

# Magnetic Behaviour of “Lithiated” $\text{Fe}_2\text{TiO}_5$

Mahadev Anapa MADARE<sup>1</sup>, Sadanand Vitthal SALVI<sup>2</sup>

<sup>1</sup>ICLES' Motilal Jhunjhunwala College, Sector 9A, A. Roye Marg,  
VASHI, NEW MUMBAI 400703

<sup>2</sup>Department of Physics, Institute of Science,  
15, Madame Cama Road, MUMBAI 400 032 INDIA

Received 01.04.2004

## Abstract

$\text{Fe}_2\text{TiO}_5$  shows a spin glass transition at 53 K and is mainly known for its semiconducting nature. A ‘LiAl’ pair is incorporated in  $\text{Fe}_2\text{TiO}_5$  by high temperature solid-state reaction.



The presence and quantity of “LiAl” is confirmed by Inductively Coupled Argon Plasma (IACP) technique. The crystalline geometry is determined by X- ray diffraction and Fourier Transform Infrared (FTIR) spectroscopy of powders. It remains orthorhombic pseudobrookite. Certain reflections of  $\text{Fe}_2\text{TiO}_5$  are observed to enhance progressively with the content of “LiAl”. The magnetic hysteresis parameters are observed to depend on the content of “LiAl”. Initial susceptibility and permeability are measured as a function of temperature. The magnetic order is discussed and explained. It is concluded that the pseudobrookite possesses a ‘spinel like network’, which is strengthened by incorporation of “LiAl”. It produces a weak long-range ferrimagnetic order in place of short-range antiferromagnetic order. Possible applications are discussed in the text.

**Key Words:** Pseudobrookite, Lithiation, Intercalation.

## 1. Introduction

A solid-state reaction between  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  forms the very stable phase  $\text{Fe}_2\text{TiO}_5$  [1]. The presence of  $\text{Fe}^{2+}$  ion is not observed in this phase [2]. Electrically, it is ‘n’ type of semiconductor [3]. This compound has been investigated extensively for its magnetic spin glass behaviour [4-7]. This compound has short-range antiferromagnetic order, which is partly broken by Ti layers, and the compound has a spin glass transition at 53 K [8]. Recently, the compound has been investigated for its large thermal expansion anisotropy [9], thermodynamic equilibrium [10] and crystallographic texture [11]. Pseudobrookite has orthorhombic symmetry [12]. The space group assigned to  $\text{Fe}_2\text{TiO}_5$  by different investigators is either “Bbmm” [11] or “Cmcm” [13]. Recently,  $\text{Fe}_2\text{TiO}_5$  has been observed to exist with monoclinic symmetry (space group C2/c) when annealed at 1570 K [14]. The compound has been used as a photocatalyst [15], a photoelectrode for electrolysis of water [16,17]. Overall one gets an impression that this compound has the potential of wide range of applications.

This has encouraged us to pursue systematic investigation of its electrical, dielectric and magnetic properties. An attempt is made to investigate the effect of lithium aluminium hydride ( $\text{LiAlH}_4$ ) on the compound.

$\text{LiAlH}_4$  is known as a reducing agent. It is proved to reduce and convert  $(\text{NiO}+2\text{MnO}_2)$ ,  $(\text{MnO}_2+\text{Fe}_2\text{O}_3)$  and  $(\text{ZnO}+2\text{MnO}_2)$  into spinels during their respective solid state reactions at  $950^\circ\text{C}$  [18]. However, a large quantity of reducing agent is observed to vaporize. Interestingly, the remaining small quantity of lithium and aluminium in equal equimolar ratio appears to enter into vacant 16c sites of the spinel, similar to lithium intercalation [18]. However, in this case it may be called as “lithium-aluminium intercalation” due to the presence of aluminium. A similar attempt on the stable phase  $\text{Fe}_2\text{TiO}_5$  failed to form the corresponding spinel. However, it has developed interesting magnetic properties. This paper reports the synthesis and magnetic properties of such a “lithiated”  $\text{Fe}_2\text{TiO}_5$ . These characteristics would widen the range of applicability of the compound.

## 1.1. Experimental procedures

$\text{Fe}_2\text{TiO}_5$  was prepared by calcinating a mixture of A. R. grade  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$  (haematite) at  $1000^\circ\text{C}$  for 24 hours followed by homogenization in an agate mortar and again was calcined at  $1000^\circ\text{C}$  for 24 hours. The X- ray diffraction of powdered sample was taken and the formation of pseudobrookite phase was confirmed. Then,  $x$  mole  $\text{LiAlH}_4$  was added to one mole of  $\text{Fe}_2\text{TiO}_5$  (where  $x = 0.50, 0.75$  and  $1.00$ ). A homogeneous mixture is heated at low temperature to decompose  $\text{LiAlH}_4$  inside the sample. Then, the mixture is calcined at  $1000^\circ\text{C}$  for 24 hours. The samples are labeled and referred as  $S_{50}$ ,  $S_{75}$  and  $S_{100}$  respectively. The presence and the quantity of “LiAl” in these samples, was confirmed by chemical analysis using Inductively Coupled Argon Plasma (ICAP) technique. “LiAl” remaining with the sample is observed to be  $x = 0.20, 0.30$  and  $0.40$  mole respectively having Li Al in 1:1 atomic proportion

The initial susceptibility ( $\chi_i$ ) of all the samples in powder form was measured as function of temperature by a double coil set up [19] generating an alternating field of 5 oersted at 300 Hz. On the other hand, the initial permeability ( $\mu_i$ ) was measured on APLAB LCR-Q meter, by winding 100 turns on the pelletized sample in the toroidal form. The initial permeability was calculated by using the relation,

$$\mu_i = L/[0.0046N^2h \log(d_2/d_1)]$$

Where  $L$  is the inductance in  $\mu\text{H}$ ,  $d_1$  and  $d_2$  is inner and outer diameters respectively of the sample in the toroidal form and  $h$  is the height of the toroid in inches. The variation of initial permeability was investigated as a function of temperature.

The saturation magnetization of the pseudobrookite sample was determined by using an alternating current electromagnetic type hysteresis loop tracer. It mainly consists of an electromagnet, a pick coil system, balancing and integrating circuits and pre-amplifier. The details of this method are given elsewhere [20].

## 2. Results and Discussion

### 2.1. Location of “LiAl” in lattice

In order to determine the origin of the ferrimagnetic order in the samples, the investigation of their structural nature is thought worthwhile. The equal atomic presence of Li and Al after the reaction process enhances the probability of lattice/interstitial sites by “LiAl” as a pair particularly on the grain boundary. The XRD analysis of the “lithiated” samples indicates that they too are pseudobrookite with orthorhombic symmetry. However, the content of “LiAl” in the sample appears to increase the anisotropy (i.e. octahedral distortion) as suggested by the decrease in lattice parameters ‘a’ and ‘b’ and increase in the value of ‘c’ (Table 1). This may be explained as follows: The ionic radius corresponding to  $(\text{LiAl})^{4+}$  ion would certainly be greater than that of  $\text{Ti}^{4+}$  ion. This implies two things: i) $(\text{LiAl})^{4+}$  ion substitutes  $\text{Ti}^{4+}$  ion along the  $c$  axis which is the easy magnetic axis of the pseudobrookite and ii) the difference between ionic radii of  $(\text{LiAl})^{4+}$

and  $\text{Fe}^{3+}$  ions is larger than that between ionic radii of  $\text{Ti}^{4+}$  and  $\text{Fe}^{3+}$  ions. This causes more distortion in octahedra and decrease in the value of ‘a’ as observed [12]. However, it is interesting to note that certain reflections corresponding to the pseudobrookite phase become increasingly stronger as the content of “LiAl” increases [Table 2b]. Many of them exist in  $\text{Fe}_2\text{TiO}_5$  as weak reflections. These reflections correspond to spinel phase as indicated in Table 2b. However, the densities in xylene of all the samples are around 4.2 g/cc. Hence, the formation of heavier spinels (theoretical density  $\sim 4.76$  g/cc) such as  $\text{LiFe}_5\text{O}_8$  or  $\text{Fe}_2\text{TiO}_4$  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 content. That  $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$  reduction by incorporation of “LiAl” is unlikely would be made clear later.

**Table 1.** Data showing effective carrier concentration, room temperature conductivity and particle size.

Sample	Assumed cation distribution on 4c sites	Concentration of donors	Concentration of acceptors (2Li content)	Effective carrier concentration and type	d. c. conductivity $\times 10^{-6}$ mho- $\text{m}^{-1}$	Particle size $\text{\AA}$
S <sub>00</sub>	Fe <sub>0.67</sub> Ti <sub>0.33</sub>	0.33	0.00	0.33(n)	3.45	305
S <sub>50</sub>	Fe <sub>0.67</sub> Ti <sub>0.13</sub> (LiAl) <sub>0.20</sub>	0.13	0.40	0.27(p)	4.20	544
S <sub>75</sub>	Fe <sub>0.67</sub> Ti <sub>0.03</sub> (LiAl) <sub>0.30</sub>	0.03	0.60	0.57(p)	6.10	485
S <sub>100</sub>	Fe <sub>0.67</sub> Ti <sub>0.00</sub> (LiAl) <sub>0.33</sub>	0.00	0.66	0.66(p)	14.00	364

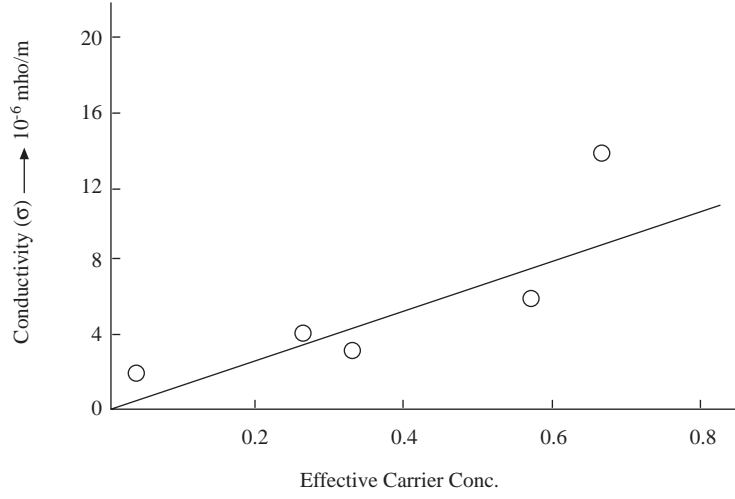
If (LiAl)<sup>4+</sup> ion replaces Ti<sup>4+</sup> ion, then the question arises about which of the two octahedral (8f and 4c) sites of  $\text{Fe}_2\text{TiO}_5$  would it prefer. In this connection it is interesting to note that the cation distribution in  $\text{Fe}_2\text{TiO}_5$  is given as  $[(\text{Fe}_{0.67}^{3+}\text{Ti}_{0.33}^{4+})_{4c}(\text{Fe}_{1.33}^{3+}\text{Ti}_{0.67}^{4+})_{8f}]$  [21]. Due to the random distribution of cations [22], Ti<sup>4+</sup> ion acts as a donor in  $\text{Fe}_2\text{TiO}_5$ . If the entire quantity of the LiAl replaces Ti on 4c sites, then acting as an acceptor, Li ion compensates the donor (Al<sup>3+</sup> ion does not contribute to the  $\text{Fe}^{3+}$  lattice due to having the same valency). On the basis of this model the carrier densities are calculated [23], and are compared with the corresponding d.c. conductivities (Table 1). The linearity of the plot (Figure 1) suggests that most of the (LiAl)<sup>4+</sup> substitutes Ti<sup>4+</sup> on 4c sites.

**Table 2a.** Lattice parameters for the S<sub>00</sub>, S<sub>50</sub>, S<sub>75</sub> and S<sub>100</sub> samples.

SAMPLE	a $\text{\AA}$	b $\text{\AA}$	c $\text{\AA}$
S <sub>00</sub>	3.729	9.782	9.980
S <sub>50</sub>	3.727	9.806	9.985
S <sub>75</sub>	3.706	9.672	9.990
S <sub>100</sub>	3.701	9.583	10.107

**Table 2b.** XRD data showing reflections corresponding to spinel phase in pseudobrookite phase

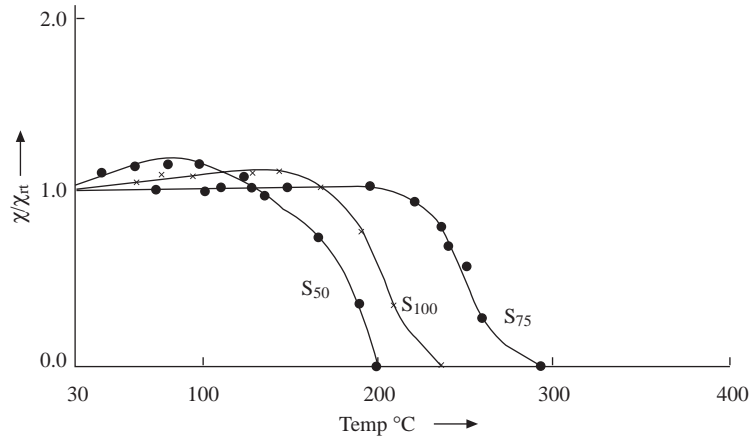
$d_{obs}$ in $\text{\AA}$				Percentage Intensity				For spinel phase $d_{cal}$ in $\text{\AA}$				
S <sub>00</sub>	S <sub>50</sub>	S <sub>75</sub>	S <sub>100</sub>	S <sub>00</sub>	S <sub>50</sub>	S <sub>75</sub>	S <sub>100</sub>	hkl	S <sub>00</sub>	S <sub>50</sub>	S <sub>75</sub>	S <sub>100</sub>
2.859	2.927	2.912	2.921	7	9	29	46	220	2.920	2.932	2.918	2.921
2.454	2.501	2.489	2.491	27	23	76	100	311	2.490	2.509	2.489	2.491
—	2.070	2.066	2.065	—	8	23	30	400	—	2.073	2.064	2.066
1.662	1.659	1.684	1.687	12	14	15	18	224	1.690	1.690	1.685	1.687
1.421	—	1.456	1.463	9	—	27	44	440	1.460	—	1.459	1.461



**Figure 1.** Plot of Carrier Concentration versus A. C. Conductivity ( $\sigma$ ) at Room Temperature at 1 MHz.

## 2.2. Initial susceptibility

$\text{Fe}_2\text{TiO}_5$  (sample  $S_{00}$ ) does not exhibit any initial susceptibility. This is attributed to its antiferromagnetic nature at ambient temperature (Curie temperature  $\sim 650$  K [24]). However, all “lithiated” pseudobrookite possessed initial susceptibility. Their room temperature values increase in  $\chi_i(S_{50}) < \chi_i(S_{75}) < \chi_i(S_{100})$  order. They exhibit the Curie temperature (Figure 2). This is probably a ferrimagnetic behaviour. The rounded nature of the curve (that is the presence of a dome) for  $S_{50}$  is attributed to a large number of single domains [25]. The curves corresponding to  $S_{75}$  and  $S_{100}$  are flat, and show a long tail around Curie temperature. These samples, therefore, may also have a substantial number of multidomain grains [26].



**Figure 2.** Plot of Normalized Susceptibility versus Temperature.

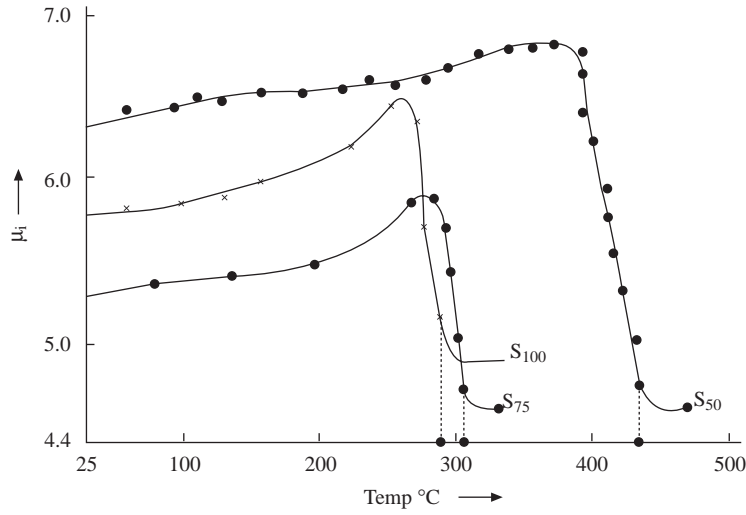
## 2.3. Initial permeability

Also for  $\text{Fe}_2\text{TiO}_5$  ( $S_{00}$ ) sample permeability is not observed. The room temperature permeability increase in  $\mu_i(S_{75}) < \mu_i(S_{100}) < \mu_i(S_{50})$  order. The variation of initial permeability versus temperature is shown in Figure 3. It shows that the initial permeability increase slowly, forms a small peak just before the Curie temperature and falls rapidly beyond the Curie temperature. The peak becomes more pronounced and fall is more rapid with the content of “LiAl” in the sample (Figure 3). The presence of peak is indicative of changing sign of anisotropy constant near Curie temperature and its height indicates the rapidity with which

it changes. Thus overall, one gets an impression that anisotropy is on the rise with the “LiAl” content as suggested earlier from the structural data. The Curie temperature obtained from the initial susceptibility and initial permeability curves are compared in Table 3.

**Table 3.** Data showing curie temperature for lithium ferrite  $S_{50}$ ,  $S_{75}$  and  $S_{100}$  samples.

Sample	Curie Temperature	
	From susceptibility	K From permeability
$\text{LiFe}_5\text{O}_8$	890	—
$S_{50}$	471	708
$S_{75}$	568	581
$S_{100}$	519	568



**Figure 3.** Plot of initial permeability versus temperature.

Both the initial susceptibility and initial permeability are dependent on the magnitude, direction [27] and frequency [28] of the applied magnetic field. The principle used in the experimental technique is also an important factor. A powdered sample was used for the measurement of the initial susceptibility; on the other hand a toroid was used while measuring initial permeability. In view of these factors, a strict comparison of the present curves (Figure 3) and Curie temperatures (Table 3) is not possible. The strict comparison is not possible also due to the possibility of randomness of location of “LiAl” in different samples. However, it is interesting to note that the Curie temperatures from the initial permeability are on the higher side in each case (Table 3). This may be due to the preferred orientation retained in the toroids. In  $S_{50}$ , such an orientation may be substantial causing a large difference between Curie temperatures of  $S_{50}$  (Table 3).

However, one may logically conclude that, inside the sample:

1. LiAl pair is likely to substitute  $\text{Ti}^{4+}$  ion particularly on the grain boundary and generates a ferrimagnetic order.
2. Domains are separated by the layers of non-magnetic Ti ions.
3. Initially, for smaller LiAl content, domains are magnetically weak yet large in size. The short-range ferrimagnetic order is sandwiched between non-magnetic Ti layers may serve as a thick domain wall. This creates a single domain like situation.

4. As the LiAl content increases, the number of ferromagnetic multidomains increases. The nonmagnetic Ti layers may act as thin domain walls. The increasing number of multidomains is known to increase Curie temperature [29]. In the present system, the presence of single domain, multidomains and their preferred orientation will decide Curie temperature.

## 2.4. Magnetic hysteresis

As a further confirmation, the hysteresis of the samples in the pellet form was studied at 50 Hz applying large fields. The corresponding parameters are included in Table 4. The small value of  $H_c$  is indicative of a soft ferrite. As has been indicated earlier from the study of initial susceptibility and initial permeability,  $S_{50}$  has the least anisotropy and the stronger SD nature. However, in both  $S_{75}$  and  $S_{100}$  a MD formation is indicated and anisotropy is maximum for  $S_{100}$ . Hence, larger  $H_c$  for  $S_{100}$  may be due to increasing part of wall energy.

**Table 4.** Magnetic data for  $S_{50}$ ,  $S_{75}$  and  $S_{100}$  samples.

sample	$M_s$	$H_c(\text{Oe})$	$M_R/M_s$	$\eta_{\beta}$ calculated from $\text{LiFe}_5\text{O}_8$ formation	$\eta_{\beta}(\text{observed})$
$S_{50}$	6	67	0.63	0.67	0.09
$S_{75}$	9	59	0.70	0.67	0.13
$S_{100}$	8	94	0.68	0.67	0.11

The small magnitude of saturation magnetization ( $M_s$ ) and number of unpaired electrons ( $\eta_{\beta}$ ) show that it is weak magnetic system. The data is compared with that of spinels, which possibly form in the system.

The only magnetic spinel, likely to form in this sample is  $\text{LiFe}_5\text{O}_8$ . However, there is equal presence of Li and Al. Moreover, the Curie temperature of Lithium Ferrite is 890 K, which is much larger than the Curie temperature determined for our samples (Table 3). Further, the number of unpaired electrons is 2.5 in  $\text{LiFe}_5\text{O}_8$ . Had  $\text{LiFe}_5\text{O}_8$  been formed in these samples, the corresponding number of unpaired electrons on 4c sites would have been 0.67, 0.67, 0.67 respectively for  $S_{50}$ ,  $S_{75}$  and  $S_{100}$ . However, the measured number of unpaired electrons is much smaller (Table 4). These facts rule out the possibility of the formation of  $\text{LiFe}_5\text{O}_8$ .

$\text{Fe}_2\text{TiO}_4$  is another spinel of interest. It is paramagnetic above its Curie temperature 142 K [29]. Both, the magnetic moment and Curie temperature of  $\text{Fe}_2\text{TiO}_4$  do not match with the values observed for our samples. Hence, it is concluded that  $\text{Fe}_2\text{TiO}_4$  spinel phase is also not formed in our samples

At low field, the magnetization increases by the shifting of domain walls. From the  $\chi_i$  data, domain wall movement is in  $\chi_i(S_{50}) < \chi_i(S_{75}) < \chi_i(S_{100})$  order at 300 Hz. However, from  $\mu_i$  data the domain wall movement is in  $\mu_i(S_{75}) < \mu_i(S_{100}) < \mu_i(S_{50})$  order at 1 kHz. Thus between the two MD samples, the wall movement becomes faster in  $S_{100}$  than in  $S_{75}$  when the applied frequency is changed from 300 Hz to 1 kHz.

## 3. Conclusion

It is concluded that the long range antiferromagnetic like order, which is partly broken by Ti layers in  $\text{Fe}_2\text{TiO}_5$ , is revived and rendered ferromagnetic by LiAl pair replacing by Ti. This strengthens the spinel like network, which is responsible for magnetic properties of these materials.

## References

- [1] S. Akimoto, T. Nagata and T. Katsura, *Nature*, **37**, (1957), 179.

- [2] E. Gurewitz and U. Atzmony, *Phys. Rev.*, **B26**, 11, (1982), 6093.
- [3] R. S. Singh, T. H. Ansari, R. A. Singh, B. M. Wanklyn and B. E. Watt, *Solid State Commun*, **94**, 12, (1995), 1003.
- [4] J. K. Srivastava, J. Hammann, K. Asai and K. Katsumata, *Phys. Lett. A*, **149**, 9, (1990), 485.
- [5] J. K. Srivastava, S. Moromoto and A. Ito, *Hyperfine, Inter*, **54**, (1990), 717.
- [6] R. L. Lichi and S. Kumar, *J. Appl. Phys.*, **63**, (8), (1988), 4351.
- [7] J. L. Tholence, Y. Yeshurun and B. Wanklyn, *Solid State Phys.*, **19**, (1986), 235.
- [8] K. Iwauchi and Y. Ikeda, *Phys Stat. Sol.*, **119**, (1990), K71.
- [9] S. W. Paulik, M. H. Zimmerman, K. T. Faber and E. R. Fuller Jr, *J. Mater. Res.*, **11**, 11, (1996), 2795.
- [10] E. Gunner, A. D. Petton, E. Woermann and A. Ender, *Ber Bun Phys. Chem.*, **100** 11, (1996), 1839.
- [11] M. H. Zimmermann, K. T. Faber, E. R. Fuller Jr., K. L. Kruger and K. J. Bowman, *J. Am. Ceram. Sc.*, **79**, (5), (1996), 1389.
- [12] G. Bayer, *J. Less-Common Metals*, **24**, (1971), 129.
- [13] M. Drogenik, L. Golic, D. Hanzel, V. Krasevec, A. Prodon, M. Blakker and D. Kolar, *J. Solid State Chem.*, **40**, (1981), 47.
- [14] D. Cordischi, N. Burriesci, F. D'Alba, M. Petrera, G. Polizzotti and M. Schiavello, *J. Solid State Chem.*, **56**, (1995), 182.
- [15] G. S. Ginley and M. A. Butler, *J. Appl. Phys.*, **48**, (5), (1977), 2019.
- [16] G. S. Ginley and R. Boughman, *J. Mater. Res. Bull*, **11**, (1976), 1539.
- [17] M. R. Parab and S. V. Salvi, *Turkish J. Phys.*, (in press).
- [18] T. R. McGuire and F. S. Ferebee, *J. Appl. Phys.*, **34**, (1963), 1821.
- [19] C. Radhakrishnamurthy, S. D. Likhite and P. W. Sahastrabudhe, *Proc. Ind. Acad., Sci.*, **87A**, (1978), 245.
- [20] D. A. Kharmov, M. A. Glazkova, V. Tu. Negy, S. S. Meshalkin, S. S. Urugov, N. S. Ovanesyan, S. S. Rusakov, *J. Magn. Magn. Mater.*, **150**, (1995), 101.
- [21] U. Atzmony, E. Gurewitz, M. Melmud, H. Pinto, H. Shaked, G. Gorodetsky, E. Hermon, R. M. Hornreich, S. Shtrikman and B. Wanklyn, *Phy. Rev. Lett.*, **43**, 11, (1979), 782.
- [22] M. A. Madare and S. V. Salvi, *Ind. J. Phys.*, **84A**, 4, (2001), 363.
- [23] C. Radhakrishnamurthy and N. G. Nandikar, *Pramana*, **13**, (1979).
- [24] U. Atzmony, G. Gorodetsky, E. Gurewitz, E. Hermon, R. M. Hornreich, M. Melamud, H. Pinto, H. Shaked, S. Shtrikman and B. Wanklyn, *J. Mag. Mag. Mater.*, **15**, (1980), 115.
- [25] S. V. Kakatkar, S. S. Kakatkar, R. S. Patil, A. M. Sankpal, N. D. Choudhary, P. K. Maskar, S. S. Suryawanshi and S. R. Sawant, *Mat. Chem and Phys.*, **46**, (1996), 96.
- [26] R. M. Bozorth Ferromagnetism, *D. Von. Nostrand Co. Inc.*, (1951), 489.
- [27] G. T. Rado, R. W. Wright and W. H. Emerson, *Phys Rev.*, **80**, (1950), 273.
- [28] I. Yoshikaza, S. Yasuhiko and S. Shoichi, *Ferrites Proc. International Conf.*, July 1970, Japan.
- [29] C. Radhakrishnamurthy, "Magnetism and Basalt", *Memoir*, 26, Geographical Society of India, 40, (1993).