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EFFECT OF TEMPERATURE AND PHASE ON PROPERTIES OF METAL PSEUDOBROOKITE

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ABSTRACT

Iron titanate is a metal pseudobrookite, which exhibits many interesting properties such as spin glass behaviour, thermal microcracking, magnetic texture and high resistivity. The polycrystalline pseudobrookite has wide range of applications. This communication presents the comparative study of electrical resistivity and dielectric properties as a function of temperature and relaxation spectra of pure iron titanates prepared by using rutile form of titanium oxide and sintered at two temperatures viz. 1000°C and 1250°C and also prepared at 1250°C using anatase form of titanium oxide.

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 as pseudobrookite having orthorhombic unit cell.

The analysis of the relaxation spectra establishes the presence of space-charge, which increases with the sintering temperature for the pseudobrookite prepared from rutile TiO_2. Also the analysis shows that the pseudobrookite prepared from anatase TiO_2 has lower dielectric and electric properties at low frequency (1 kHz) and shows pronounced hysteresis indicating lower microcrack healing. The changes in the resistivity, dielectric constant and dielectric loss are discussed and analysed on the basis of structural changes.

Key words: Pseudobrookite, Electrical properties, Dielectric properties.

INTRODUCTION

A solid state reaction between Fe_2O_3 and TiO_2 forms the very stable phase Fe_2TiO_5[1]. Electrically, it is an n-type semiconductor[2]. This is mainly due to the random distribution of Fe^{3+} and Ti^{4+} ions $[(Fe^{3+}_{0.67}\ Ti^{4+}_{0.33})_{4c}\ (Fe^{3+}_{1.33}\ Ti^{4+}_{0.67})_{8f}]$ among two octahedral sites (viz. 8f and 4c) where Ti^{4+} ion acts as donor. This compound exhibits magnetic spin glass behaviour[3].

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The antiferromagnetic order is rendered short range by Ti layers and the compound has spin glass transition at about 55 K. This antiferromagnetic order is finally destroyed above 650 K. This compound has also been investigated for large thermal expansion anisotropy[4] thermodynamic equilibrium[7] and crystallographic texture[8]. This pseudobrookite exists in a orthorhombic or monoclinic phase[5]. TiO_2 exists in three different forms; anatase, rutile and brookite. Rutile is the stable form while the other two are meta stable. Anatase on heating transforms irreversibly to rutile. This transformation does not have a transformation temperature since there is no phase equilibrium involved. This transformation temperature varies, which strongly depends on many factors such as presence of impurity, deviation of stoichiometry, surface area, particle size, atmosphere, etc. Impurities having inhibiting action are chloride, sulphate and fluoride, whereas transition metal oxides like Fe_2O_3, CuO, MnO_2, etc. have accelerating power[6]. Fe_2TiO_5 compound has the potential of a wide range of applications such as photocatalyst[10] and photoelectrode for electrolysis of water[11,12]. This has encouraged us to pursue systematic investigation of electrical and dielectric properties of pure Fe_2TiO_5 prepared from rutile and anatase TiO_2 and sintered at two temperatures viz. 1000°C and 1250°C. These characteristics would increase the range of applications of the compound.

EXPERIMENTAL

The mixture of fine powders of A.R.grade α-Fe_2O_3, rutile TiO_2 was first presintered at 950°C for 24 hours followed by homogenizing in a agate mortar and sintered at 1000°C for 24 hours. Another mixture of α-Fe_2O_3, anatase TiO_2 was similarly prepared by ceramic technique. Both the mixtures are further finally sintered at 1250°C for 24 hours. Powdered samples were used for X-ray powder diffraction. The samples are labeled and referred to as F_{r1000}, F_{r1250} and F_{a1250}. Dielectric constant (K'), dielectric loss (K") and a.c. resistivity are determined by using LCR-Q meter at an internal frequency 1 kHz by measuring the capacity of parallel plate capacitor with pellet of sample as a dielectric medium; within the range of temperature 300 K-850 K. Also, K' and K" are determined at room temperature in the range of 10 kHz-1000 kHz using an auto-computing LCR-Z meter (4277A Hewlett Packard).

RESULTS AND DISCUSSION

Structural properties

The Table 1 shows the lattice parameters (a, b, c), volume of the unit cell (V), densities by XRD, practical densities, average particle size, pore factor and inhomogeneity of the samples F_{r1000}, F_{r1250} and F_{a1250} under study.

Table 1

Sample	F_{r1000}	F_{r1250}	F_{a1250}
a (Å)	9.782	9.778	9.795
b (Å)	9.980	9.961	9.992
c (Å)	3.729	3.726	3.732
V ($Å^3$)	364.04	362.91	365.26
XRD density (g/cc)	4.370	4.384	4.356
Practical density (g/cc)	3.364	3.999	3.741
Pore factor	0.22	0.09	0.14
Inhomogeneity	-0.012	-0.002	-0.038
Average particle size (Å)	305	540	636

All the samples are pseudobrookite having orthorhombic unit cell and space group Bbmm. The Table 2 shows the observed (d) values and relative intensities of some planes for the samples under study. It shows that in case of the sample F_{r1250} the spacing between the planes (d)is decreases as compared to sample F_{r1000}, where it increases as in case of the sample $F_{a1250.}$

Table 2

	F_{r1000}		F_{r1250}		F_{a1250}	
Hkl	d_{obs}	I/I_o	d_{obs}	I/I_o	d_{obs}	I/I_o
101	3.485	100	3.482	100	3.488	100
230	2.749	68	2.747	86.9	2.753	44
200	-	-	4.888	41.2	4.898	26
002	1.864	28	1.863	29.6	1.867	26
301	2.455	27	2.451	17.1	2.456	21
131	2.407	25	2.403	22.7	2.408	16

Dielectric characteristics at room-temperature

The dielectric constant (K') and dielectric loss (K") measured at room temperature and at 1 kHz, 10 kHz and 1000 kHz are given in the Table 3. Also the a.c. conductivity measured at 1 kHz is given in the Table 3. It indicates that the presence of space-charge is more for the sample F_{r1250} compareed to the other samples. This results into large dielectric constant and large conductivity for the sample $F_{r1250.}$

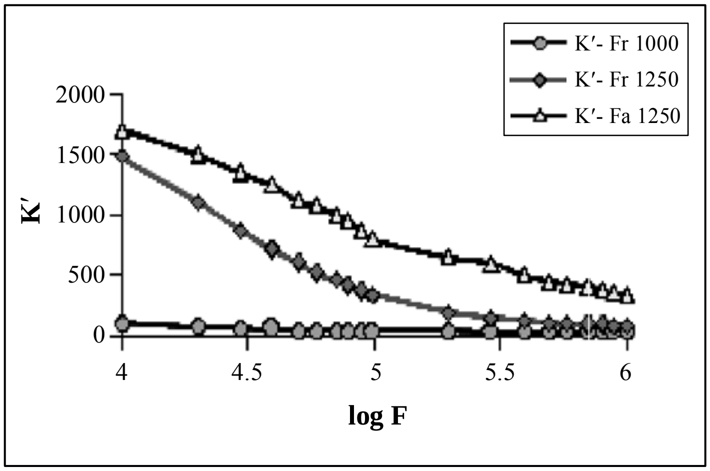

Fig. 1: K' vs. log F

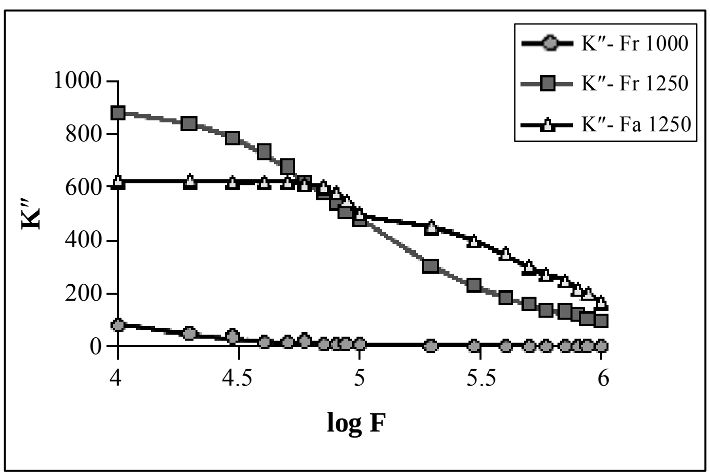

Fig. 2: K'' vs. log F

Table 3

	F_{r1000}	F_{r1250}	F_{a1250}
K'_{1kHz}	389	3407	166
K''_{1kHz}	957	3248	199.5
K'_{10kHz}	105	1484	1700
K''_{10kHz}	86	884	625
$K'_{1000kHz}$	32	76	339
$K''_{1000kHz}$	3.3	99.4	167
$\sigma_{1kHz\ mho/m}$	1.43×10^{-6}	1.8×10^{-4}	1.18×10^{-6}

The comparison with the sample F_{r1000} shows that the dielectric constants increase ten times due to higher sintering temperature (1250^{o}C). Similar trend is observed in case of dielectric loss. The a.c. conductivity at 1 kHz is also found to increase about ten times due to higher sintering temperature. The changes in K', K'' and σ may be due to interfacial polarization[13].

In this connection, it may be noted that Fe_2TiO_5 possesses a short range antiferromagnetic order[5], which may be destroyed due to higher sintering temperature. This may release more $Fe^{2+} \leftrightarrow Fe^{3+}$ space-charge. This mechanism is absent for the sample F_{a1250} resulting in low K', K" and σ.

Relaxation spectra

In order to obtain more information about space-charge, the relaxation spectra of the samples are also investigated. The plots (i) K' v/s frequency and (ii) K" v/s frequency, known as relaxation spectra of the samples are given in Figures 1-2. The nature of the curves is similar to shown by Maxwell-Wagner model for space-charge[13].

From Figures 1-2, it is clear that the value of dielectric constant K' is maximum for sample F_{r1250}. The curve falls rapidly with frequency. Hence, the relaxation frequency of the space-charge of F_{r1250} may be lower than 10 kHz but close to 10 kHz. For the remaining samples, the space-charge is observed to be very small.

It is also clear from the Figures 1-2 that K" is largest for the sample F_{r1250}. Therefore, the largest conductivity term corresponds to F_{r1250}. The conductivity terms are much smaller for remaining samples.

Variation of dielectric constant (K') with temperature at 1 kHz

Variation of dielectric constant (K') with temperature (300 K-850 K) is investigated to find if there exists ferroelectric/ diffused phase or any other transition. The variation of K' with temperature is shown in Figure 3-6 for all the samples. The curve corresponding to sample F_{r1000} shows that K' increases slowly from 300 K. It shows discontinuity at 500 K and then increases rapidly. This discontinuity agrees with antiferro to paramagnetic transition[9]. Hence, above 500 K, space-charge is available in large quantity and therefore, K' increases rather rapidly. The curve corresponding to sample F_{r1250} shows that there is escape of this transition, which may be due to higher sintering temperature. Therefore, there may be large space-charge is available, which results into higher value for K'.

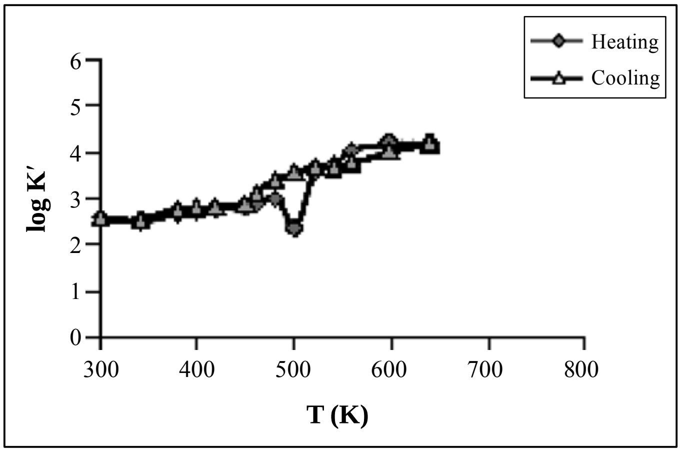

Fig. 3: log K' vs. T (K) of F_{r1000}

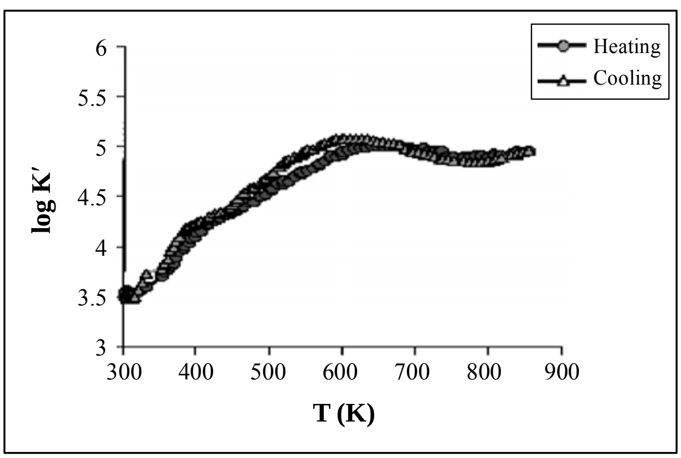

Fig. 4: log K' vs. T (K) of F_{r1250}

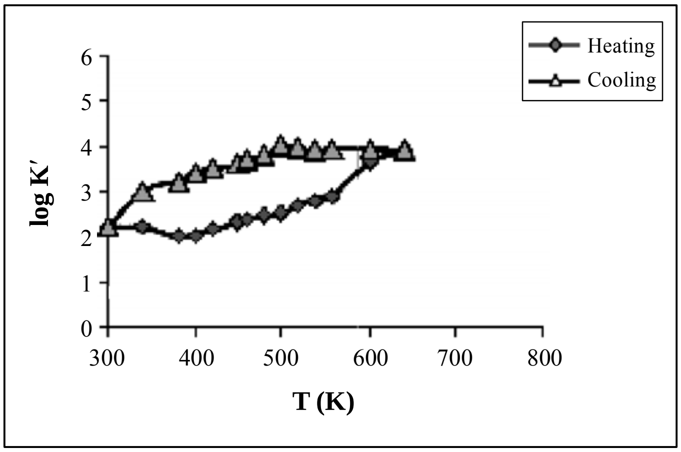

Fig. 5: log K' vs. T (K) of F_{a1250}

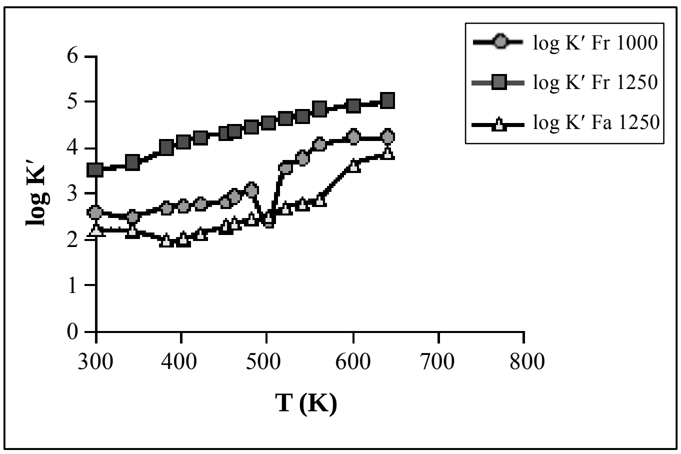

Fig. 6: log K' vs. T (K)

It increases rather rapidly from 350 K. The curve corresponding to sample F_{a1250} is rather well separated from the other curves. The dielectric constant corresponding to sample decreases from 300 K to 350 K. Beyond 350 K, its value increases rather slowly. It is interesting to note that the increase is rapid after 550 K. The dielectric hysteresis curves in Figures 3-5 shows that the hysteresis loss is minimum for the sample F_{r1250}, whereas it is maximum for the sample F_{a1250}.

Variation of dielectric loss (K") with temperature at 1 kHz

Variation of dielectric loss (K") with temperature (300 K-850 K) is investigated. The variation of K" with temperature is shown in Figure 7 for all the samples. The curve corresponding to sample F_{r1250} increases rapidly from 300 K. The curves corresponding to F_{r1000} and F_{a1250} show decrease with temperature from 300 K-350 K, after that they show rapid increase with temperature. This confirms the large space-charge for the sample F_{r1250}.

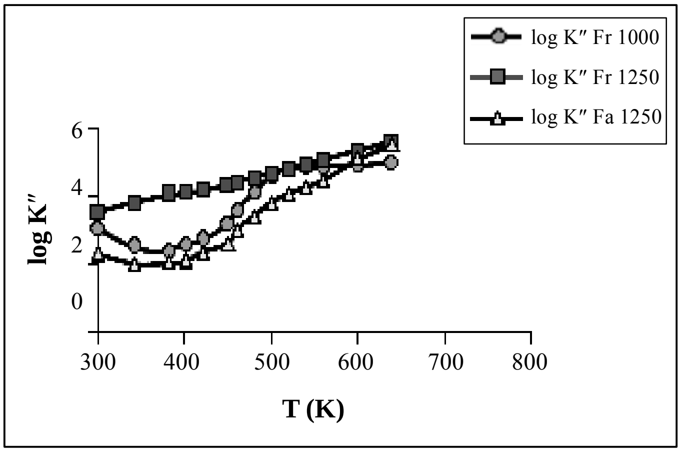

Fig. 7: log K'' vs. T

CONCLUSIONS

From the above discussion, we may conclude that -

(i) The pseudobrookite prepared from rutile TiO_2 has larger contribution of interfacial polarization at low frequencies. However, at high frequencies, the contribution of dipolar polarization is more in the pseudobrookite prepared from anatase TiO_2.

(ii) As the sintering temperature is increased for the sample prepared from rutile TiO_2, the K', K" and σ show considerable increase.

(iii) Dielectric hysteresis loss is minimum for rutile as compared to that for the anatase samples.

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