

Characerization of Intercalated Iron Titanate BasedISSN: 0474-9030
Vol-68-Issue-30-February-2020**Materials****S.S. GURAV**

Department of Physics, K.E.S. Anandibai Pradhan Science College, Nagothane (M.S.)

Abstract: 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. It is observed 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 interesting to note that certain reflections corresponding to the pseudobrookite phase become increasingly stronger as the content of "(LiAl)⁴⁺" increases. Inter-planer distance, Miller indices and relative percentage intensities of these reflections match closely with those of spinel phase. Hence there exists a spinel like network within the pseudobrookite phase and gets increasingly ordered and stronger with the "(LiAl)⁴⁺" content.

Key words: Intercalation, Pseudobrookite.

1 INTRODUCTION

The association of Li⁺ and Al³⁺ in a magnetic environment has been investigated extensively in ferrites, spinels and garnets [1]. It is found that a magnetic spinel establishes a long range magnetic ordering by linking its octahedral and tetrahedral sites [2]. Lithium ferrite and substitutions such as Al, Ti, Mn and Ge have been studied for their magnetic structure [2]. The magnetic structure of Li-Al Ferrite has been investigated by J. Maknani et al. [1]. Mossbauer studies with and without applied field have been performed on LiFe_xAl_{5-x}O₈ ferrite system and a canted structure is demonstrated [1].

The phase equilibria in Li₂O-Fe₂O-TiO₂ system have been studied by I. E. Grey et al. [3]. The pseudobrookite showed deviation from M₃O₅ stoichiometry towards metal-rich compositions which increased with increasing substitution of Li¹⁺+Ti⁴⁺ for Fe³⁺, from Fe₂TiO₅ to Li_{0.81}Fe_{0.27}Ti_{2.09}O₅ (= M_{3.17}O₅). Titanium is ordered in

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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 octahedra 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. Magnetic properties of Li^+ substituted manganese ferrite have been studied by T. R. Mc Guire and F. S. Ferebee [9]. The structure of Li_4TiO_4 has been determined by R. P. Gunawardane et al. [10] Ladislav Kavan et al. [11] have studied Li^+ insertion into $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (spinel) and found that Li^+ -diffusion coefficients decreased by orders of magnitude if the average particle size drops from $1\mu\text{m}$ to 9nm . Hence it is thought possible to intercalate " $(\text{LiAl})^{4+}$ " in Fe_2TiO_5 to incorporate magnetic ordering [5]. 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:

2.1 STRUCTURAL PROPERTIES:

In this article the investigation on $\text{Fe}_2\text{TiO}_5 + \{0.5 \text{LiAl}\}$ i.e. [FTL₁R] and $\text{Fe}_2\text{TiO}_5 + \{1.0 \text{LiAl}\}$ i.e. [FTL₂R] is reported. Fe_2TiO_5 i.e. [FTR] is included to facilitate the comparison. All the samples are synthesized by using rutile TiO_2 . The XRD data of [FTR], [FTL₁R] and [FTL₂R] shows that all the samples are pseudobrookites with orthorhombic symmetry. The retention of quantity and proportion of lithium and aluminium is confirmed by



Inductively Coupled Plasma (ICP) and XRF analysis. The structural properties of the samples are reported in the

Table .1.

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

Sample	Order parameter λ'	Inhomogeneity	Debye Particle Size (Å)	Avg. grain size (µm)	XRD density g/cc	Practical Density g/cc	Porosity	Unit cell volume $V(\text{Å})^3$	Relative % intensity of (040) plane
[FTR]	0.31	-0.002	540	3	4.38	3.99	0.09	362.9	1.6
[FTL ₁ R]	0.81	-0.005	338	19	5.02	3.59	0.23	357.8	45.2
[FTL ₂ R]	1.00	-0.004	328	19	5.05	3.44	0.32	359.7	52.9

However, it is felt necessary first to locate the position of “(LiAl)⁴⁺” in [FTL₁R] and [FTL₂R]. It is observed from the XRD data that relative intensity of (040) plane passing through interstices (Figure. 1) increases from 1.6 in [FTR] to 45.22 in [FTL₁R] and 52.9 in [FTL₂R] (Table . 1). Thus “(LiAl)⁴⁺” appears to enter the interstices of Fe₂TiO₅. It is termed as the intercalation of “(LiAl)⁴⁺”.

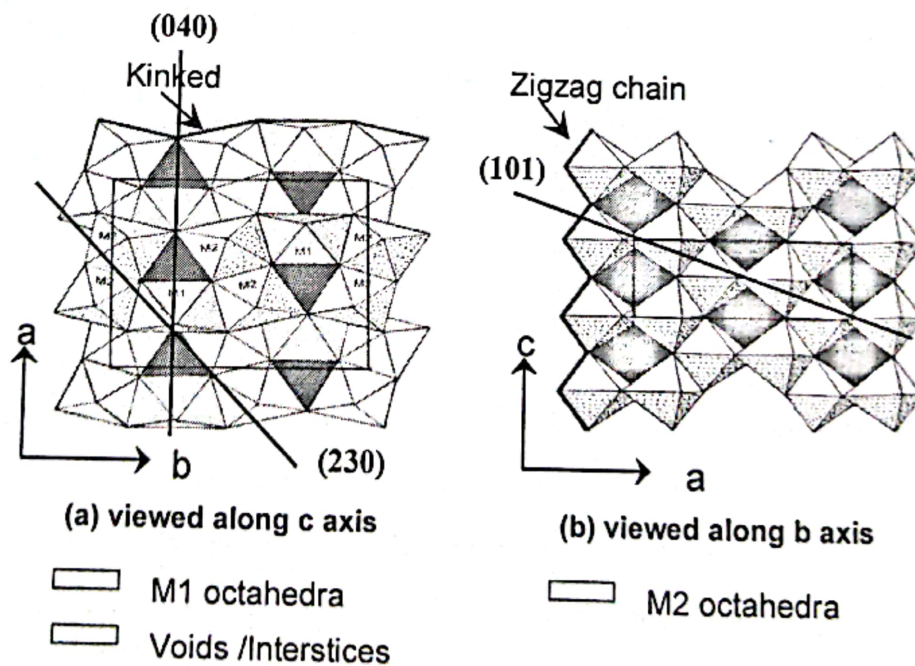


Figure .1: The pseudobrookite structure. [12]

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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.

2.2 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 .2. It is interesting to note that sample [FTR] is tending towards inverse ordered structure $[Fe_1]_{M1} [Fe_1 Ti_1]_{M2} O_5$ and intercalation of “(LiAl)⁴⁺” helps to achieve it. The cation distribution shows that as the content of “(LiAl)⁴⁺” increases the content of Fe³⁺ on the M2 site decreases. This appears to increase the symmetry of the structure and correspondingly the unit cell volume decreases (Table.1). The ordering of the structure depends on the lower tetrahedral symmetry associated with Fe³⁺ in the octahedral site.

Table .2: 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 Fe³⁺ on M2 site – Amount of Fe³⁺ on M1 site. But it is observed that, when amount of Fe³⁺ on M2 site = 1.5 and that of Fe³⁺ 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' .

2.2.1: The Fourier Transform Infra Red Spectra:

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The FTIR spectra of these samples exhibit two nearby bands of frequencies ν_1 (630- 690 cm^{-1}) and ν_2 (430- 510 cm^{-1}) which correspond to the octahedral M1 and M2 sites [5] respectively (Figure .2 and Table.3). 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 " $(\text{LiAl})^{4+}$ " decreases the frequency ν_1 . This may be due to $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ 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 ($\nu_1 - \nu_2$) corresponding to M1 and M2 octahedral sites is less for " $(\text{LiAl})^{4+}$ " intercalated samples (Table. 3). It implies a stronger link between the M1 and M2 sites perhaps due to the affinity of Li^{1+} in the interstices adjacent to M1 site and Fe^{3+} on the M2 site.

Table.3: Assignment of two major bands of frequencies ν_1 and ν_2 .

Bands	Frequency for the sample (cm^{-1})			Possible octahedral assignment
	[FTR]	[FTL ₁ R]	[FTL ₂ R]	
ν_1	690	638	630	M1
ν_2	490	510	530	M2
$\nu_1 - \nu_2$	200	128	100	

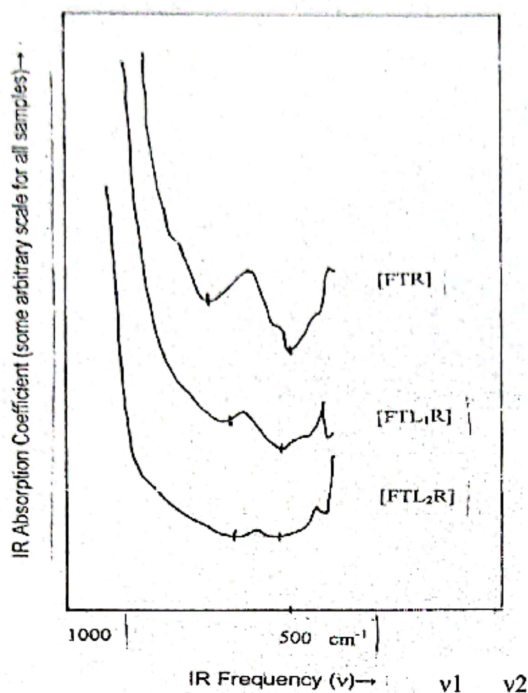
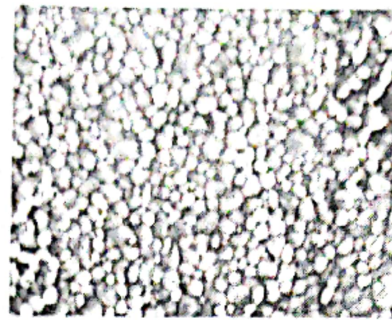


Figure. 2: IR-Spectra for the samples.

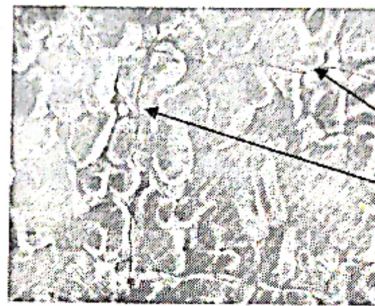
2.2.2: Scanning Electron Micrographs (SEM):

The Micrographs of the samples under study obtained from the SEM technique are as shown in Figure. 3. From these SEMs we can see the presence of microcracking in the samples and the grain size of the material is observed to increase (Table. 1) by the intercalation of $(LiAl)^{4+}$ in the pseudobrookite.

Figure.3: Scanning Electron Micrographs (SEM) for the samples.



20 μm



[FTRI]

[FTL₁R]

Microcracks

50 μm



[FTL₂R]

50 μm

2.3. 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. 4). 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. 6. However, the densities of all the samples are small (around 3.5 g / cc). Hence, the formation of highly denser spinels such as Li Fe₃O₄ or Fe₂TiO₄ as an additional phase seems unlikely.

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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, as has been 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 Fe₂TiO₅. 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 MI sites [4]. It is similar to occupancy of vacant octahedral sites in spinels by excess of lithium [2, 6].

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

For pseudobrookite phase (Å)				d _{obs}	Relative Percentage intensity			For spinel phase d _{cal} (Å)			
[FTR]	[FTL ₁ R]	[FTL ₂ R]	hkl		[FTR]	[FTL ₁ R]	[FTL ₂ R]	hkl	[FTR]	[FTL ₁ R]	[FTL ₂ R]
2.8502	2.9096	2.8990	121	6.4	9.67	21.6	220	2.9158	2.9054	2.8974	
2.4866	2.4777	2.4709	040	1.6	45.22	52.9	311	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	14.4	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)⁴⁺" appears to enter the interstices of Fe₂TiO₅. It is termed as the intercalation of "(LiAl)⁴⁺". 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 interesting to note that certain reflections corresponding to the pseudobrookite phase become increasingly stronger as the content of "(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 "(LiAl)⁴⁺" content.

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