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GAS and Pressure Sensing Fe_2TiO_5 Based Materials

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Abstract – In order to study the applications of the Fe_2TiO_5 based materials 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 magnetic hysteresis and susceptibility measurement shows that LiAl enhances the magnetic ordering. The intercalated samples are sensitive to pressure as well as gases (O_2 and CO_2).

Key Words: Intercalation, Pseudobrookite, Pressure Sensitivity, Gas Sensitivity.

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1. INTRODUCTION:

The association of Li^+ and Al^{3+} 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 $LiFe_XAl_{5-X}O_8$ ferrite system and a canted structure is demonstrated [1].

The phase equilibria in Li_2O-Fe_2O-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 Li^{1+}+Ti^{4+} for Fe^{3+}, from Fe_2TiO_5 to $Li_{0.81}Fe_{0.27}Ti_{2.09}O_5$ (= $M_{3.17}O_5$). 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 $Fe^{3+} \rightarrow Fe^{2+}$ reduction and oxygen deficiency.

From the single crystal refinement of Fe_2TiO_5, Tiedemann and Muller-Buschbaum [4] have reported a statistical distribution of 2/3Fe + 1/3Ti 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.

Hence it is thought possible to intercalate "$(LiAl)^{4+}$" in Fe_2TiO_5 to incorporate magnetic ordering [5-8]. 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 "$(LiAl)^{4+}$" intercalated samples [FTL_1R] and [FTL_2R]. All the samples are sintered at 1250^oC.

Magnetic properties of Li^+ substituted manganese ferrite have been studied by T. R. Mc Guire and F. S. Ferebee [9]. The result of substituting lithium for manganese is to lower the magnetic moment and raise the Curie temperature. The variation of magnetic moment with concentration is consistent with about 90% of Li^+ going on B sites. From previous work, it is known that lithium goes into solid solution from 10 to 50 atomic% in both rock salt and spinel structures. In each substitution the Li^+ is balanced by divalent ions that go to a higher valency. In the reported manganese lithium ferrite [9], both divalent manganese and iron become trivalent as Li^+ is introduced. For higher values of x in the system $Mn_{1-X}Li_X Fe_2O_4$, there is an increased amount of iron on the A-sites which gives rise to stronger A-B interaction and the Curie temperature rises [9-11].

2. RESULTS AND DISCUSSION:

2.1 Structural Properties:

In this article the investigation on Fe_2TiO_5 + {0.5 LiAl} i.e. [FTL_1R] and Fe_2TiO_5+{1.0 LiAl} i.e. [FTL_2R] 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], [FTL_1R] and [FTL_2R] 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: Debye particle size, Average Grain size, XRD and Practical density, Porosity, Unit cell volume and Relative % intensity of (040) plane.

Sample	Debye Particle Size (Å)	Avg. grain size (μm)	XRD density g/cc	Practical Density g/cc	Porosity	Unit cell volume V (Å)³	Relative % intensity of (040) plane
[FTR]	540	3	4.38	3.99	0.09	362.9	1.6
[FTL_1R]	338	19	5.02	3.59	0.23	357.8	45.2
[FTL_2R]	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 [FTL_1R] and [FTL_2R]. 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 [FTL_1R] and 52.9 in [FTL_2R] (Table . 1). Thus "$(LiAl)^{4+}$" appears to enter the interstices of Fe_2TiO_5 . It is termed as the intercalation of "$(LiAl)^{4+}$".

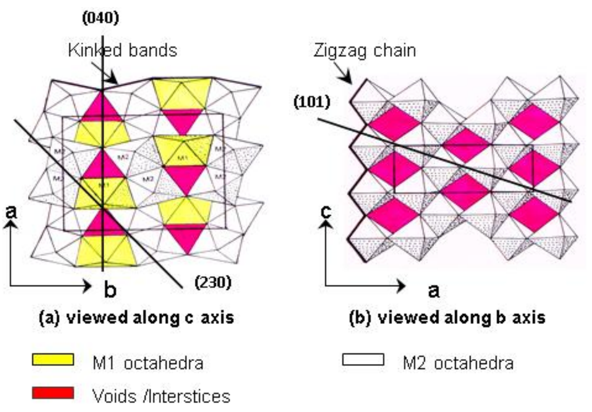

Figure .1: The pseudobrookite structure. [12,13]

It is interesting to note that the intercalation has resulted into the increase in the porosity and the decrease in Debye particle size.

2.2.: Scanning Electron Micrographs (SEM):

The Micrographs of the samples under study obtained from the SEM technique are as shown in Figure. 2.

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.

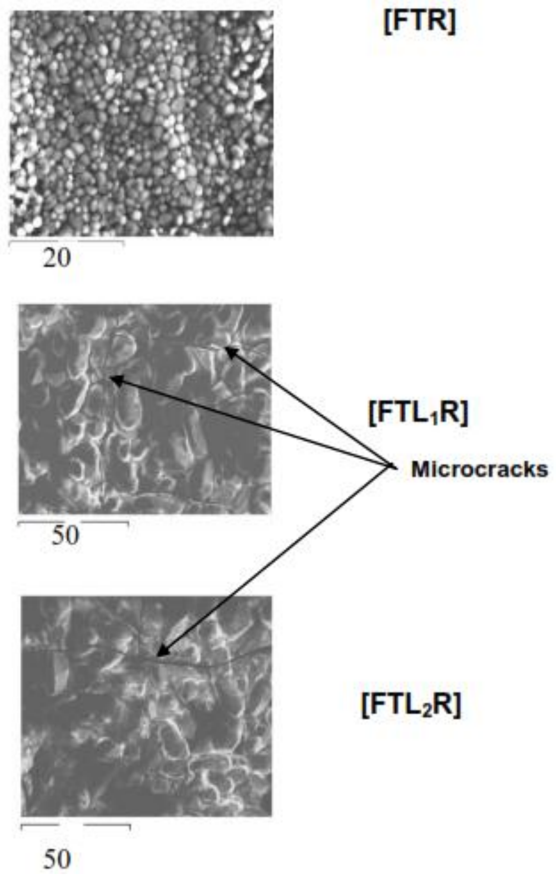

Figure.2: Scanning Electron Micrographs (SEM) for the samples.

2.3 MAGNETIC PROPERTIES:

2.3.1 Location of LiAl in Fe_2TiO_5:

It is interesting to note that certain reflections corresponding to the pseudobrookite phase become increasingly stronger as the content of "$(LiAl)^{4+}$" increases (Table. 2). Many of them exist in Fe_2TiO_5 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. 2. However, the densities of all the samples are small (around 3.5 g / cc). Hence, the formation of highly denser spinels such as Li Fe_5O_8 or Fe_2TiO_4 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, 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

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

For pseudobrookite phase d_{obs} (Å)				Relative Percentage intensity			For spinel phase d_{cal} (Å)			
[FTR]	[FTL_1R]	[FTL_2R]	hkl	[FTR]	[FTL_1R]	[FTL_2R]	hkl	[FTR]	[FTL_1R]	[FTL_2R]
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

2.3.2 Magnetic Behaviour:

With the existence of the spinel like network in the pseudobrookite it is decided to investigate whether these spinels posses a magnetic ordering particularly in the presence of lithium and iron. Accordingly the samples are tested for the existence of magnetic hysteresis and Curie-Weiss law. Interestingly, both [FTL_1R] and [FTL_2R] exhibit hysteresis curves (Figures.3, 4) respectively. From the shape of these hystereses it is concluded that the samples [FTL_1R] and [FTL_2R] possess a Ferrimagnetic ordering [14-17] having the presence of Single Domain + Multi Domain (S.D. + M. D.). However, the magnetic moment is small (Table. 3). The magnetic susceptibility is not detected for sample [FTR]. A small coercive force (H_c~250 Oe) which is a measure of the field required to rotate the magnetizing vector of [FTL_1R] and [FTL_2R] indicates that they are soft ferrites [18].

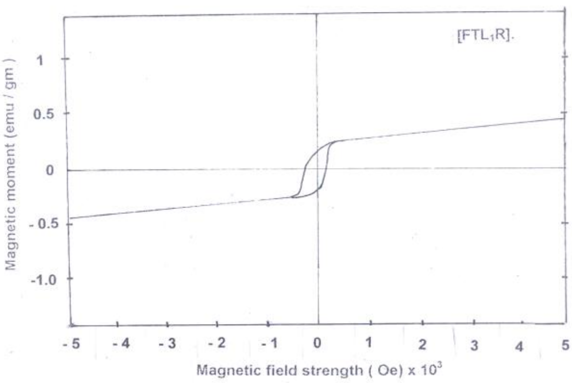

Figure 3: Magnetic Hysteresis at room temperature for sample[FTL_1R]

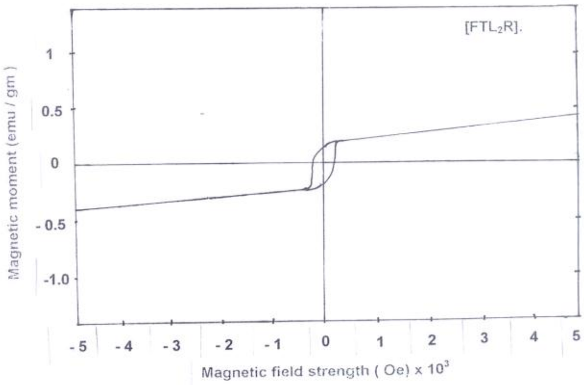

Figure 4: Magnetic Hysteresis at room temperature for sample [FTL_2R]

The type of domains may also be judged from the grain size. The spinels having grain size smaller than 3μm are of single domain type [19] and for grain size larger than 3μm the spinels have multi domain structure [20].

Since these are pseudobrookites the grain size limits are different. However, sample [FTR] may not have domain formation and hence no hysteresis. Since the grain sizes of [FTL_1R] and [FTL_2R] are much larger (19μm), therefore on the basis of the grain size the samples may have multi domain structure. The initial a. c. susceptibility Vs temperature (χ/χ_{rt} Vs T) plots corresponding to samples [FTL_1R] and [FTL_2R] are shown in Figures .5 and 6 respectively.

This and the shapes of curves means N-type Ferrimagnetic behaviour [21] which also means the existence of multi domains. The Curie temperature is around ($T_c \approx 347$ K) which is not well defined and implies the co-existence of multiple curie temperatures. This may be due to the distribution of strength of exchange interaction. The exchange interaction also reduces the space charge considerably. At Curie temperature perhaps the oxygen loss is recovered and the space charge is minimized.

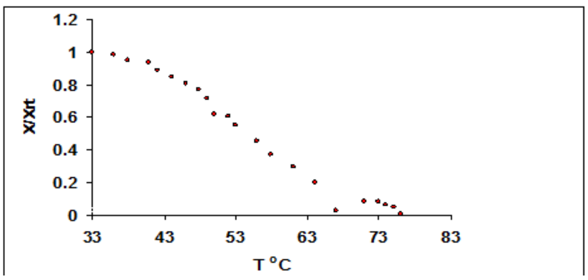

Figure 5: Plot of initial a.c. susceptibility Vs temperature for sample [FTL_1R]

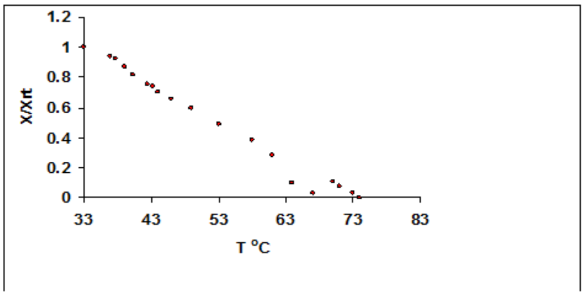

Figure . 6: Plot of initial a.c. suseptibility Vs temperature for sample[FTL_2R]

Therefore the samples [FTL_1R] and [FTL_2R] are soft magnetic (dilute magnetic systems) which is also reflected in the low values of coerceivity H_c and Curie temperature T_c.

Table 3: Magnetic data for samples [FTL_1R] and [FTL_2R].

Samples Sample	Initial a. c. susceptibility χ_i at 300Hz at room temperature emu	Hc Oe	M_S emu / gm	M_R / M_S
[FTL_1R]	0.0041	260	0.44	0.28
[FTL_2R]	0.0032	217	0.40	0.39

3. APPLICATIONS: EXPERIMENTAL:

The samples are investigated for their pressure and gas sensitivity property. For this special type of experimental set up as shown in the Figure 7 and 8 are used. The experimental results are reported in the Table.4.

3.1: Pressure Sensing:

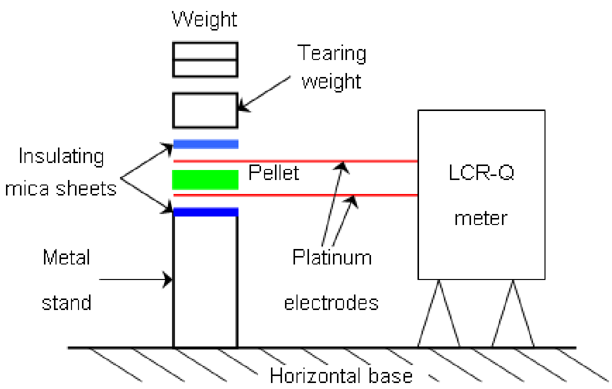

Figure 7: Experimental set up for Pressure sensitivity Measurements.

The effect of pressure on the dielectric and electric parameters of the Pseudobrookite has not been studied so far. In order to investigate the dependence of capacitance of the samples on pressure, the pressure cell [22] Shown in Figure. 7, is used. The pellets are silvered on flat circular faces.

The circular faces of the silvered pellets are sandwiched between platinum foil electrodes. The system is insulated from the surroundings by using thin mica sheets. This system is rested on horizontal base. The pressure (weight/area of pellet) is applied vertically from the top. The measurements are carried out at room temperature in dry air. The pressure applied on the sample is between the range 9000 and 100000 Pa. The capacitance and resistance of the samples are measured at 1 kHz by using Digital LCR-Q meter.

3.2 Gas Sensing:

The experimental set up for measuring the gas sensitivity of the samples is shown in Figure 8. The two-probe capacitance and resistance measurement set up constructed in the laboratory is used to measure the variation of sample capacitance with oxygen gas pressure. Before every cycle of readings, care is taken to clean and polish the electrodes of the sample holder. Prior to the dielectric measurements, the sintered pellets are polished to obtain flat, smooth and parallel surfaces.

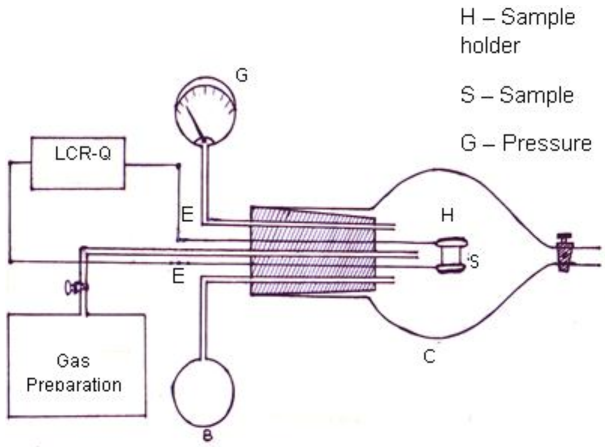

Figure 8. Experimental set up for gas

The two surfaces are converted into electrodes with high purity and the ultra fine silver particle paste, which give OHMIC contacts. Through the chamber, dry gas is passed at different pressures. The pressure of the gas is varied manually between 1 atm. To 1.15 atm. and is measured by pressure gauge. The well-established method in chemical lab is used for the generation of gas. The capacitance and resistance are recorded using Digital LCR-Q meter at 1 kHz at room temperature. From the experimental data we may conclude that the samples [FTL_1R] and [FTL_2R] are sensitive to pressure as well as gas (O_2 and CO_2). These properties are due to the intercalation of "$LiAl^{4+}$", which causes reduction of Fe_2TiO_5 to Fe_2TiO_4 to satisfy its oxygen requirement.

Table . 4: Structural, Magnetic Parameters and Sensitivity of the samples.

Sample	Relative % Intensity of (040) plane	Magnetic moment (emu/g)	Curie Temp. Tc (K)	O_2 Gas Sensitivity		CO_2 Gas Sensitivity		Pressure Sensitivity	
				% ΔC	% ΔR	% ΔC	% ΔR	% ΔC	% ΔR
[FTL_2R]	52.9	0.40	347	-0.5	+8.8	-6.0	+8.9	+2.7	-8.0
[FTL_1R]	45.22	0.44	350	-2.4	+7.8	+2.6	-8.7	+16.6	-19.6
[FTR]	1.6	-	-	-1.5	+4.0	-0.5	+0.9	+1.2	-1.0

The experimental data also reveals that the gas sensitive properties depend on the relative percentage intensity of (040) plane of the pseudobrookite.

4. 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 [FTL_1R] and 52.9 in [FTL_2R].Thus "$(LiAl)^{4+}$" appears to enter the interstices of Fe_2TiO_5. It is termed as the intercalation of "$(LiAl)^{4+}$". It is interesting to note that the intercalation has resulted into the increase in the porosity and the decrease in Debye particle size. From the shape of the hystereses it is concluded that the samples [FTL_1R] and [FTL_2R] possess N-type Ferrimagnetic ordering having the presence of Single Domain + Multi Domain (S.D. + M. D.). However, the magnetic moment is small. The Curie temperature is around ($T_c \approx 347$ K) which is not well defined and implies the co-existence of multiple curie temperatures.

Lastly we may conclude that to get gas sensitive property maximize we have to mainly intercalate the pseudobrookite such that relative percentage intensity of (040) plane is maximize. Whereas the pressure sensitive properties of these materials are mainly depending on their magnetic behaviour.

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