{1.0}] _{M1} [Fe _{2.0} Ti ₀] _{M2} O ₅	0.03683	1.3333	
R _{2 [18]}	[Fe _{0.67} Ti _{0.33}] _{M1} [Fe _{1.33} Ti _{0.67}] _{M2} O ₅	0.03818	0.9985	
R 3 [19]	[Fe _{0.88} Ti _{0.12}] _{M1} [Fe _{1.12} Ti _{0.88}] _{M2} O ₅	0.03824	0.9069	
R _{4 [20]}	{(Li) _{0.08} }[Fe _{0.69} Li _{0.31}] _{M1} [Fe _{0.57} Ti _{1.43}] _{M2} O ₅	0.03873	0.6406	
R _{5 [20]}	{(Li) _{0.11} }[Fe _{0.49} Li _{0.51}] _{M1} [Fe _{0.13} Ti _{1.87}] _{M2} O ₅	0.03909	0.5032	
R _{6 [20]}	{(Li) _{0.17} }[Fe _{0.16} Li _{0.64} Ti _{0.20}] _{M1} [Fe _{0.11} Ti _{1.89}] _{M2} O ₅	0.03933	0.4866	

Table 1 : Cation Distribution of the Reported samples obtained from the reported data.

$$q_1/q_2 = \{(2006.2) \ x^2 - (230.02) \ x + (8.7843)\}10^5 x - 11172.75$$

(3.1)

Where, x = c/ab

Before giving cation distribution of the samples under study it is felt necessary to locate the position of "(LiAl)^{4+"} in Fe₂TiO₅. It is observed from the XRD data that relative intensities of (040) plane passing through interstitials have increased (Table 3). This confirms that the "(LiAl)^{4+"} enters the interstitials of Fe₂TiO₅ may also be termed as the intercalation. Also the FTIR spectra

indicate that the absorption corresponding to M1 sites of "(LiAI)^{4+"}containing samples tends to equal the absorption corresponding to M2 site (Figure 2). Therefore applying empirical formula (3.1) to the XRD data in Table 2, the cation distribution of the samples under study is obtained as given in the Table 3.

Table 2 : Lattice parameters, (c/ab), Charge ratio (q1/q2), Avg. particle size and XRD density.

Sample	a (Å)	В (Å)	c (Å)	c/ab (Å) ⁻¹	q_1/q_2	Avg. particle size (Å)	XRD density g/cc
[FTR]	9.7780	9.9608	3.7262	0.03826	0.90	540	4.38
[FTL₁R]	9.7282	9.9253	3.7055	0.03838	0.83	338	5.02
[FTL₂R]	9.7547	9.9222	3.7162	0.03840	0.82	328	5.05

Table 3 : Relative % intensities of (040) plane and Cation Distribution of the samples.

Sample	Cation distribution obtain from the suggested Model	Relative % intensity of (040) plane
[FTR]	[Fe _{0.78} Ti _{0.22}] _{M1} [Fe _{1.22} Ti _{0.78}] _{M2} O ₅	1.6
[FTL₁R]	{(LiAl) _{0.5} } [Fe _{0.95} Ti _{0.05}] _{M1} [Fe _{1.05} Ti _{0.95}] _{M2} O ₅	45.2
[FTL₂R]	$\{(\text{LiAI})_{1,0}\}$ [Fe $_1$ Ti $_0$] _{M1} [Fe $_1$ Ti $_1$] M2 O5	52.9

b) Effect of LiAl on Dielectric Properties

i. Relaxation Spectra

In [FTR], the dielectric constant (K') decreases considerably with frequency (Table 4, Figure 3). Which indicates the presence of large quantity of space charge. The nature of this relaxation spectrum is similar to the two media model for the space charge [21]. The presence of a broad tan δ maximum (Figure 4) implies that the dielectric material has conducting ellipsoids (perhaps vacant interstitials) surrounded by an insulating material. In [[FTL₁R] and [FTL₂R] the quantity

of space charge is insignificant (Table 4, Figure 3) and the conducting medium is almost absent due to the intercalation of "(LiAl)^{4+"}.

ii. Variation of Dielectric Constant with Temperature

Variation of K' with temperature (300-850 K) at 1kHz is investigated as shown in the Figures5-7. For the samples [FTL₁R] and [FTL₂R] the dielectric constant K' first decreases from 300K to 350Kand after 350K, A loop is observed in the temperature range in which the microcrack healing is reported. The loop areas are larger corresponding to the intercalated samples.

d) Electrical Transport Properties

Table 4 : Restivities, activation energies, band gaps and dielectric constants at room temperature.

Sample	pac at 1 kHz	pdc (MΩm)	Activation Energy at	Band Gap	Dielectric constant (K') at			
	(KΩm)		high temp. (eV)	(eV)	1 KHz	10 KHz	100 KHz	1000 KHz
[FTR]	5.5	6.6	0.75	1.50	3407	1484	339	75.8
[FTL ₁ R]	19.3	10.4	0.80	1.60	887	169	69	43.2
[FTL ₂ R]	15.2	10.7	0.83	1.66	897	192	74	46.4

The room temperature resistivities have increased considerably with intercalation of "(LiAl)^{4+"} this is due to lowering of space charge. The variation of a.c. resistivity (1kHz) with temperature is measured (300-850K) for all the samples and is shown in the Figures 8-10. From 300K to approximately 350K the curve shows PTCR effect for LiAl containing samples. Above 350K all the curves show two distinct activation energies. The activation energy at high temperature corresponds to the band gap (Table 4). The band gaps are larger corresponding to the intercalated samples.

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d) Magnetic Properties

From the shape of hysteresis curves (Figures11, 12) the samples [FTL₁R] and [FTL₂R] may have long range magnetic ordering [22-25] of super paramagnetic (S.P.) type, however the magnetic moment is small. The magnetic susceptibility is not detected in [FTR]. The susceptibility Vs temperature plots corresponding to samples [FTL₁R] and [FTL₂R] are shown in Figures 13,14. The curie temperature (~74°C) is not well defined, which implies the co-existence of multiple curie temperatures. This may be due to the distribution of strength of exchange interaction, which reduces the space charge considerably. At curie temperature the exchange interaction vanishes and the space charge minimizes. The magnetic transition is well depicted as a dip in dielectric constant (Figures 6, 7) and the end of PTCR region (Figures 9, 10) at around 350K.

IV. Conclusions

The space charge and therefore Dielectric constant is considerably less for LiAl containing samples. The ac and dc resistivities increased with intercalation of LiAl. The energy band gaps increased with intercalation of LiAl. The PTCR effect is observed in LiAl containing samples. The magnetic transition is well depicted as a dip in dielectric constant and the end of PTCR region at around 350K. In LiAl containing samples long range magnetic ordering of super paramagnetic type is observed, however the magnetic moment is small.

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Figure 8 : The variation of a.c. resistivity with temperature of sample [FTR].









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Magnetic Field Strength (Oe)x 103





Magnetic Field Strength (Oe)x 10³

Figure 12 : The magnetic hysteresis of sample $[FTL_2R]$.



Figure 13 : The variation of magnetic susceptibility with temperature of sample[FTL₁R].



Figure 14 : The variation of magnetic susceptibility with temperature of sample [FTL₂R].

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