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Influence of Intercalation on Dielectric Behaviour of Pseudobrookites

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Abstract: In order to study the influence of intercalation of LiAl on the dielectric behavior of Fe_2TiO_5 pseudobrookites, 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.

Keywords: Intercalation, dielectric constant, relaxation spectra, Pseudobrookite.

1 INTRODUCTION:

Mossbauer studies with and without applied field have been performed on $\text{LiFe}_x\text{Al}_{5-x}\text{O}_8$ ferrite system and a canted structure is demonstrated [1]. The crystal chemistry and phase relations in the system $\text{Li}_2\text{O}-\text{Fe}_2\text{O}_3-\text{TiO}_2$ have been studied by Yu-Chyi Yau et al. [2]. They have concluded that above 755 °C, compounds along the spinel join $\text{LiFe}_5\text{O}_8-\text{Li}_4\text{Ti}_5\text{O}_{12}$ form a complete solid solution (s. s.) and below that temperature a two phase region separates the ordered LiFe_5O_8 and the disordered spinel phase. The phase equilibria in $\text{Li}_2\text{O}-\text{Fe}_2\text{O}_3-\text{TiO}_2$ system have been studied by I. E. Grey et al. [3]. The pseudobrookite showed deviation from M_3O_5 stoichiometry towards metal-rich compositions which increased with increasing substitution of $\text{Li}^{1+}+\text{Ti}^{4+}$ for Fe^{3+} , from Fe_2TiO_5 to $\text{Li}_{0.81}\text{Fe}_{0.27}\text{Ti}_{2.09}\text{O}_5$ ($=\text{M}_{3.17}\text{O}_5$). Titanium is ordered in the eight fold M2 / (8f) site while lithium together with minor iron and titanium is ordered in the four fold M1 / (4c) site. The excess lithium (0.17 per formula unit) is located in interstitial sites in the structure, having square pyramidal coordination and implies the $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ reduction and oxygen deficiency.

From the single crystal refinement of Fe_2TiO_5 , Tiedemann and Muller-Buschbaum [4] have reported a statistical distribution of $2/3\text{Fe} + 1/3\text{Ti}$ in M1 and M2 sites and they have concluded that the polyhedral distortion of the M1 site of Fe_2TiO_5 is more than that of M2 site and the volume of the interstices associated with M1 site is very large.

Therefore, M1 site is capable of accommodating cations of large size and the interstices are large enough to intercalate the excess of cations.

The system $\text{LiFeO}_2\text{-Fe}_2\text{O}_3$ has been studied by Stickler and Roy [6]. They have found a cubic form of LiFe_5O_8 which exists stably from 500°C to at least 1400°C . The spinel LiFe_5O_8 is also found to have a crystallographic order-disorder transition at 735 to 755°C .

Roth et al. [7] have described the structure of $\text{Li}_2\text{Ti}_3\text{O}_7$ as related to the rutile structure by having octahedral rearranged to provide holes for Li^+ ions. Effects of Li^+ losses and oxygen losses on magnetic and crystallographic properties of spinel lithium ferrite have been investigated by D. H. Ridgley et al. [8]. They found that magnetic moments and lattice parameters increased with increasing sintering temperature.

Hence it is thought possible to intercalate " $(\text{LiAl})^{4+}$ " in Fe_2TiO_5 to incorporate some new properties. In the present work the systematic investigation of these properties of pseudobrookite [FTR] prepared from rutile phase of TiO_2 is made and its properties are compared with those of " $(\text{LiAl})^{4+}$ " intercalated samples [FTL₁R] and [FTL₂R]. All the samples are sintered at 1250°C .

2 RESULTS AND DISCUSSION:

It is interesting to note that the intercalation has resulted into the increase in the inhomogeneity and porosity and the decrease in Debye particle size. The increased inhomogeneity implies the increased stress which perhaps increases porosity and decreases the particle size.

2.1 DETERMINATION OF CATION DISTRIBUTION:

Applying an empirical formula (IV.1) proposed in Chapter-IV of the Ph.D. thesis [13] to the XRD data, the cation distributions for the samples are obtained as given in the Table .1. It is interesting to note that sample [FTR] is tending towards inverse ordered structure $[\text{Fe}_1]_{\text{M1}} [\text{Fe}_1 \text{Ti}_1]_{\text{M2}} \text{O}_5$ and intercalation of " $(\text{LiAl})^{4+}$ " helps to achieve it. The cation distribution shows that as the content of " $(\text{LiAl})^{4+}$ " increases the content of Fe^{3+} on the M2 site decreases.

This appears to increase the symmetry of the structure and correspondingly the unit cell volume decreases. The ordering of the structure depends on the lower tetrahedral symmetry associated with Fe^{3+} in the octahedral site.

Table .1: Cation Distribution, Lattice parameters, (c/ab) and Charge ratio (q1/q2) for the samples.

Sample	Cation distribution	a (Å)	b (Å)	c (Å)	(c/ab) (Å) ⁻¹	q1/q2
[FTR]	$[Fe_{0.78} Ti_{0.22}]_{M1} [Fe_{1.22} Ti_{0.78}]_{M2} O_5$	9.7780	9.9608	3.7262	0.03826	0.95
[FTL ₁ R]	$\{(LiAl)_{0.5}\} [Fe_{0.95} Ti_{0.05}]_{M1} [Fe_{1.05} Ti_{0.95}]_{M2} O_5$	9.7282	9.9253	3.7055	0.03838	0.87
[FTL ₂ R]	$\{(LiAl)_{1.0}\} [Fe_1 Ti_0]_{M1} [Fe_1 Ti_1]_{M2} O_5$	9.7547	9.9222	3.7162	0.03840	0.86

Therefore, an order parameter corresponding to the lower tetrahedral symmetry is defined as, "Order Parameter λ " = Amount of Fe^{3+} on M2 site – Amount of Fe^{3+} on M1 site. But it is observed that, when amount of Fe^{3+} on M2 site = 1.5 and that of Fe^{3+} on M1 site = 0.5, the structure is fully symmetric ($\lambda_0 = 1$). Therefore, the "Order Parameter λ' " is redefined as

$$\lambda' = (\lambda - \lambda_0)^2$$

The order parameter corresponding to the *inverse ordered* cation distribution $[Fe_1]_{M1} [Fe_1 Ti_1]_{M2} O_5$ is $\lambda' = 1$. Interestingly, Debye particle size, practical density and volume decrease whereas the inhomogeneity, theoretical density and porosity increase with the order parameter λ' .

2.2: The Fourier Transform InfraRed Spectra:

The FTIR spectra of these samples exhibit two nearby bands of frequencies $\square 1$ (630- 690 cm^{-1}) and $\square 2$ (430- 510 cm^{-1}) which correspond to the octahedral M1 and M2 sites [5] respectively (Figure .1 and Table.2). The number of M2 sites is twice that of M1 sites. This means the number of dipoles is more on M2 sites and therefore the IR-band corresponding to M2 site is more intense as expected.

It is interesting to note that the intercalation of "(LiAl)⁴⁺" decreases the frequency ν_1 . This may be due to Fe³⁺ → Fe²⁺ reduction caused by the intercalation whereas, this shifts the frequency ν_2 to the high frequency side.

It is also interesting to note that the separation between two frequencies (ν_1 - ν_2) corresponding to M1 and M2 octahedral sites is less for "(LiAl)⁴⁺" intercalated samples (Table. 2). It implies a stronger link between the M1 and M2 sites perhaps due to the affinity of Li⁺ in the interstices adjacent to M1 site and Fe³⁺ on the M2 site.

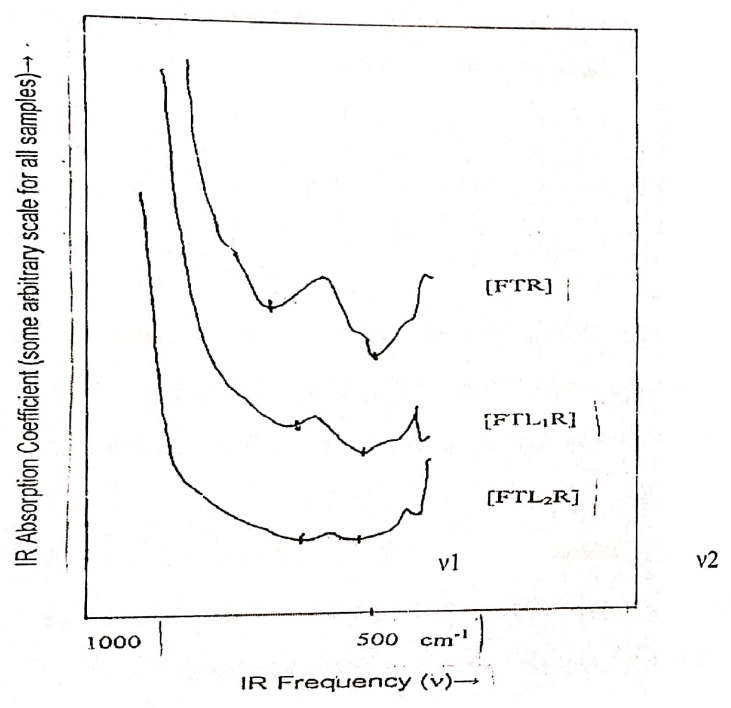


Figure. 1: IR-Spectra for the samples.

Table.2: Assignment of two major bands of frequencies

Bands	Frequency for the sample (cm ⁻¹)			Possible octahedral assignment
	[FTR]	[FTL ₁ R]	[FTL ₂ R]	
ν_1	690	638	630	M1

2.3: DIELECTRIC PROPERTIES:

Table.3: Unit cell volume V, Porosity, Inhomogeneity, Debye Particle size, Order parameter, Loop area of Dielectric hysteresis, Dielectric Constants at various frequencies at room temperature.

Sample	V (Å) ³	Porosity	Inhomogeneity	Debye Particle Size (Å)	Order parameter λ'	Loop area of K' hysteresis (Sq. Units)	Space Charge K' _{1kHz} -K' _{1MHz}	Dielectric constant (K') at			
								1 kHz	10 kHz	100 kHz	1000 kHz
[FTR]	362.9	0.088	-0.002	540	0.31	3.02	3331	3407	1484	339	75.8
[FTL ₁ R]	357.8	0.234	-0.005	338	0.81	0.76	843.8	887	169	69	43.2
[FTL ₂ R]	359.7	0.319	-0.004	328	1.00	1.16	850.6	897	192	74	46.4

The values of the room temperature Dielectric constant K' measured at different frequencies are reproduced in Table. 3. It is observed that both the contributions due to the space charge (K'_{1 kHz} - K'_{1000kHz}) and the dipolar polarization (K'_{1000kHz}) are decreased considerably by the intercalation.

This is because LiAlH₄ being a reducing agent may have reduced Fe³⁺ to Fe²⁺ totally after intercalation, leaving no scope for Fe³⁺ ↔ Fe²⁺ space charge to form. The decrease in the space charge in the intercalated samples is also reflected by the corresponding increase in their porosity, inhomogeneity and decrease in their particle size. The possibility of oxidation may turn these materials into the gas / pressure sensitive ones.

2.4: Relaxation Spectra:

In order to obtain more information about the space charge the relaxation spectra of the samples are also investigated. The plots (i) K' v/s log (frequency) and (ii) K'' v/s log (frequency) and (iii) tan (δ) Vs log (frequency), known as relaxation spectra of the samples are given in Figures .2 to 4 respectively. The nature of the curves is similar to that shown by Maxwell-Wagner model for the space charge [14].

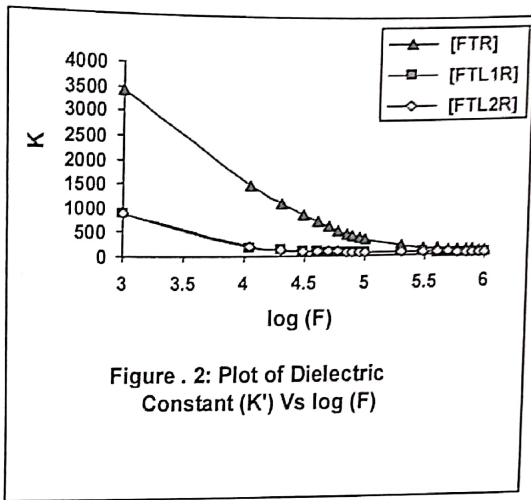


Figure . 2: Plot of Dielectric Constant (K') Vs $\log(F)$

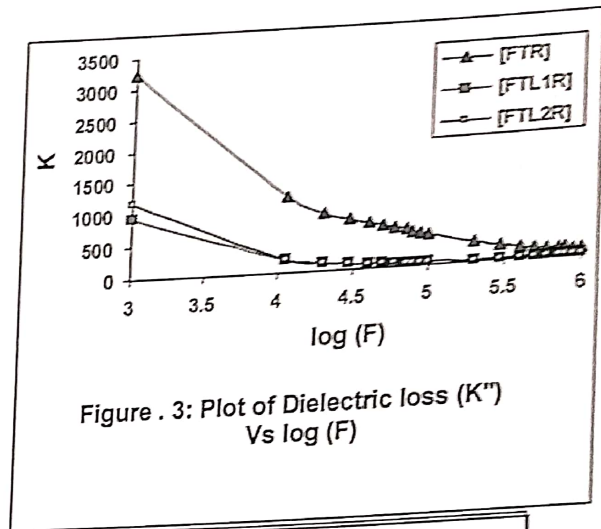


Figure . 3: Plot of Dielectric loss (K'') Vs $\log(F)$

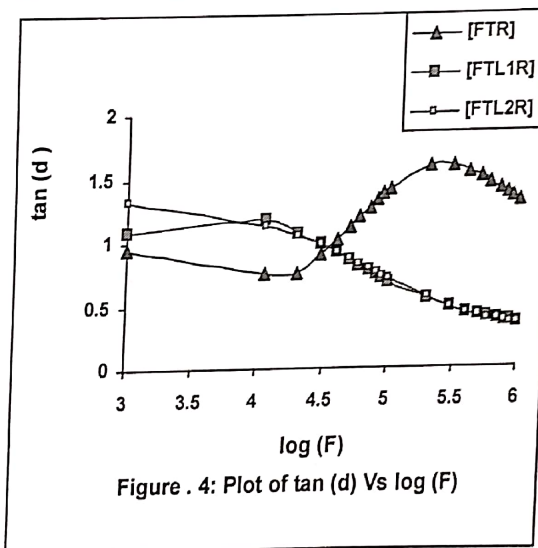


Figure . 4: Plot of $\tan(\delta)$ Vs $\log(F)$

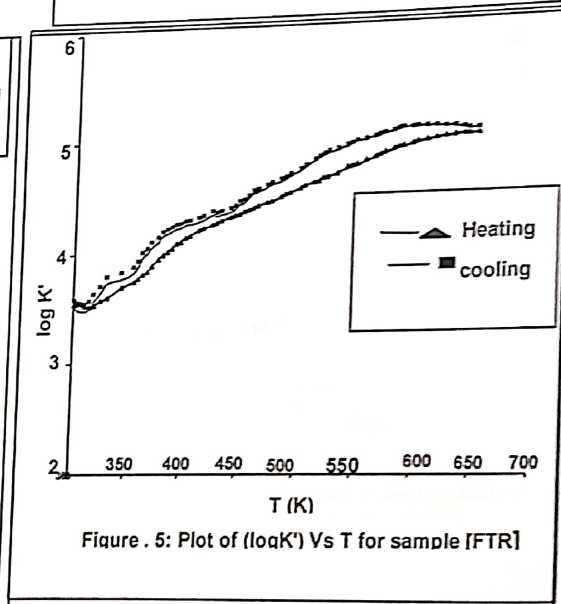


Figure . 5: Plot of $(\log K')$ Vs T for sample [FTR]

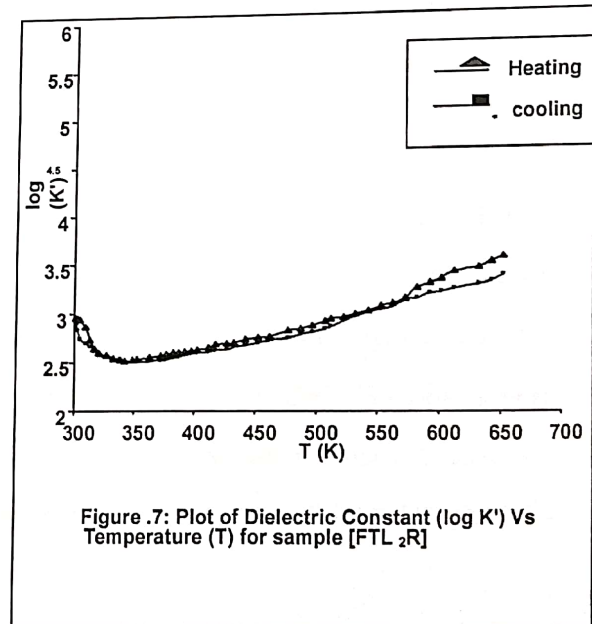
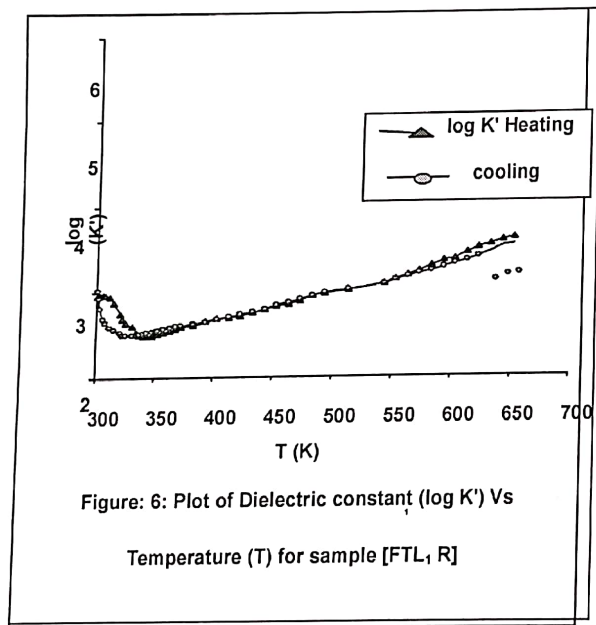
In [FTR] the presence of a broad $\tan(\delta)$ maximum (Figure. 4) implies that the dielectric material has conducting ellipsoids (perhaps vacant interstices) surrounded by an insulating material. In [[FTL₁R] and [FTL₂R] the quantity of space charge is insignificant (Table.3,Figure.4) and the conducting medium is almost absent due to the intercalation of“(LiAl)⁴⁺”.

2.5: Variation of Dielectric Constant with Temperature:

The variation of dielectric constant (K') with temperature (300-650 K) at 1 kHz is investigated and the curves for [FTR], [FTL₁R] and [FTL₂R] are reproduced in the Figures 5 to 7 respectively. For the samples [FTL₁R] and [FTL₂R] the dielectric constant (K') first decreases from 300 K to 350 K and after 350 K it increases with

temperature. The intercalated samples have perhaps caused the reduction of Fe_2TiO_5 to Fe_2TiO_4 (a spinel) which on heating above room temperature regains oxygen and dielectric constant starts decreasing. This gives a hint of existence of magnetic ordering in $[\text{FTL}_1\text{R}]$ and $[\text{FTL}_2\text{R}]$.

A large dielectric hysteresis is observed for $[\text{FTR}]$ corresponds to the appearance and disappearance of microcracks [15] whereas the samples $[\text{FTL}_1\text{R}]$ and $[\text{FTL}_2\text{R}]$ exhibit antihystereses. The loop areas (Table.3) for these intercalated samples are far less. Both the loop area and the space charge decrease as the order parameter λ' increases, once again underlining the importance of the cation distribution.



2.6: ELECTRICAL PROPERTIES: The a. c. resistivities at room temperature have increased considerably on intercalation of " $(\text{LiAl})^{4+}$ ". Also it is observed that the d. c. resistivities at room temperature are larger in the intercalated samples (Table. 4). The complementary dependence between the resistivities and the space charge means the conduction is mainly from the space charge.

Table 4: Order parameter, loop area of (ρ_{ac}) hysteresis, Space charge, Inhomogeneity, d. c. and a. c. Resistivities at room temperature, Transition temperatures, Activation energies and Band gap for the samples.

Sample	Order parameter λ'	Loop area of ρ_{ac} hysteresis (Sq. Units)	Space Charge K'_{1kHz} - K'_{1MHz}	Inhomogeneity	ρ_{dc} (K Ω m)	ρ_{ac} (1kHz) K Ω m	Transition temperature (K)		Activation Energy (eV)			Band gap (eV) (550-650)
							T ₁	T ₂	Ea ₁ (400-550)	Ea ₂ (550-650)	Ea ₃ (650-850)	
[FTR]	0.31	1.17	3331	-0.002	6565	5.5	400	710	0.14	0.38	0.73	0.76
[FTL ₁ R]	0.81	1.65	843.8	-0.005	10373	19.3	550	650	0.25	0.62	0.57	1.24
[FTL ₂ R]	1.00	2.25	850.6	-0.004	10701	15.2	540	640	0.28	0.91	0.36	1.82

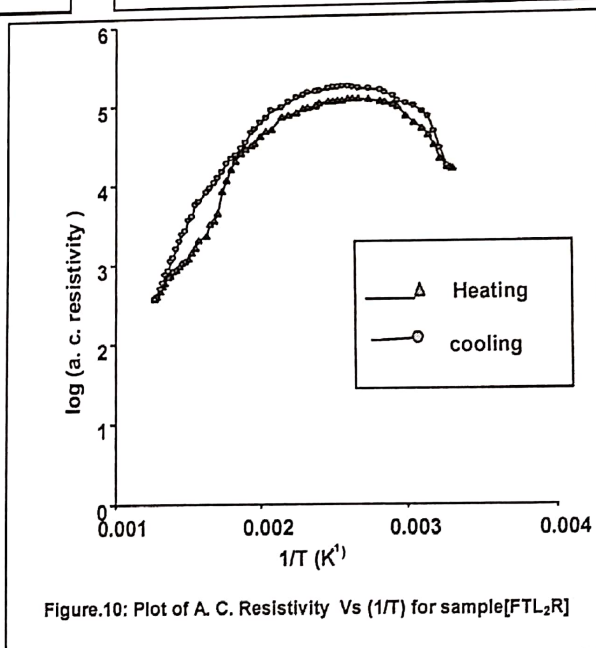
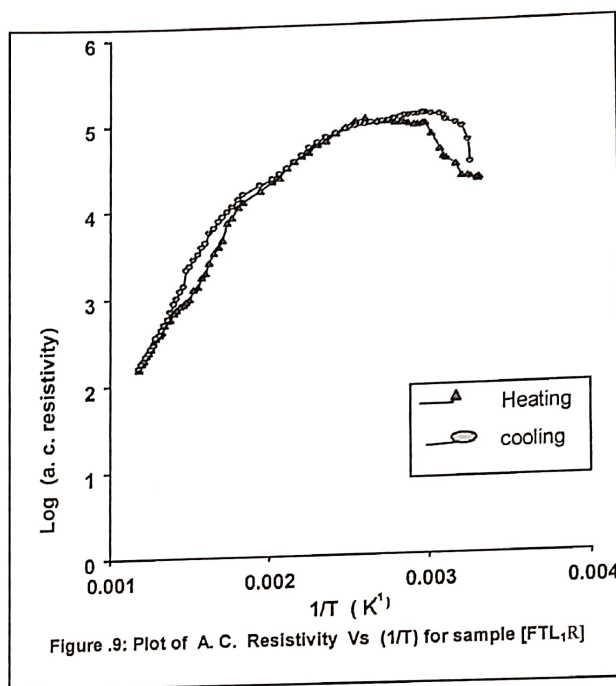
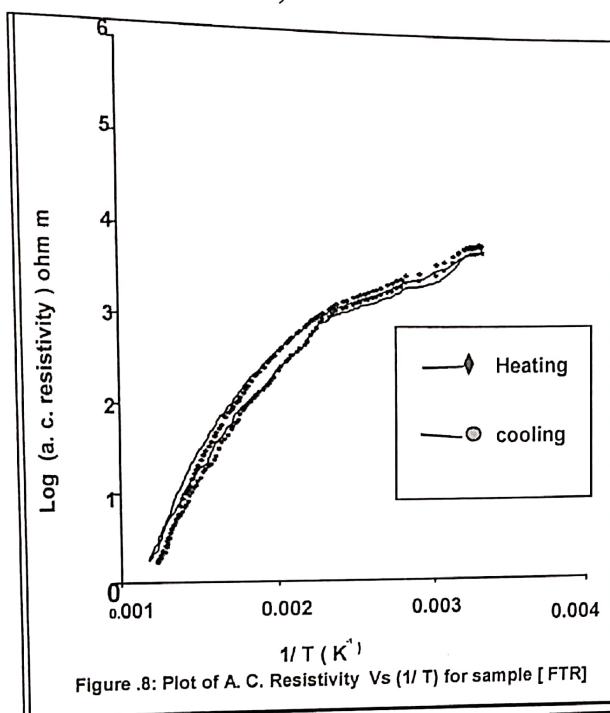
2.7: Variation of a.c. resistivity (1 kHz) with temperature:

The variation of a.c. resistivity (1 kHz) with temperature (300-850 K) is measured for the samples [FTR], [FTL₁R] and [FTL₂R] and is reproduced as plot of log (ρ_{ac}) Vs 1/T in the Figures .8 to 10 respectively.

From 300 K to approximately 350 K the curves show a Positive Temperature Coefficient of Resistance (PTCR) effect [16] i.e. increase in resistivities for “(LiAl)⁴⁺” containing samples [FTL₁R] and [FTL₂R]. In this temperature region the dielectric constant decreases which means presence of space charge. Above 350 K these curves show two transition temperatures T₁ (400-550 K) attributed to extrinsic-intrinsic transition and T₂ (650-710 K) attributed to antiferro-paramagnetic transition [17] and hence three distinct activation energies are observed and are shown (Table. 4) as (Ea₁), (Ea₂) and (Ea₃) corresponding to the temperature regions (i) 400- 550 K, (ii) 550- 650 K and (iii) 650- 850 K respectively.

The activation energy (Ea₂) of the intrinsic region corresponds to the band gap (= 2 Ea₂). The energy band gaps are much larger for the intercalated samples. The loop area of (ρ_{ac}) hysteresis increases with the content of “(LiAl)⁴⁺” implying the increase in the width of microcracks.

It is interesting to note that the samples [FTL₁R] and [FTL₂R] exhibit antihystereses and Ea₃< Ea₂ for these samples. Hence we may conclude that that these antihystereses are due to tunneling effect [18].



2.8: Location of LiAl in Fe₂TiO₅:

It is interesting to note that certain reflections corresponding to the pseudobrookite phase become increasingly stronger as the content of “(LiAl)⁴⁺” increases (Table. 5). Many of them exist in Fe₂TiO₅ as weak reflections. Inter-planer distance, Miller indices and relative percentage intensities of these reflections match closely with those of spinel phase as indicated in Table.5. However, the densities of all the samples are small (around 3.5 g / cc). Hence, the formation of highly denser spinels such as Li Fe₃O₈ or Fe₂TiO₄ as an additional phase seems unlikely.

Hence it may be concluded that there exists a spinel like network within the pseudobrookite phase and gets increasingly ordered and stronger with the $(LiAl)^{IV}$ content.

Also, as has been observed from the XRD data that relative intensities of (040) plane passing through interstices have increased. This confirms that the $(LiAl)^{IV}$ enters the interstices of Fe_2TiO_5 . It is termed as the intercalation of the pseudobrookite.

This is quite possible here because of bipyramidal geometry of interstices which have very large volume and adjacent to M1 sites [4]. It is similar to occupancy of vacant octahedral sites in spinels by excess of lithium [2, 6].

Table.5: XRD Data Showing Reflections Corresponding to Spinel Phase in Pseudobrookite Phase.

For pseudobrookite phase (Å)				d_{obs}	Relative Percentage intensity			For spinel phase d_{ref} (Å)		
[FTR]	[FTL ₁ R]	[FTL ₂ R]	hkl		[FTR]	[FTL ₁ R]	[FTL ₂ R]	hkl	[FTR]	[FTL ₁ R]
2.8502	2.9096	2.8990	121	6.4	9.67	21.6	220	2.9154	2.9054	2.8974
2.4866	2.4777	2.4709	040	1.6	45.22	52.9	111	2.4866	2.4777	2.4709
-	2.0556	2.0483	141	-	9.16	12.1	400	-	2.0544	2.0487
1.6618	1.6536	1.6551	(060)	14	15.41	16.4	224	1.6834	1.6774	1.6728
-	1.4542	1.4478	630	-	14.1	54.4	440	-	1.4527	1.4487

3: CONCLUSIONS:

It is observed from the XRD data that relative intensity of (040) plane passing through interstices increases from 1.6 in [FTR] to 45.22 in [FTL₁R] and 52.9 in [FTL₂R]. Thus $(LiAl)^{IV}$ appears to enter the interstices of Fe_2TiO_5 . It is termed as the intercalation of $(LiAl)^{IV}$.

It is interesting to note that the intercalation has resulted into the increase in the inhomogeneity and porosity and the decrease in Debye particle size. The increased inhomogeneity implies the increased stress which perhaps increases porosity and decreases the particle size.

It is observed from the values of the room temperature Dielectric constant (K') measured at different frequencies that both the contributions due to the space charge (K'_{sc} and K'_{intra}) and the dipolar polarization

($K'_{1000\text{Hz}}$) are decreased considerably by the intercalation. This is because LiAlH_4 being a reducing agent may have reduced Fe^{3+} to Fe^{2+} totally after intercalation, leaving no scope for $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$ space charge to form.

From the variation of dielectric constant (K') with temperature (300-650 K) at 1 kHz it is concluded that the intercalated samples have perhaps caused the reduction of Fe_2TiO_5 to Fe_2TiO_4 (a spinel) which on heating above room temperature regains oxygen and dielectric constant starts decreasing. A large dielectric hysteresis observed for [FTR] corresponds to the appearance and disappearance of microcracks. [FTL₁R] and [FTL₂R] exhibit antihystereses. The loop areas for the intercalated samples are far less. Both the loop area and the space charge decrease as the order parameter λ' increases, once again underlining the importance of the cation distribution.

The loop area of (ρ_{ac}) hysteresis increases with the content of " $(\text{LiAl})^{4+}$ " implying the increase in the width of microcracks. It is interesting to note that the samples [FTL₁R] and [FTL₂R] exhibit antihystereses and $E_{a3} < E_{a2}$ for these samples. Hence we may conclude that these antihystereses are due to tunneling effect.

It is interesting to note that certain reflections corresponding to the pseudobrookite phase become increasingly stronger as the content of " $(\text{LiAl})^{4+}$ " increases. Inter-planer distance, Miller indices and relative percentage intensities of these reflections match closely with those of spinel phase.

Hence it may be concluded that there exists a spinel like network within the pseudobrookite phase and gets increasingly ordered and stronger with the " $(\text{LiAl})^{4+}$ " content.

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