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Investigation of Effect of Sintering Temperature / Phase on Electrical Properties of Iron Titanates

Dr. Sandesh. Suryakant Gurav

Head Department of Physics K.E.S.Anandibai Pradhan Science College, Nagothane,
Tal.Roha, Dist-Raigad, Maharashtra State, India

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Abstract: It has been observed that the semiconducting metal oxides and / mixed metal oxides show changes in the electrical properties with sensitivity to humidity and / or various gases .Therefore attention of the research workers in solid state physics has been attracted towards the semiconducting oxide environmental sensors due to the growing concern towards the pollution control. Iron titanium oxides have received considerable attention as possible electrode materials for photo electrolysis of water. Also they are of interest to geologists, being the primary ceramics of rock magnetism. Recently, Fe_2TiO_5 has attracted attention due to its thermal expansion anisotropy and spontaneous microcracking. However, the data on its electrical transport as well as dielectric properties of this is scarce. . Electrical properties as a function of temperature and relaxation spectra are discussed in this paper. At temperatures 1000^0C and 1250^0C samples of Fe_2TiO_5 using rutile and anatase titanium oxide are sintered. Ceramic technique is used to synthesize these samples. The XRD and FTIR techniques are used for the confirmation of pseudobrookite phase of the samples. All the samples have orthorhombic structure. Relaxation spectra showed the space-charge, which is higher for higher sintering temperature for the sample prepared from rutile TiO_2. The sample prepared from anatase TiO_2 has lower dielectric and electric properties at low frequency (1kHz). The parameters such as dielectric constant, dielectric loss and resitivity are discussed and analysed on the basis of structural changes.

Keywords: *Iron Titanate, Phase, Resistivity, Order Parameter.*

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I. INTRODUCTION

A stable phase of Fe_2TiO_5 is formed by solid-state reaction between Fe_2O_3 and TiO_2 [1]. This compound exhibits magnetic spin glass behaviour [2]. The short range antiferro-magnetic order is rendered by Ti layers and above 650 K it is destroyed [3,4]. Also for thermal, thermodynamic and crystallographic properties Fe_2TiO_5 has been investigated [5,6,7]. Orthorhombic or monoclinic phases are observed in this compound [8]. The random distribution of Fe^{3+} and Ti^{4+} ions in M1 and M2 sites which are octahedral makes this compound electrically an n-type semiconductor [9]. Many factors such as the sintering temperature, allotropes and purity of the starting materials used to synthesize Fe_2TiO_5 are likely to affect the cation distribution, randomization of this distribution, distortion and therefore the physical properties. TiO_2 has three different allotropes, (i) anatase, (ii) rutile and (iii) brookite [10]. The rutile form is stable at all temperatures and pressures up to 60 k bar whereas other two forms are metastable. On heating irreversible transformation from anatase to rutile takes place and the enthalpy is as low from -1.3 to -6.0 kJ / mol [10]. Kinetically, at room the transformation of the anatase into the rutile does not occur and required temperature varies, it depends on many factors such as atmosphere, purity of material, stoichiometry, particle size , area of the surface, surface defects [11].

II. EXPERIMENTAL

The A. R. grade α-Fe_2O_3, rutileTiO_2 fine powders were throughly mixed and mixture was first presintered at 950^0C for 24 hours. The presinterd mixture was homogenized in a mortar and then sintered at 1000^0C for 24 hours. By similar method another mixture of α-Fe_2O_3, anatase TiO_2 was prepared . Finally the mixtures are sintered at 1250^0C for 24 hours. The samples are labeled as $[FTR]_{1000}$, [FTR] and [FTA]. By X-ray diffraction these samples are analysed . LCR-Q meter was used at frequency 1 kHz to measure a.c. resistivity, Dielectric constant (K') and dielectric loss (K") within the range of temperature 300K-850K. Also, LCR-Z meter was used to measure K' and K" at room temperature in the frequency range 10 kHz-1000 kHz.

III. RESULTS AND DISCUSSION

A. Electrical Properties

The room temperature d. c. resistivities ($\rho_{d.c}$) which correspond to the grain boundary are much larger than their corresponding a. c. resistivities ($\rho_{a.c}$) implying the insulating nature and the presence of microcracks on the grain boundary (Table 1). The room temperature d. c. resistivities ($\rho_{d.c}$) which correspond to the grain boundary are much larger than their corresponding a. c. resistivities ($\rho_{a.c}$) implying the insulating nature and the presence of microcracks on the grain boundary (Table 1).

Table 1: Inhomogeneity, Space charge, Loop area of $\rho_{a.c}$ hysteresis, Room **temperature a. c. and d. c. resistivities, , Transition temperatures, Activation energies and Band gap.**

Sample	**Inhomo-geneity**	**Space charge K'_{1kHz} - K'_{1MHz}**	**Loop Area of ρ_{ac} hysteresis Sq. Units**	**ρ_{ac} (1kHz) KΩm**	**ρ_{dc} KΩm**	**Transition temperature (K)**		**Activation Energy (eV)**			**Band gap (eV) (430K-525K)**
						T_1	**T_2**	**Ea_1 (335K-430K)**	**Ea_2 (430K-525K)**	**Ea_3 (525K-850K)**	
[FTA]	-0.0038	791	17	849	1040	400	710	0.22	0.45	0.80	0.90
$[FTR]_{1000}$	-0.012	357	2.71	700	5835	335	525	0.25	0.69	0.40	1.38
[FTR]	-0.002	3331	1.17	5.5	6565	400	710	0.14	0.38	0.73	0.76

The very small values of a. c. resistivities ($\rho_{a.c}$) highlight the presence of large carrier concentration inside the grain. There is a strong correlation between a. c. resitivity ($\rho_{a.c}$) and space charge as well as inhomogeneity. Also the ($\rho_{a.c}$) is the most for the anatase sample $[FTA]_{1250}$ which has the least space charge contribution. Therefore, it is concluded that the a. c. resistivity ($\rho_{a.c}$) corresponds mainly to the space charge.

B. Measurement of A. C. Resistivity (1 Khz) With Temperature :

The variation of a. c. resitivity with temperature in the range 300 to 850 K for the samples is measured at 1 kHz frequency. The log ($\rho_{a.c}$) Vs 1/T plots in the Figures 1,2 and 3 correspond to $[FTR]_{1000,}$ [FTR] and [FTA] respectively. The two temperatures T_1 (335-400 K) and T_2 (525-710 K) attributed to extrinsic-intrinsic and antiferro-paramagnetic transition [4] are shown in the curve. Table1 shows three distinct activation energies as (Ea_1), (Ea_2) and (Ea_3) corresponding to the three temperature regions. Ea_1 (335K-430K) occurs near room temperature and likely to correspond to the extrinsic conduction from impurities by polaron hopping [9,16].

Ea_2 (430K-525K), therefore corresponds to the intrinsic conduction giving a band gap of the order of 1 -1.4 eV. This agrees well with the earlier reports [9,16, 17]. There is a third activation energy Ea_3 (525K-850K). The transition from Ea_2 to Ea_3 occurs (Table 1) round a temperature T_2 (525-710 K) at which antiferromagnetic ordering breaks [4]. Therefore, this activation energy corresponds to the paramagnetic samples.

It is Interesting to note that $[FTR]_{1000}$ exhibits thermal antihysteresis in the log ($\rho_{a.c}$) Vs 1/T plot. Its cation distribution implies the possibility of the coexistence of two species namely fully disordered and fully (normal/ inverse) ordered adjacent to one another, which may activate the tunneling effect [18] giving rise to antihysteresis. It is also interesting to note that $Ea_3 < Ea_2$ for this sample (Table1). The loop area of thermal hysteresis of a. c. resistivity ($\rho_{a.c}$) is the largest for the sample [FTA]. The magnitudes of loop area corresponding to the dielectric and resistivity hystereses follow the same trend. Therefore, it is concluded that the origin of both the dielectric and resistivity hystereses lies in the presence of microcracks.

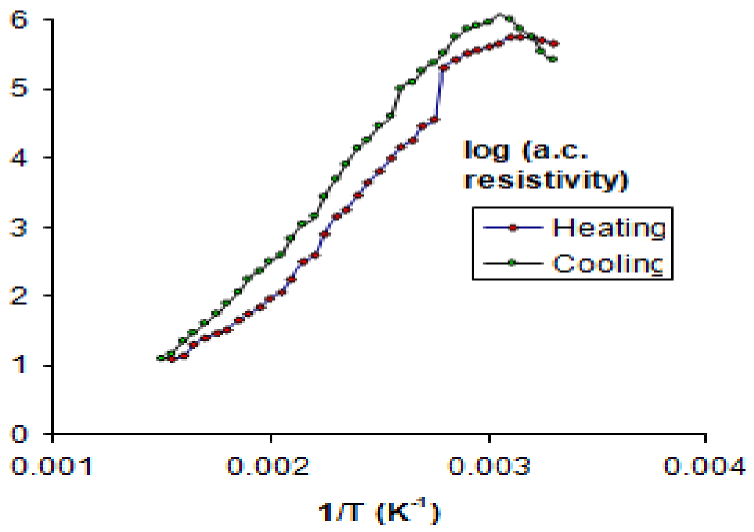

Figure 1 : Plot of A. C. Resistivity Vs Reciprocal of Temperature For sample $[FTR]_{1000}$

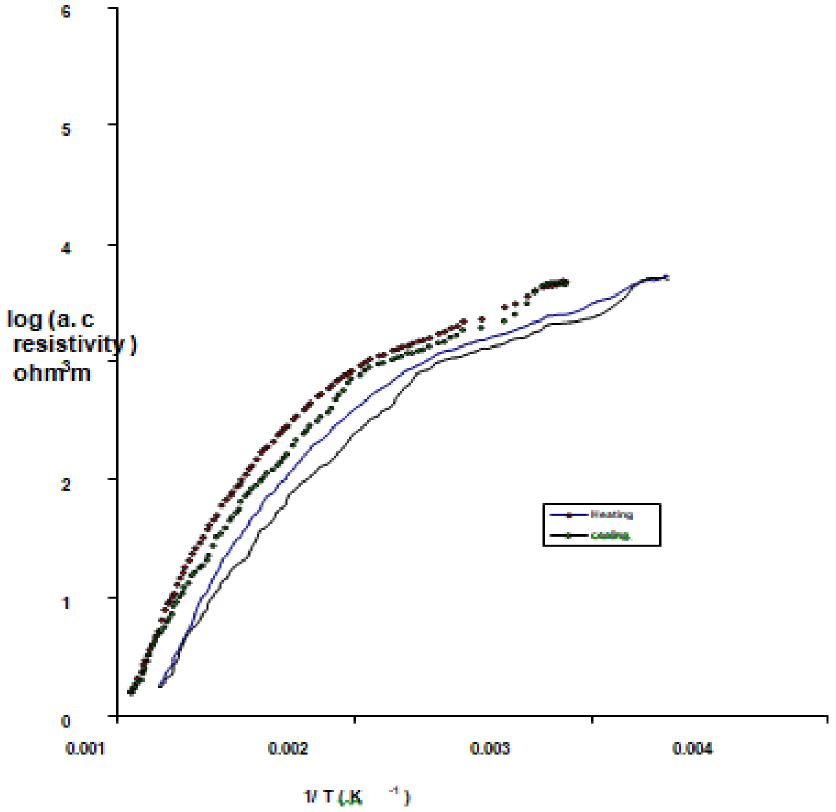

Figure 2: Plot of A. C. Resistivity Vs Reciprocal of Temperature (1/ T) for sample [FTR]

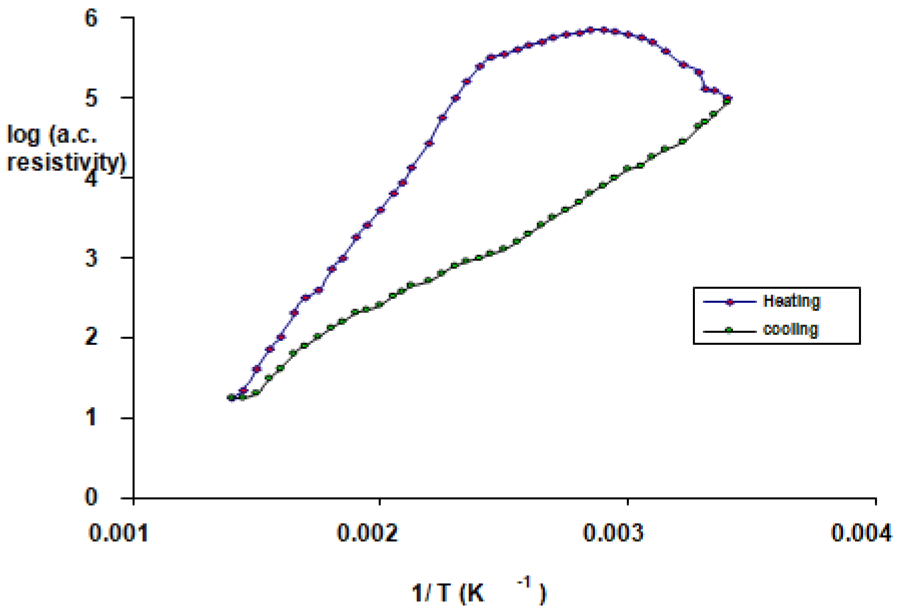

Figure 3: Plot of A. C. Resistivity Vs Reciprocal of Temperature for sample [FTA]

C. The Correlation Between Structural, Dielectric And Electrical Parameters:

A very interesting picture emerges out in the case of Fe_2TiO_5. The Fe^{3+} always prefers a lower i. e. tetrahedral symmetry. At the same time it prefers an octahedral bonding. A Fe_2TiO_5 has two octahedral sites and therefore Fe^{3+} is capable of entering into any one of these sites. However, due to its preference for tetrahedral symmetry it distorts the octahedral site. The two octahedral sites of Fe_2TiO_5 being adjacent will have the opposing effect. Therefore, an order parameter is defined as,

λ = Fe^{3+} on M2 site - Fe^{3+} on M1 site.

when Fe^{3+} on M2 site = 1.5 and Fe^{3+} on M1 site = 0.5, the structure is fully symmetric ($\lambda_o = 1$).

Therefore for inverse ordered cation distribution $\lambda' = (\lambda - \lambda_o)^2$

Therefore, the order parameter corresponding to the ordered cation distribution

$[Ti_1]\ [Fe_2]\ O_5$ is $\lambda = 1$.

Similarly, corresponding to the inverse ordered cation distribution $[Fe_1]\ [Fe_1\ Ti_1]\ O_5$ is $\lambda' = 1$.

Table 2: The correlation between structural, Dielectric and Electrical parameters.

Sample	**Order Parameter λ'**	**Space Charge**	**Inhomo-geneity**	**Loop area of K' hysteresis (Sq. Units)**	**Loop area of $\rho_{a.c}$ hysteresis (Sq. Units)**	**$\rho_{a.c}$ (KΩm)**	**$\rho_{d.c}$ (KΩm)**
[FTA]	0.04	791	-0.0038	4.00	17.00	849	1040
$[FTR]_{1000}$	0.14	357	-0.012	3.83	2.71	700	5835
[FTR]	0.31	3331	-0.002	3.02	1.17	5.5	6565

It is clear from the Table 2 that as the order parameter **(λ')** increases there is lowering of tetrahedral symmetry which results into increase in d. c. resistivity ($\rho_{d.c}$) and space charge and decrease in a. c. resistivity ($\rho_{a.c}$), loop area of K' hysteresis, loop area of $\rho_{a.c}$ hysteresis and inhomogeneity. A strong correlation between $\rho_{a.c}$ and space charge shows that the conduction is mainly due to the space charge.

IV. CONCLUSIONS

The comparison of sample [FTR] with sample $[FTR]_{1000}$ shows that, the Debye particle size and densities increase with the increase in the sintering temperature and inhomogeneity, porosity decrease. In short, growth of material improves with the sintering temperature. The higher sintering temperature also causes more Fe^{3+} to go to M1 site lowering its symmetry.

At higher sintering temperature (1250°C) the dielectric constant has increased about nine times. It is also observed that dielectric loss has increased about three times.

When [FTR] is compared with anatase sample [FTA], it is observed that the use of anatase increases inhomogeneity, porosity, Debye particle size, room temperature a. c. resistivity and the dipolar contribution at high frequencies and decreases densities. The cation distribution shows that in [FTA] Fe^{3+} prefers M2 site lowering its symmetry, which results into the increase in volume.

The sample $[FTR]_{1000}$ exhibits thermal antihysteresis in the log ($\rho_{a.c}$) Vs 1/T plot. Its cation distribution implies the possibility of the coexistence of two species namely fully disordered and fully (normal/ inverse) ordered adjacent to one another, which may activate the tunneling effect giving rise to antihysteresis. It is interesting to note that $Ea_3 < Ea2$ for this sample.

The loop area of thermal hysteresis of resistivity ($\rho_{a.c}$) is the largest in case of the sample [FTA]. It is observed that as the order parameter **(λ')** increases there is lowering of tetrahedral symmetry which results into increase in d. c. resistivity ($\rho_{d.c}$), space charge and decrease in a. c. resistivity ($\rho_{a.c}$), loop area of K' and $\rho_{a.c}$ hysteresis and inhomogeneity. A strong correlation between $\rho_{a.c}$ and space charge shows that the conduction is mainly due to the space charge. The magnitudes of loop area corresponding to the dielectric and resistivity hysteresis follow the same trend. Therefore, it is concluded that the origin of both the dielectric and resistivity hysteresis lies in the presence of microcracks and the sintering temperature reduces microcracking whereas the use of anatase widens microcracks.

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