Investigation of Effect of Lial Intercalation and Tin Substitution on Magnetic Properties of Fe_2TiO_5

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Abstract—**The association of tin with lithium is found to be advantageous in lithium-ion rechargeable batteries. The Substitution of titanium by tin in Fe_2TiO_5 enhances the dielectric properties. The polycrystalline pseudobrookite exhibits many interesting properties such as spin glass behaviour, thermal microcracking, magnetic texture, high resistivity and has wide range of applications.This communication presents the characterization of LiAl intercalated and Tin containing iron titanates prepared by using rutile titanium oxide and sintered at 1250^0C. The iron titanates are synthesized by usual standard ceramic technique using A.R. grade oxides. The single-phase formation is confirmed by XRD and FTIR techniques. Structurally all the samples remain pseudobrookite having orthorhombic unit cell. It is observed from the XRD data that the relative intensities of (040) plane passing through interstices have increased. That there is no loss of either Li^{1+} or Al^{3+} is confirmed by the Inductively Coupled Plasma (ICP) and XRF technique. The magnetic hysteresis data for one of the samples shows that it is a soft ferrite. The Curie temperature of this sample is (Tc = 602 K).**

Index Terms—**Pseudobrookite, Intercalation, Tin Substitution, Iron Titanate.**

I. INTRODUCTION:

Tin alloys extensively with lithium to form alloys of the form $Li_{22}Sn_5$ [1], which gives rise to anode material of high theoretical capacity of 991mAh/g.The reversible reaction of lithium with tin can be given by [2]

$Li^+ + Sn + e^- \rightarrow Li_xSn$ (x< 4.4)

According to Courtney and Dahn [2], during first discharge lithium bonds to oxygen that was initially bonded to Sn, thereby breaking up the oxide and leaving Sn metal and Li_2O. The rest of the Sn metal can reversibly alloy with Li until the theoretical limit of $Li_{4.4}Sn$. Based on this hypothesis, they have observed that the first cycle discharge capacity increased with increase in Sn-valence. Due to the variation in the oxygen content, the discharge capacity changes with temperature of heating. The Substitution of titanium by tin in Fe_2TiO_5 enhances the dielectric properties [3]. Intercalation of "$(LiAl)^{4+}$" in Fe_2TiO_5 establishes long range magnetic ordering [4]. Hence it is thought possible to have a material with dielectric as well as magnetic properties by intercalation of "$(LiAl)^{4+}$" in $Fe_2Ti_{0.75}Sn_{0.25}O_5$. Where the intercalation is achieved by treating the pseudobrookite with the reducing agent viz. $LiAlH_4$. The crystallographic and magnetic characteristics of the lithium aluminium ferrite have been investigated [5, 6] in order to understand the site preference for Al^{3+} and the magnetic interactions in the spinel lattice. The Mossbauer studies [7] of lithium aluminates have shown central quadrupole doublet superimposed on a magnetic sextet and its intensity was sensitive to Al concentration. U. N. Trivedi et al. [8] have studied the effect of substitution of Fe^{3+} by Al^{3+} and Cr^{3+} in $Li_{0.5}Fe_{2.5}O_4$ on its structural and magnetic properties. The Cr^{3+} ions have marked preference for octahedral B-sites and it is assumed that Li^+ ion preferentially occupies the B (octahedral)-sites [9]. Contrary to the earlier reports the results have shown that Al^{3+} ions were almost equally distributed among octahedral and tetrahedral sites. The system exhibited canted spin structure.

The crystal structure and magnetic properties of Al and Cr co-substituted disordered spinel series $NiAl_xCr_xFe_{2-2x}O_4$ (x = 0.0 - 0.9) have been investigated by Urvi V. Chhaya et al. [10]. The manner of changing of lattice constant with Cr-Al content has indicated that the spinel series had an inverse spinel structure as long as x<0.5, and it changed gradually to normal as x increases from 0.5 to 0.9. Both hyperfine fields (H_A and H_B) decreased with the increase in x,demonstrating a reduction in ferromagnetic behaviour with increasing x values. The collinear magnetic structure was found for x = 0.1 to 0.5, while for x = 0.6 to 0.9 significant canting exists on B-sites suggesting magnetic structure to be non-collinear. The change of spin ordering from collinear to non-collinear displayed a strong influence on the variation of saturation magnetic moment per molecule.

II. EXPERIMENTAL:

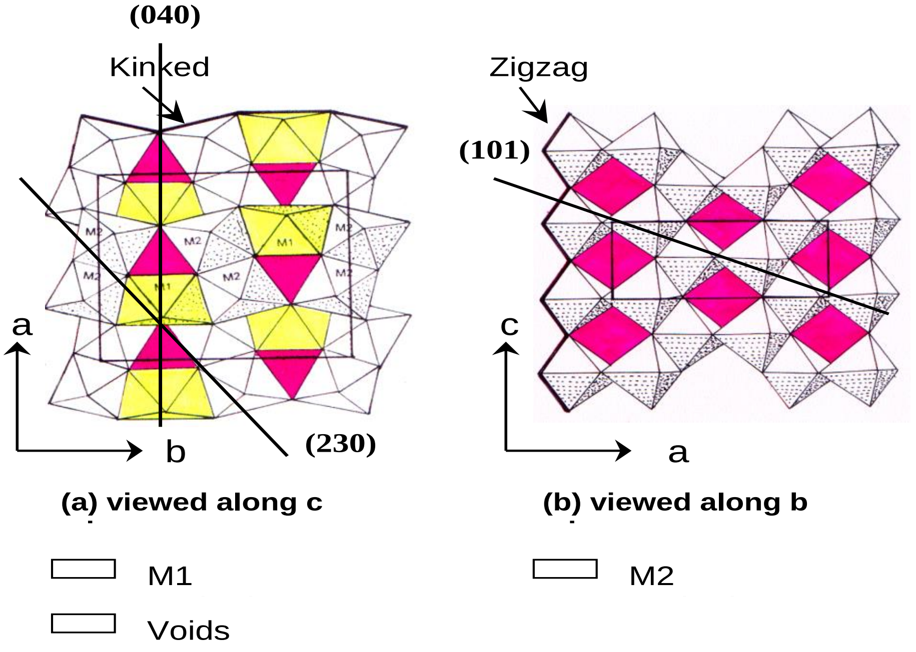
The A. R. grade α-Fe_2O_3, rutile TiO_2 fine powders were throughly mixed and mixture was first presintered at 950 ^{0}C for 24 hours. The presinterd mixture was homogenized in a mortar and then sintered at 1250 ^{0}C for 24 hours. Fe_2TiO_5. i.e. [FTR], By similar method other mixtures of $Fe_2Ti_{0.75}Sn_{0.25}O_5$. i. e. [FTSR], $Fe_2Ti_{0.75}Sn_{0.25}O_5$ +0.5LiAl, i. e. [$FTSL_1R$]and $Fe_2Ti_{0.75}Sn_{0.25}O_5$ +1.0LiAl, i. e. [$FTSL_2R$]. are synthesized. By X-ray diffraction these samples are analyzed. FTIR spectra are also obtained and analysed for the characterization of these samples. That there is no loss of either Li^{1+} or Al^{3+} is confirmed by the Inductively Coupled Plasma (ICP) and XRF technique.

III. RESULTS AND DISCUSSION:

3.1 STRUCTURAL PROPERTIES:

The XRD data and analysis of [FTR], [FTSR], [$FTSL_1R$] and [$FTSL_2R$] indicates that [$FTSL_1R$] and [$FTSL_2R$] too are pseudobrookites with orthorhombic symmetry. The data analysis corresponding to [FTR] and [FTSR] are included to facilitate the comparison. It is observed from the XRD data that the relative intensities of (040) plane passing through interstices (Figure 1) have increased (Table 1). This confirms that Sn^{4+} occupies the M1 sites and the "$(LiAl)^{4+}$" enters the interstices of $Fe_2Ti_{0.75}Sn_{0.25}O_5$. It is termed as intercalation of "$(LiAl)^{4+}$". That there is no loss of either Li^{1+} or Al^{3+} is confirmed by the Inductively Coupled Plasma (ICP) and XRF technique.

It is interesting to observed (Table 1) that on one hand Sn^{4+} increases the unit cell volume, on the other hand "$(LiAl)^{4+}$" increasingly decreases it. However, it remains larger than that of the pure sample [FTR]. Both the Sn^{4+} and "$(LiAl)^{4+}$" inhibit the Debye particle size. The XRD/ theoretical density is increased by Sn^{4+} because of its greater atomic mass and by "$(LiAl)^{4+}$" because it occupies interstices. Whereas, Sn^{4+} lowers the porosity, "$(LiAl)^{4+}$" raises it. While Sn^{4+} increases the inhomogeneity slightly, "$(LiAl)^{4+}$" increases it considerably.



(a) viewed along c

(b) viewed along b

Figure 1: The Pseudobrookite Pseudobrookite Structure. [1

Table 1: Unit cell volume, Order parameter, Debye particle size, Average Grain size, XRD and Practical density, Inhomogeneity, Porosity and Relative percentage intensity of (040) plane.

Sample	Unit cell volume V (Å)^3	Order Parameter	Debye Particle Size(Å)	Avg. grain size μm)	XRD density g/cc	Practical Density g/cc	Inhomo-geneity	Porosity	Relative % intensity of (040) plane
[FTR]	362.9	0.31	540	3	4.38	3.99	-0.002	0.09	1.6
[FTSR]	385.1	1	450	9	4.44	4.29	-0.0025	0.03	38.5
[FTSL$_1$R]	378.8	1	340	9	4.81	3.61	-0.0086	0.25	43.9
[FTSL$_2$R]	374.4	0.81	336	9	5.16	3.78	-0.014	0.27	156.1

3.2. DETERMINATION OF CATION DISTRIBUTION:

Table 2: Cation Distribution, Parameter (c/ab), Charge ratio q1/q2 and Separation between IR-bands for the samples

Sample	Cation distribution obtain from the Empirical Model	(c/ab) (Å)$^{-1}$	q_1/q_2	Separation between IR bands (ν1-ν2) cm^{-1}
[FTR]	$[Fe_{0.78}\ Ti_{0.22}]_{M1}$ $[Fe_{1.22}\ Ti_{0.78}]_{M2}\ O_5$	0.03826	0.95	200
[FTSR]	$[Fe_{0}\ Ti_{0.75}\ Sn_{0.25}]_{M1}$ $[Fe_{2}\ Ti_{0}]_{M2}O_5$	0.03739	1.41	185
[FTSL$_1$R]	$\{(LiAl)_{0.5}\}\ [Fe_{0}\ Ti_{0.75}\ Sn_{0.25}]_{M1}\ [Fe_{2}\ Ti_{0}]_{M2}O_5$	0.03753	1.37	131
[FTSL$_2$R]	$\{(LiAl)_{1.0}\}\ [Fe_{0.10}\ Ti_{0.65}\ Sn_{0.25}]_{M1}\ [Fe_{1.9}\ Ti_{0.1}]_{M2}O_5$	0.03774	1.27	123

The cation distribution in Fe_2TiO_5 and related compounds has been reportedly determined by using Reitveld Refinement technique [11-15]. It is observed that lattice parameters of these compounds depend on the cation distribution as also in other cases [16]. However, the magnitudes of the lattice parameters depend on the heat treatment, fineness and purity of the powder, etc. Therefore, a new empirical model, which is dependent on the relative values of lattice parameters of the reported samples, is proposed here,

$$q_1 / q_2 = \{(2006.2)\ x^3 - (230.02)\ x^2 + (8.7843)\}\ 10^5\ x - 11172.75$$

Where, x = (c/ab).

The cation distribution of the samples under study is obtained (Table 2). The implication of the increase in the relative percentage intensity of (040) plane that Sn^{4+} occupies the M1 site and "$(LiAl)^{4+}$" occupies interstices is satisfied fully in this cation distribution. Almost the entire Fe^{3+} is seen to shift to the M2 site. The FTIR spectra of these samples are depicted in Figure 6, which show two major bands of frequencies ν1and ν2 corresponding to the octahedral sites M1 and M2 respectively [3, 4].

In [FTR] the band corresponding to M2 sites is more intense due to larger number of dipoles available at M2. However, as the charge on M1 increases due to Sn^{4+} and number of dipoles on M1 increases due to the occupancy of interstices by "$(LiAl)^{4+}$" , the IR-band corresponding to M1 also becomes equally intense. Also, the bands are broadened by Sn^{4+} as well as "$(LiAl)^{4+}$".

The frequencies of the bands are listed in the Table 3. The frequency ν1 shifts to lower side by Sn^{4+} perhaps due to its heavy mass. It lowers further by "$(LiAl)^{4+}$". On the other hand, the frequency ν2 shifts to higher side both by Sn^{4+} and "$(LiAl)^{4+}$" which force Fe^{3+} to the M2 sites (Tables 2 and 3). Perhaps the lower tetrahedral symmetry of Fe^{3+} increases the values of ν2.

The frequency difference (ν1-ν2) decreases by Sn^{4+}. It decreases further as "$(LiAl)^{4+}$" content increases.

This means that Sn^{4+} and “$(LiAl)^{4+}$” strengthens the interaction between the M1 and M2 sites.

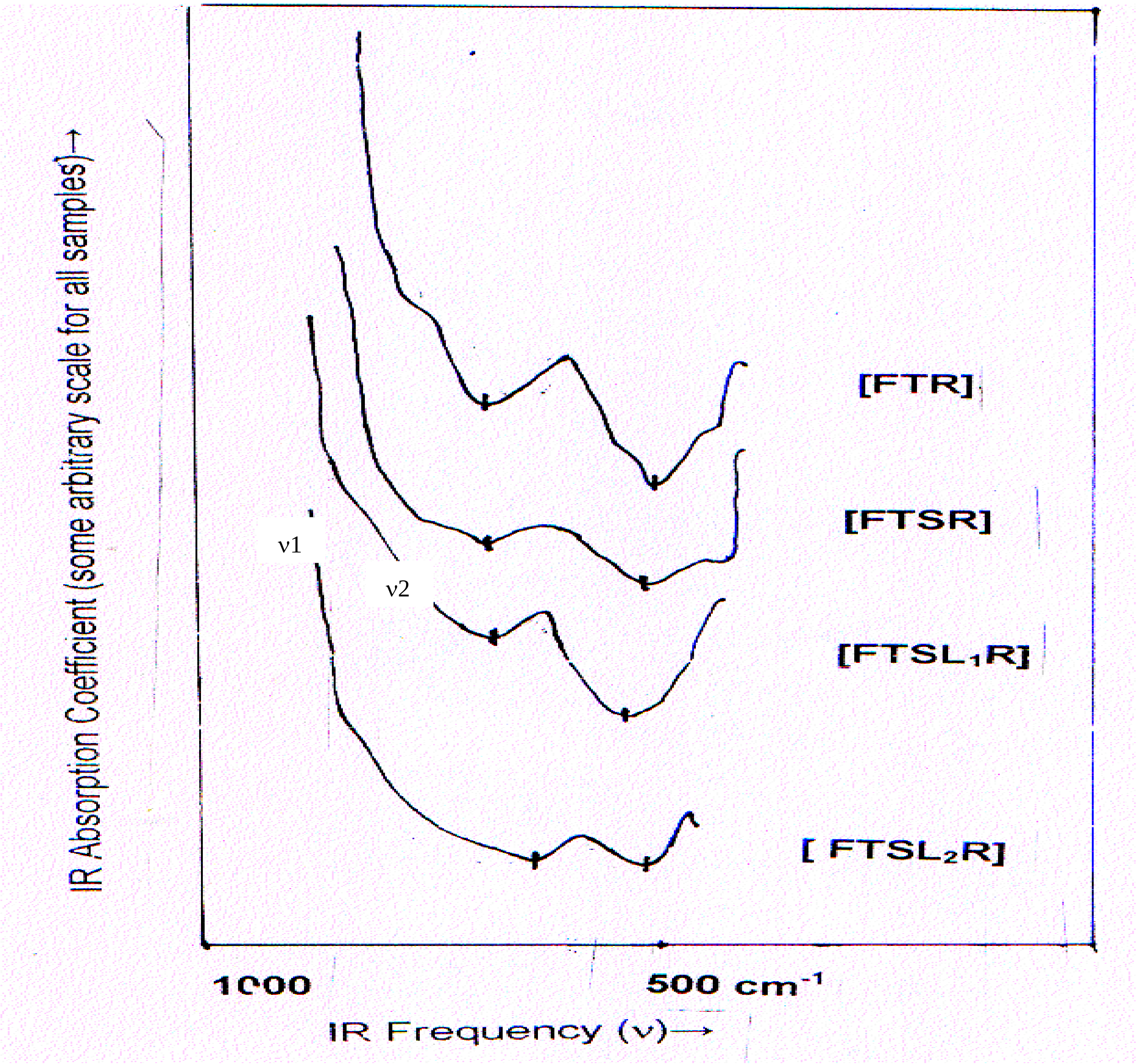


Figure 2: IR-Specra for the samples.

Table 3: Assignment of two major bands of frequencies ν1and ν2 corresponding to the octahedral sites M1 and M2 respectively for the pseudobrookites.

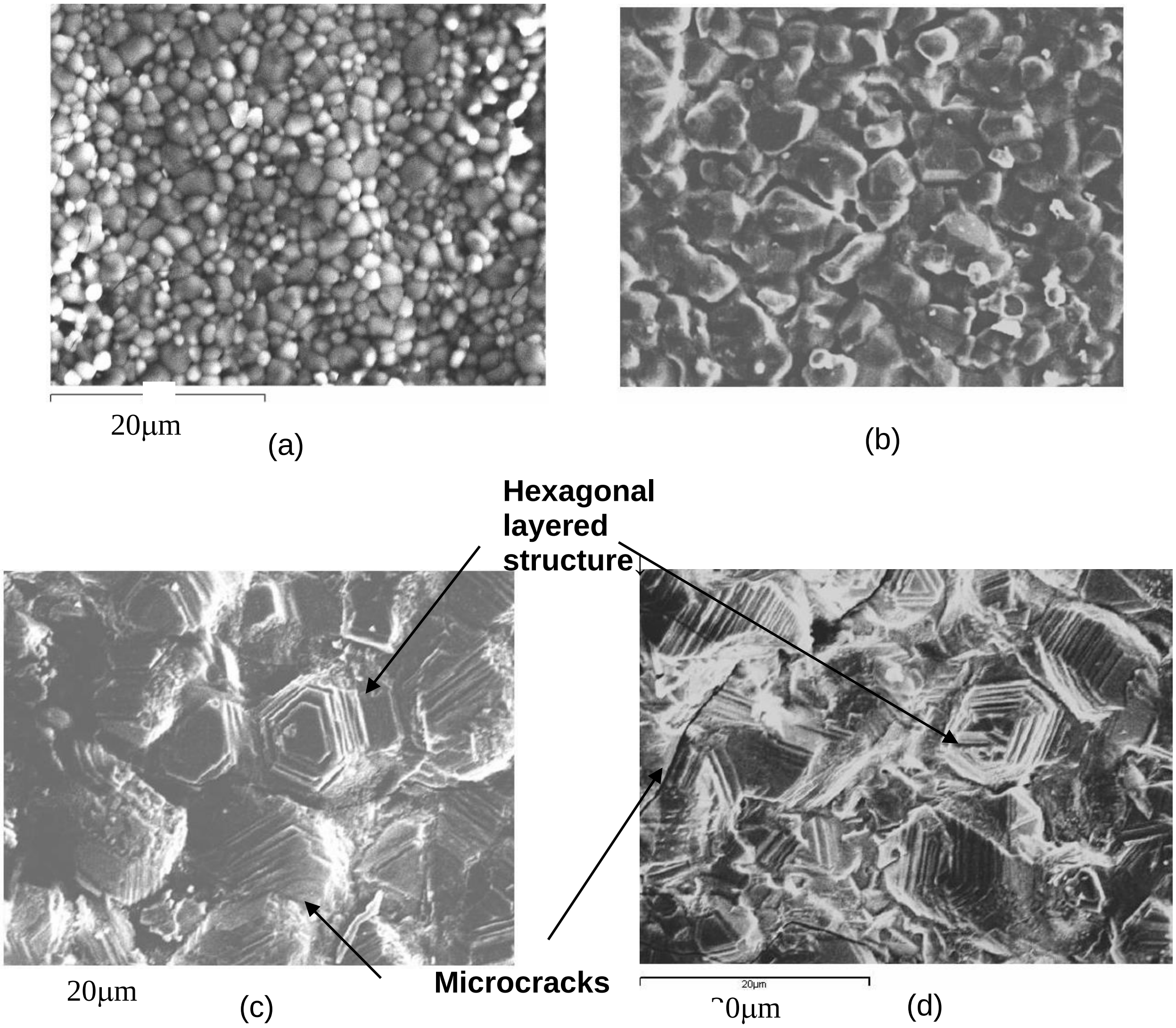
Bands	Frequency (cm^{-1})				Possible octahedral assignment
Sample □	[FTR]	[FTSR]	[FTSL$_1$R]	[FSTL$_2$R]	
ν1	690	688	680	638	M1
ν2	490	503	549	515	M2
(□1-□2)	200	185	131	123	

3.3: Scanning Electron Micrographs (SEM):

The micrographs of the samples under study obtained from the Scanning Electron Microscopy (SEM) technique are as shown in the Figures 3 (a, b, c, d).

20μm

Figure 3: Scanning Electron Micrographs for samples



(a)[FTR], (b) [FTSR], (c) [$FTSL_1R$] and (d) [$FTSL_2R$].

The SEMs show the presence of microcracking in the samples. The grain size of the material is observed to increase by the substitution of Ti^{4+} by Sn^{4+} and it is controlled even after intercalation of "$(LiAl)^{4+}$" in the pseudobrookite. The hexagonal layers observed increase with the content of "$(LiAl)^{4+}$" in the intercalated samples [$FTSL_1R$] and [$FTSL_2R$].

3.4: MAGNETIC PROPERTIES:

3.4.1: Location of "$(LiAl)^{4+}$" in $Fe_2Ti_{0.75}Sn_{0.25}O_5$:

The XRD analysis of the samples indicates that they too are pseudobrookites with orthorhombic symmetry. It is interesting to note that certain reflections corresponding to the pseudobrrokite phase become increasingly intense as the content of "$(LiAl)^{4+}$" increases. Many of them exist in Fe_2TiO_5 as weak reflections. The (d) values along with the relative percentage intensities of these reflections appear to match with those of the spinel phase as indicated in Table 4.

Table 4: XRD Data Showing Reflections Corresponding to Spinel Phase in Pseudobrookite Phase.

For pseudobrookite phase d_{obs} (Å)	Percentage intensity	For spinel phase d_{cal} (Å)

[FTR]	[FTSR]	[$FTSL_1R$]	[$FTSL_2R$]	hkl	[FTR]	[FTSR]	[$FTSL_1R$]	[$FTSL_2R$]	hkl	[FTR]	[FTSR]	[$FTSL_1R$]	[$FTSL_2R$]
2.8502	-	2.9458	2.9352	121	6.4	-	11.67	68.06	220	2.9158	-	2.9023	2.9299
2.4866	2.4885	2.4751	2.4986	40	1.6	38.5	43.92	156.12	311	2.4866	2.4885	2.4751	2.4986
-	-	-	2.0679	141	-	-	-	35.08	400	-	-	-	2.0717
1.6618	1.6526	1.6437	1.6836	60	14	14.28	23.33	23.76	224	1.6834	1.6847	1.6757	1.6916
-	1.4308	1.4592	-	630	-	8.6	13.7	-	440	-	1.459	1.4512	-

Since the pseudobrookites have been treated with $LiAlH_4$ the formation of any spinel is unlikely. Also, the densities of all the samples are small (around 3.7 g/ cc). Hence, the formation of spinels such as Li Fe_5O_8 or Fe_2TiO_4 having higher densities 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 "$(LiAl)^{4+}$" content. Also, it is observed from the XRD data that relative intensities of (040) plane passing through interstices have increased (Figure 1 and Table 1). This confirms that the "$(LiAl)^{4+}$" enters the interstices of Pseudobrookite and is termed as the intercalation similar to occupancy of vacant octahedral sites in spinels by excess of lithium [6]. This is quite possible because of bi-pyramidal geometry of interstices which have very large volumes and they are equal in number to M1 sites [11].

3.4.2: Magnetic Behaviour:

Due to the availability of a spinel like network to cations such as Li^{1+} and Fe^{3+}, it is thought worthwhile to investigate the magnetic behaviour of the intercalated pseudobrookites viz. [$FTSL_1R$] and [$FTSL_2R$]. The samples are tested for the magnetic hysteresis and Curie-Weiss law. Interestingly, the sample [$FTSL_1R$] possesses both the characters. The magnetic susceptibility is not detected for the sample [$FTSL_2R$] perhaps due to the presence of excess of Li^{1+}.

The Table5 shows the magnetic hysteresis data for the sample [$FTSL_1R$]. On the basis of coerceivity (Hc), the ferrites are characterized as

I) Hard Ferrites (Hc > 1.5 kOe),
ii) Moderate Ferrites (1.5 kOe > Hc > 100 Oe), and
iii) Soft Ferrites (100 Oe > Hc).

Obviously, [$FTSL_1R$] is a soft ferrite.

Table 5: Magnetic data for sample [$FTSL_1R$].

Sample	Initial a. c. Susceptibility χ_I at 300Hz at room temp. (emu)	Hc (Oe)	M_S (emu / gm)	M_R / M_S
[$FTSL_1R$]	0.001	90	0.61	0.45

The soft ferrites are useful as transformer cores for telecommunications, televisions and in numerous applications in industrial electronics like inverters, SMPS, EMI filters, etc. [23]. According to the above discussion the sample [$FTSL_1R$] may have applicability as soft ferrite.

The comparative study of hysteresis (Figure 4) and thermal variation of magnetization study (Figure 5) of the sample helps a lot to pin point its domain nature [24-27]. The dome shaped curve of initial a. c. susceptibility Vs temperature (χ/χ_{rt} Vs T) for the sample [$FTSL_1R$] (Figure 5) indicates that it is *Ferrimagnetic* and there is a good proportion of *S. D. particles* interacting between themselves [28]. The Curie temperature of this sample is ($T_c = 602\ K$). The type of domain may also be judged from the grain size. The spinels having grain size smaller than 3μm are of single domain type [29, 30] and for grain size larger than 3μm the spinels have multi domain structure. The single domain nature of sample [$FTSL_1R$] indicates that the critical size may be around *9μm* in case of our samples. This may be true for all pseudobrookites.

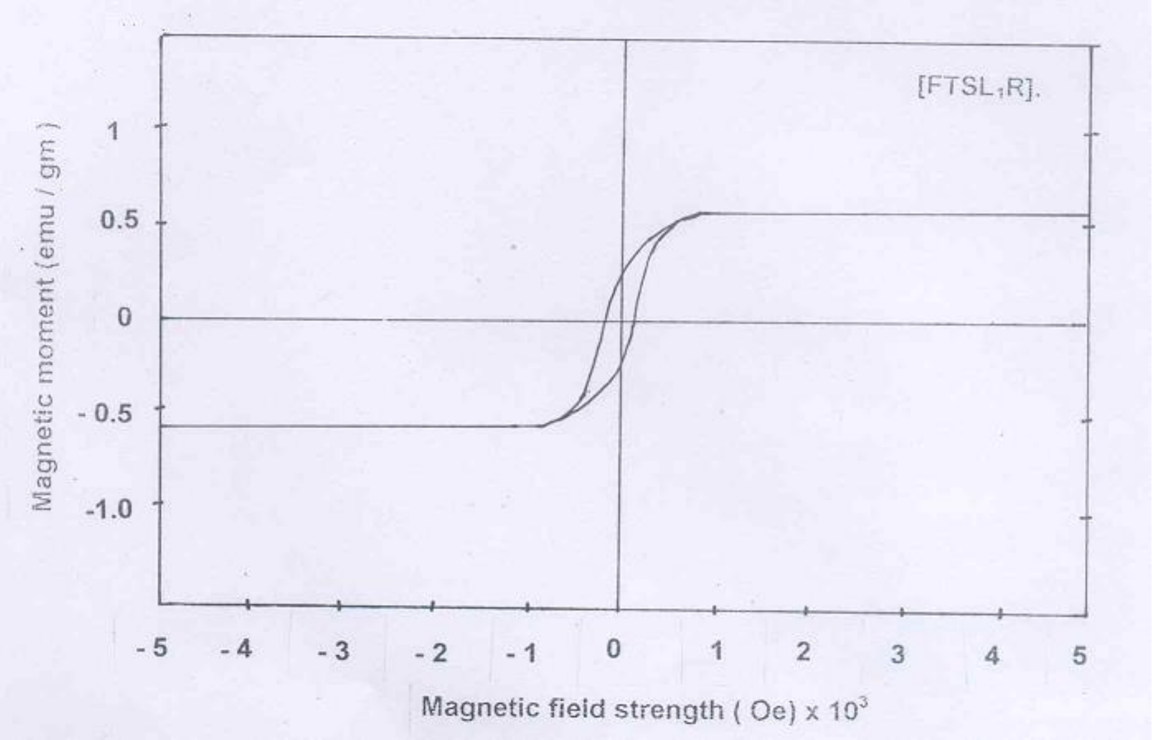


Figure 4: Magnetic Hysteresis for the sample [FTSL$_1$R] measured at room temperature.

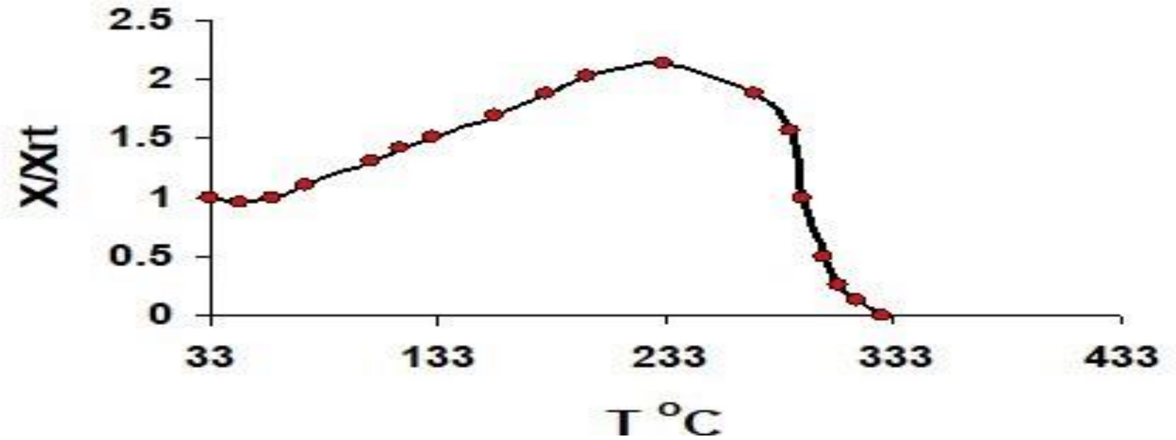


Figure 5: Plot of initial a.c. susceptibility Vs. Temp. For the sample [FTSL$_1$R]

IV. CONCLUSIONS:

The XRD data and analysis of [FTSL$_1$R] and [FTSL$_2$R] indicates that they too are pseudobrookites with orthorhombic symmetry. It is also observed from the XRD data that the relative intensities of (040) plane passing through interstices have increased. This confirms that Sn^{4+} occupies the M1 sites and the "$(LiAl)^{4+}$" enters the interstices of $Fe_2Ti_{0.75}Sn_{0.25}O_5$. It is termed as intercalation of "$(LiAl)^{4+}$". It is interesting to observed that on one hand Sn^{4+} increases the unit cell volume, on the other hand "$(LiAl)^{4+}$" increasingly decreases it. However, it remains larger than that of the pure sample [FTR].

It is interesting to note from the XRD analysis that certain reflections corresponding to the pseudobrrokite phase become increasingly intense as the content of "$(LiAl)^{4+}$" increases. Many of them exist in Fe_2TiO_5 as weak reflections. The (d) values along with the relative percentage intensities of these reflections appear to match with those of the 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 "$(LiAl)^{4+}$" content.

The dome shaped curve of initial a. c. susceptibility Vs temperature (χ/χ_{rt} Vs T) for the sample [$FTSL_1R$] indicates that it is Ferrimagnetic and there is a good proportion of S. D. particles interacting between themselves. The Curie temperature of this sample is (Tc = 602 K). The magnetic hysteresis data for the sample [$FTSL_1R$] shows that it is a soft ferrite.

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