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An investigation on electrical properties of microwave treated natural ilmenite ($FeTiO_3$)

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It has been observed that microwaves of 2.45 GHz heat dielectric materials. On subjecting natural ilmenite to microwave irradiation, the mineral is observed to heat, with a surface temperature in proportion to the irradiation time. With irradiation times from 40 to 240 seconds (increased in steps of 40 sec), the surface temperature measured on the samples were between 280 and 520 K. Electrical measurements made on the samples before and after irradiation show that the electrical properties are modified by the microwave irradiation. The real conductivity (σ'), dielectric constant (ε') and the dielectric loss (ε'') plotted against frequency generally showed universal dielectric behaviour [1 and references therein] similar to that observed in other systems studied in the literature but using conventional heating techniques. Plots of σ', ε' and ε'' against the surface temperature of the sample showed frequency independent peaks around 460 K. The experimental dielectric loss (ε'') results fit a peak function of the form:

$$\varepsilon'' = \varepsilon_0 + \frac{A}{\omega_0 T\sqrt{2\pi}} \exp\left(-\frac{\left(\ln\left(\frac{T}{T_p}\right)\right)^2}{2\omega_0^2}\right)$$

where ε_0, A, and ω_0 are constants. The fitting of the dielectric loss results gives a frequency independent peak temperature (T_p) as 464 ± 5 K. Plotting the dielectric (γ') and dielectric loss (γ'') exponents against temperature also gives an estimate of T_p close this value. The possibility of a ferroelectric transition in the samples is investigated by comparison with previous results obtained from synthetic ilmenite samples as it is the case with well known ferroelectric systems such as $BaTiO_3$ [2]. *© 2006 Springer Science + Business Media, Inc.*

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1. Introduction and theoretical background

When relatively high frequency (GHz) electromagnetic energy is incident on a dielectric material, some of the energy may be reflected, absorbed or transmitted by the substance. The amount of energy absorbed is dependent on the frequency of the radiation and the dielectric properties of the material. The interaction of the absorbed energy with the material can manifest itself through quantifiable and measurable parameters such as surface temperature, which is transmitted throughout the material by diffusion from inside the material.

From a theoretical point of view, it could be of interest to look at the interaction(s) between the crystal waves i.e. phonons and the incident microwave radiation as waves, where the energy from the incident radiation could be considered a perturbation on the crystal structure. The understanding of such complex interactions (possibly through theoretical modelling) could have important spin-offs on the optimization of the use of microwave energy in the mineral processing field.

Experimentally however, it is necessary to focus on the effect of the microwave radiation on the measurable properties of the material and try to quantify to what extent the properties are influenced by the irradiation. In the present work, the measurable properties of the material detected are changes in the temperature, dielectric constant and conductivity. Such changes may be a result of phase transformation in the material, leading to phases

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which may exhibit different and/or superior properties. In some cases, mechanical changes due to thermal stresses set up within the material can promote selective liberation of certain mineral components from the host ore. Several authors [3–5] have discussed the use of microwave energy in mineral processing by looking at the possible benefits and challenges of applying the technology. Among other things, previous work has highlighted that the dielectric constant/loss is a fundamental property which is central to microwave heating [4, 5 and references therein]. Its study and characterisation would therefore contribute towards the optimum use of microwave technology.

The dielectric response of any material may be defined in terms of the time dependence of the depolarizing current following a sudden removal of a steady polarizing field. The frequency dependent dielectric constant ($\varepsilon(\omega)$), where ω is the angular frequency, is given by:

$$\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) \tag{1}$$

The symbols ε' and ε''represent the real and imaginary (dielectric loss) parts respectively. Another parameter linked to the dielectric behaviour of a material is the frequency dependent conductivity ($\sigma(\omega)$), expressed as:

$$\sigma(\omega) = \sigma'(\omega) + i\sigma''(\omega) \tag{2}$$

$\sigma'$and σ'' are the real and imaginary parts of the conductivity respectively. The conductivity and dielectric constant are generally found to obey a power law dependence on frequency, regardless of the specific physical and chemical nature of the material being studied [1]. Maxwell [6] and Wagner [7] observed that a solid consisting of phases (components) with different conductivity has an overall conductivity which increases with frequency due to the difference in the frequency response of the different phases or components. The behaviour is summarised by;

$$\sigma' \propto \omega^x \quad \text{and} \quad \varepsilon' \propto \omega^{-\gamma'}. \tag{3}$$

The parameters x and γ' are exponents which take values between 0 and 1 and can be used to characterise the system under study (i.e. in terms of conduction mechanism). In most disordered solids, x varies between 0.6 and 1.0 [8]. The range of exponents includes almost flat responses from low-loss materials to strongly dispersive materials, in which ε' and ε'' vary almost inversely with frequency. The universality of the power law does suggest that there could be a common mechanism (possibly many-body interaction) controlling dielectric relaxation in most materials [1, 8].

In systems associated with electronic hopping mechanism, the ac conductivity is expressed as:

$$\sigma(\omega) = \bar{\sigma}_0 + \omega\varepsilon''(\omega) \tag{4}$$

and

$$\varepsilon''(\omega) \propto \omega^{-\gamma''}; \quad 0 < \gamma'' < 1 \tag{5}$$

The parameter σ_0 corresponds to the dc contribution to the conductivity, which is independent of frequency, hence the flattening of the conductivity curves at low frequency. It has since been observed that the same power law is applicable to ionic conductors and also holds above the loss peak frequency in dipolar solids. In hopping systems, it is not easy to find a relation between the dc and ac components of the conductivity as more often the dc conductivity is much more strongly temperature dependent than ac. It is also difficult to make a distinction between dipolar and the charge carrier contributions. However, on the basis of temperature dependence, the charge carrier contribution is found to be stronger.

Although the potential for microwave technology in the mineral industry has been looked at by several authors, very few systematic studies of the dielectric constant have been carried out on natural mineral samples. As a continuation of test work on natural Ilmenite processing, samples were subjected to microwave irradiation and their dielectric properties studied. Natural ilmenite as mined in South Africa is a good source of titanium dioxide which has important applications in the paint industry. Previous measurements of the dielectric constant (ε') and dielectric loss (ε'') have been carried out on powder samples of synthetic $FeTiO_3$, from 4.2 K to room temperature in the frequency range of 0.1 to 100 kHz [9]. Plotted against frequency (10^2–10^5 Hz), the dielectric constant shows a decrease similar to what has been observed in other multi-component systems [1, 10]. In the work of Iwauchi *et al.* the dielectric loss showed a broad peak at a temperature of 52.5 K. Both the dielectric constant and dielectric loss were found to increase with temperature as the conductivity is increased due to electrons hopping between Fe^{2+} and Fe^{3+} sites. The relaxation mechanism was suggested to be arising from the Maxwell-Wagner interfacial polarization of heterogeneous phases in the sample. Viswanath and Seshadri [11] studied the ferroelectric properties of synthetic $FeTiO_3$ by measuring the conductivity and dielectric constant in the temperature range of 300 to 650 K. The Curie temperature (corresponding to the ferroelectric transition) in their samples was found to be around 600 K while a plot of log σ vs. $1/T$ showed two linear regimes (corresponding to different activation energies) with a change in slope around 560 K. At this temperature, the material was observed to change from ferroelectric to the paraelectric state.

In all the above studies, the variation of dielectric loss (constant) with temperature had the characteristics of a peak function. Such a function could be of the form:

$$\varepsilon'' = \varepsilon_0 + \frac{A}{\omega_0 T\sqrt{2\pi}} \exp\left(-\frac{\left(\ln\left(\frac{T}{T_p}\right)\right)^2}{2\omega_0^2}\right) \tag{6}$$

In the present notation, the function shows a variation of ε'' (dielectric loss) with T (temperature in K), with T_p corresponding to the dielectric loss peak temperature. The parameters ε_0, A, and ω_0 are constants. The results obtained in the present study will be fitted to Equation 6 in order to check for consistency and extract the value/s of T_p.

2. Experimental procedure

2.1. Sample preparation

The samples were prepared by irradiating natural ilmenite powder samples (18.7 g each) in 100 ml beakers in a 2.45 GHz, 1 kW microwave applicator for different times. The position of the sample in the oven cavity was fixed while the exposure time was varied in steps of 40 sec up to and including 240 sec. The surface temperature of the samples was measured by means of a Eurotron Infrared non contact thermometer.

2.2. Electrical characterisation of the samples

Electrical measurements were made on powder samples of natural Ilmenite (before and after irradiation), which had been prepared as in Section 2.1 above. The powder samples were placed in a custom made holder which could hold a sample of 15 mm in diameter and 7.5 mm thick with brass contacts on either side on the flat faces. The sample was lightly squeezed between the contacts by means of a hand tightened screw. The measurements reported here were all done at room temperature (295 K) using a Broadband Dielectric spectrometer, within a frequency range of 10^{-2} Hz to 10^6 Hz. The Novocontrol Spectrometer is especially designed for ac conductivity measurements and is capable of measuring far smaller loss components in the dielectric and or insulating phase (equivalent to 10^{14} Ω at 10^{-2} Hz and 10^8 Ω at 10^5 Hz in parallel with an ideal capacitor) and has a better resolution of the loss or phase angle (a maximum of tan δ of $>10^3$ and a minimum of 10^{-3}). The properties measured on the ilmenite samples include the electrical conductivity, dielectric constant and dielectric loss. These results were then plotted in various forms as shown in the following sections.

3. Results and discussion

3.1. Temperature profile

Fig. 1 shows the variation of temperature with exposure or irradiation time for the ilmenite samples. The temperature measured on the surface of the samples was found to vary from room temperature (295.5 K) to about 520 K. The results show that the temperature increases nonlinearly with irradiation time. It is worth noting that unavoidable fluctuations in the electromagnetic field inside the oven can lead to non-uniform heating and fluctuations in the surface temperature measured. In addition, it was also difficult to measure the temperature accurately and in situ without risking radiation leak. However, the profile shown in Fig. 1 indicates that there is a good correlation between the surface temperature and irradiation time. A third order polynomial fit (which is not unique) to the data in Fig. 1 gives an expression of temperature (T) as a function of time (t) in the form:

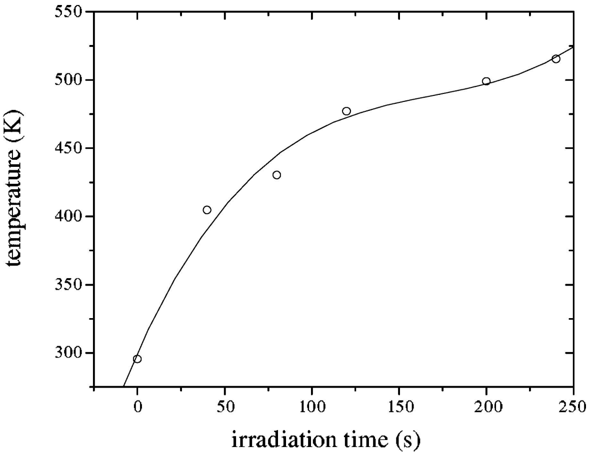

Figure 1 Variation of surface temperature with irradiation time for the ilmenite samples (○). The solid line is a third order polynomial fit to the data, which gives the expression given in the text.

$$T = 299.623 + 2.854t - 0.015t^2 + 3.028t^3, \quad (7)$$

which shows that the temperature is always increasing for the range of times used in the experiment (note the positive coefficient of the cubic term). The standard deviations in the coefficients are ±14, 0.58, 0.0063 and 1.804 × 10^{-5} respectively. Attempts to fit the data to second, fourth and fifth order polynomials yielded a similar trend but with the exceptions that: a fifth degree polynomial fit gave a zero standard deviation with a sharp increase in temperature after the last point and the curve is not smooth. The expression is:

$$\begin{aligned} T &= 295.5 + 6.15188t - 0.13172t^2 + 0.0014t^3 \\ &\quad -6.142361 \times 10^{-6}t^4 + 1.04913 \times 10^{-8}t^5. \end{aligned}$$

Second ($T = 308.92667 + 1.98633t - 0.00485t^2$) and fourth order ($T = 297.34167 + 3.417t - 0.02772t^2 + 1.12871 \times 10^{-4}t^3 - 1.70811 \times 10^{-7}t^4$) polynomial fitting gave standard deviations of ±17, 0.4, 0.001 and ±19, 1.4, 0.026 1.70 × 10^{-4}, 3.48 × 10^{-7} respectively in addition to a decreasing trend in temperature after the last point. The third order polynomial fit was then chosen as a better representation of the experimental results (Fig. 1).

The increase of temperature with irradiation time in these samples agrees well with the results of Wright *et al.* [12]. Wright *et al.* observed that microwave heating of ilmenite samples showed a temperature peak after 75 min of irradiation with microwaves before decreasing with further irradiation. Since the present study was done well under 75 min (range 0–3 min), the increase in temperature as shown in Fig. 1 is reasonable as it appears to be heading towards a peak.

3.2. Electrical conductivity

The electrical conductivity results plotted against frequency are shown in Fig. 2. These results indicate an increase in the electrical conductivity of the samples with microwave irradiation time i.e. with the surface temperature. Such evidence arises from the fact that the curve of the untreated sample is well separated from those of the irradiated samples by an order of magnitude at the lowest frequency. The increase in conductivity in the treated samples shows that the microwave radiation (heating) has a significant influence on the electrical properties of the samples. The curves of all the samples are qualitatively consistent with the Maxwell and Wagner theory of conduction in disordered or multi-component systems [6, 7], where the conductivity increases with frequency.

At lower values of frequency, the conductivity curve appears to flatten towards a finite value (which is normally regarded as the dc or zero frequency value, σ_0). It is clear that for these samples, the dc conductivity value is not reached at the lowest frequency (10^{-2} Hz) used in the experiment. Note that the samples were in powder form (only sandwiched or lightly squeezed between the electrodes by a hand tight screw) and therefore there is a substantial amount of air trapped between the grains. This could lead to the separation of the relatively high conductivity ilmenite grains and dielectric regions (essentially air) as in percolation systems close to but below the critical volume fraction [10, and references therein]. When the frequency increases, however, the impedance of the capacitive regions decreases to the point where their conductivity becomes comparable to that of the conducting grains and so the overall conductivity of the sample increases, hence the upward turn in all the curves as shown in Fig. 2. This response has been widely observed in other multi-component systems studied in the literature [1, 8, 10, and references therein] and universal laws have been put forward to explain the behaviour. Note that the conducting regions themselves are also likely to be multiphase in nature.

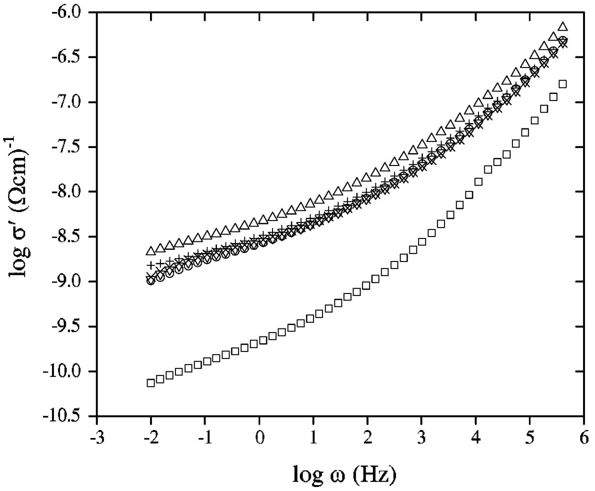

Figure 2 A log-log plot of the conductivity against frequency for the Microwave treated Ilmenite samples. The conductivity increases with frequency according to Equation 3. The symbols correspond to the measured surface temperatures: 295.5 K (□), 404.8 K (○), 430.3 K ( ), 477.1 K (+), 499.0 K (∇), 515.5 K (×).

Natural ilmenite does contain a significant amount of hematite (Fe_2O_3) as observed in previous studies [13]. The natural ilmenite is therefore essentially a composite (or solid solution) of ilmenite ($FeTiO_3$) and hematite (Fe_2O_3). In addition, components such as Uranium, Thorium, Chromium Oxide, Manganese Oxide and Silica are also present, albeit in smaller quantities. Previous studies on ilmenite-hematite solid solutions [14] have shown that addition of hematite (Fe_2O_3), even at small concentrations, to ilmenite ($FeTiO_3$) increases the conductivity of the solid solution due to the increase in the number of pairs of (Fe^{2+}, Fe^{3+}) and (Ti^{3+}, Ti^{4+}). The number of these pairs was found to depend only on the concentration of ilmenite and hematite in the solid solution. Further studies showed that the peak in conductivity is reached when the volume fraction of hematite lies between 0.20 and 0.40 and that hematite-doped ilmenite has more well defined grain boundaries (giving rise to non-linear I-V characteristic) than pure ilmenite. While the studies of Zhou *et al.* [14] were done at fixed (room) temperature and variable hematite concentration, the present study involved variation of temperature at fixed hematite volume fraction. The change in temperature is then envisaged to have an effect on the grain boundaries which could lead to an increase in conductivity as more carriers hop between the $Fe^{2+}$and Fe^{3+} sites (Fig. 2).

It is interesting to notice that the sample corresponding to 430.3 K has the highest conductivity after which σ' decreases at the higher temperatures. The presence of the conductivity peak (at a lower temperature) could be attributed to the depletion of some intermediate phase that has a higher value of conductivity. It is suggested that the phases could affect the relative concentration of the Fe^{2+} and Fe^{3+} ions in the system which are responsible for the conduction mechanism [5, 9, 14] as charges hop between the two sites. The conductivity behaviour is better illustrated in Fig. 3, where it is plotted against the temperature of the sample at three chosen frequencies. Clearly defined peaks of conductivity are observed at 1×10^3 Hz and 1×10^5 Hz while an almost flat response is observed at 10^{-2} Hz, which is expected as the ac conductivity decreases with frequency. In fact the low frequency conductivity could be regarded as essentially dc (σ_{dc}), which is independent of ω. While the conductivity peak is more pronounced at the higher frequency, the peak temperature appears to be independent of frequency (Fig. 3).

Fig. 4 shows an Arrhenius type plot for the conductivity data for three chosen frequencies. All the three plots show linear regions of different slopes. From the expression: $\sigma' = \sigma_0 \exp\left(-\frac{E_a}{kT}\right)$; we note that the slope is

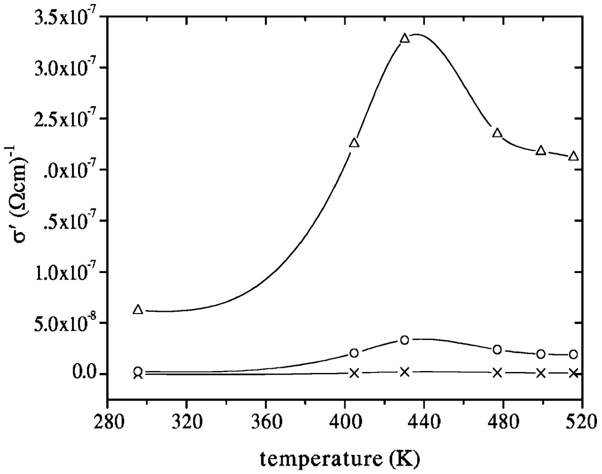

Figure 3 A plot of the real conductivity against temperature for the Microwave treated Ilmenite samples at three chosen frequencies (10^{-2} (×), 10^3 (○) and 10^5 Hz ( )). The solid line is a spline fit to the data showing a peak temperature (T_p) around 440 K.

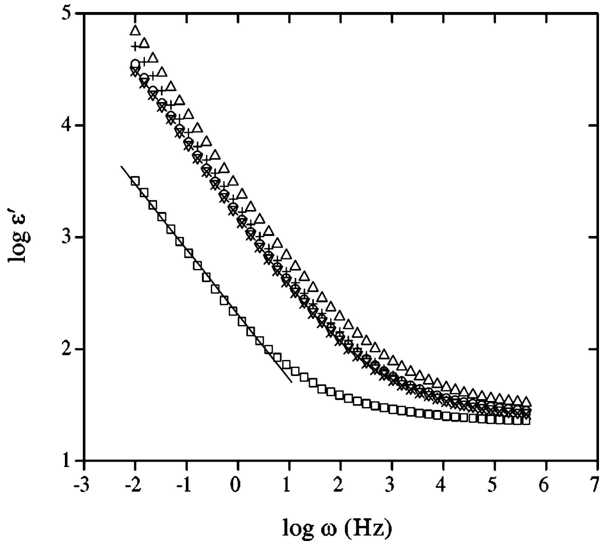

Figure 5 A log-log plot of the real dielectric constant against frequency for the Microwave treated Ilmenite samples. The linear fit gives exponent γ' according to Equation 3. The symbols correspond to the measured surface temperatures: 295.5 K (□), 404.8 K (○), 430.3 K ( ), 477.1 K (+), 499.0 K (∇), 515.5 K (×).

equivalent to $-\frac{E_\mathrm{a}}{k}$, where E_a is the activation energy and k is Boltzmann's constant. σ_0 is a pre-exponential factor or in this case the high temperature limit of σ'. Strictly speaking, this type of plot is normally done using the dc (or zero frequency) conductivity. However the similarity in the behaviour of the curves at the three different frequencies appears to indicate the existence of a general trend which could also hold at zero frequency. The values of E_a obtained from Fig. 4 for the three frequencies are $E_a = 0.115 \pm 0.008$ eV (10^{-2} Hz), $E_a = 0.085 \pm 0.004$ eV (10^3 Hz), $E_a = 0.056 \pm 0.002$ eV (10^5 Hz). It is worth noting that the activation energies decrease as the frequency increases, suggesting that probably the high frequency leads to higher hopping rates of the charge carriers at a given temperature. Viswanath and Seshadri [11] observed two linear regions (corresponding to two values of E_a) in a similar plot of the dc conductivity results from their samples of synthetic ilmenite. Unfortunately, the actual values of E_a were not calculated in their article so no quantitative comparison can be made with the present results (Fig. 4).

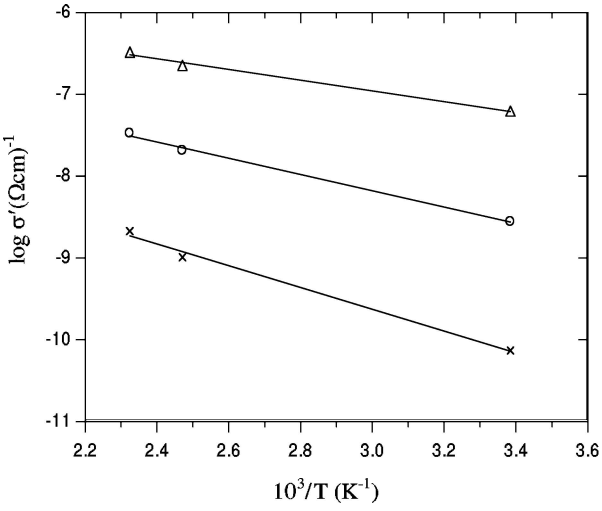

Figure 4 A plot of log conductivity against inverse temperature for the Microwave treated Ilmenite samples at three chosen frequencies (10^{-2} (×), 10^3 (○) and 10^5 Hz ( )). The solid line is a fit to the Eq. given in the text, which gives the values of E_a for the different frequencies.

3.3. Dielectric properties

Fig. 5 shows the real part of the dielectric constant (ε') plotted against the frequency of the applied signal. This type of response is typical of all materials with some polarizing species, whether they are dipoles, electrons and hopping charge carriers. At high frequency the dipoles cannot follow the rapid variation of the electric field, hence the dielectric response is smaller. As the frequency decreases, the dipoles have sufficient time to align with the field and the dielectric response increases accordingly. This behaviour has been observed in so many systems that it is referred to as universal dielectric response [15]. However subtle differences do occur in different systems and are realised through the dielectric exponent (γ'), which is discussed later.

Fig. 6 shows the dielectric constant results from all the samples plotted versus temperature, from which peak behaviour is also observed around 440 K, similar to the conductivity. Unfortunately the lack of sufficient data points around this region makes it difficult to determine the exact location of the peak in both cases. Note that the dielectric constant increases with decreasing frequency, in contrast to the conductivity. This behaviour is consistent with Equation 3 (Fig. 5).

The peak shown by the dielectric constant (when the latter is plotted as a function of temperature) is a common

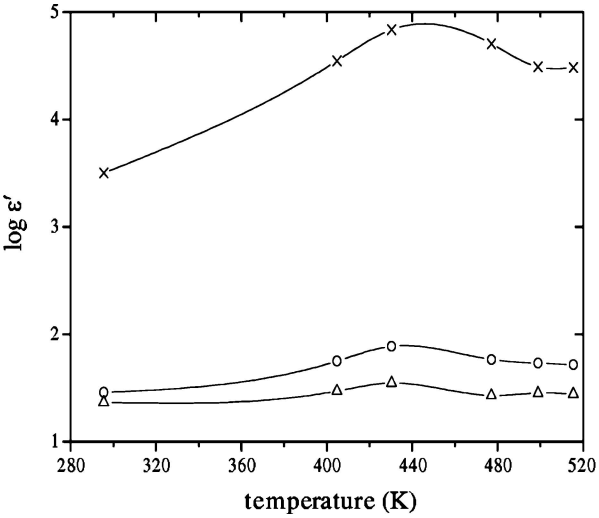

Figure 6 A plot of the dielectric constant against temperature for the Microwave treated Ilmenite samples at three chosen frequencies (10^{-2} (×), 10^3 (○) and 10^5 Hz ( )). The solid line is a spline fit to the data from which T_p can be estimated around 440 K.

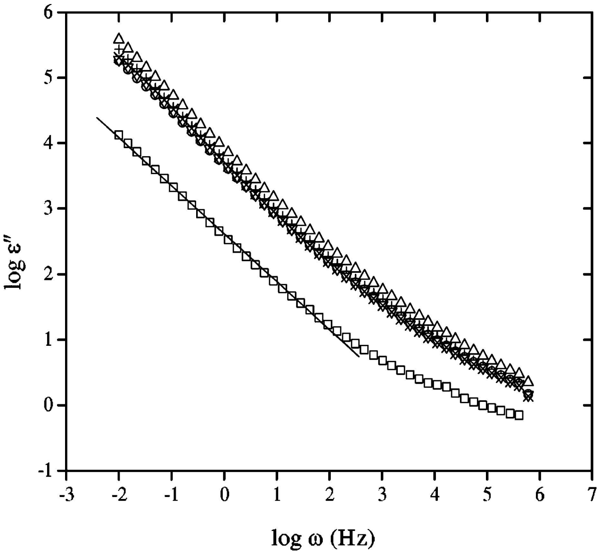

Figure 7 A log-log plot of the real dielectric loss against frequency for the Microwave treated Ilmenite samples. The linear fit gives exponent γ'' in accordance with Equation 5. The symbols correspond to the measured surface temperatures: 295.5 K (□), 404.8 K (○), 430.3 K ( ), 477.1 K (+), 499.0 K (∇), 515.5 K (×).

feature in titanate systems with a perovskite structure [2]. For example in $BaTiO_3$, the dielectric peak temperature (T_p) has been found to coincide with the ferroelectric transition (T_c). In such systems, the ferroelectric phenomena and dielectric peak is linked to the formation of dipoles, arising from the difference in size between the cations Ba^{2+} and Ti^{4+}. In this case the Ba^{2+} is much larger than the Ti^{4+}, which results in the non-centrosymmetric arrangement of ions in the unit cell, giving rise to a permanent electric dipole moment. The small Ti^{4+} ion is located at the centre of the octahedron consisting of six oxygen atoms, where it is free to translate in the presence of an external electric field, leading to the formation of dipoles (Fig. 6).

Viswanath and Seshadri [11] also observed ferroelectric behaviour in samples of synthetic $FeTiO_3$ (which has a non-perovskite structure) around 600 K, which also coincided with the dielectric peak. The ilmenite structure is more ordered than the perovskite and the cations Fe^{2+} and Ti^{4+} are very close in size. The origin of ferroelectricity in such systems is therefore not straightforward. The dielectric peak in the microwave treated samples in the present study occurs around 440 K, which is way below T_p (T_c) measured in the synthetic samples. In comparing these results, it is important to take cognisance of the differences between the systems and the manner in which the experiments were conducted. The samples in the present study are of natural ilmenite and have been treated with microwaves at different times. As mentioned earlier, the natural ilmenite contains between 10 and 20% hematite [13] which has been found to influence the conductivity [14]. It is therefore suggested that the presence of hematite could be playing a part in changing the value of T_p. Microwave treatment of ilmenite samples with varying amounts of hematite could be used to investigate this role (if any) played by hematite in influencing T_p. The treatment with microwaves (rather than conventional heating of the samples) could also be the reason for the smaller value of T_p in the present study. It is proposed that Microwave heating could be so efficient (in affecting the hematite-induced grain boundaries) that T_p is then attained at a lower temperature than in the conventionally heated samples. In addition, the role of the other components of lower concentration present in our natural ilmenite sample cannot be ruled out. Unfortunately there are no previous dielectric studies involving microwave treated synthetic or natural ilmenite samples for comparison with the present study.

Figs 7 and 8 show the dielectric loss plotted against the frequency and temperature respectively. The dielectric

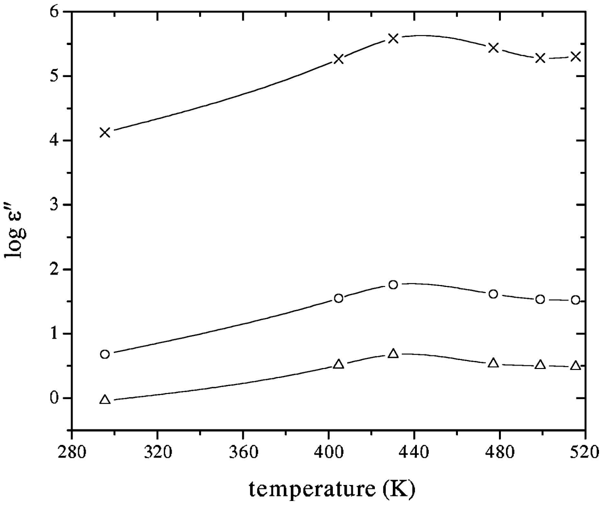

Figure 8 A plot of the dielectric loss against temperature for the Microwave treated Ilmenite samples at three chosen frequencies (10^{-2} (×), 10^3 (○) and 10^5 Hz ( )). The solid line is a spline fit to the data. T_p is around 440 K.

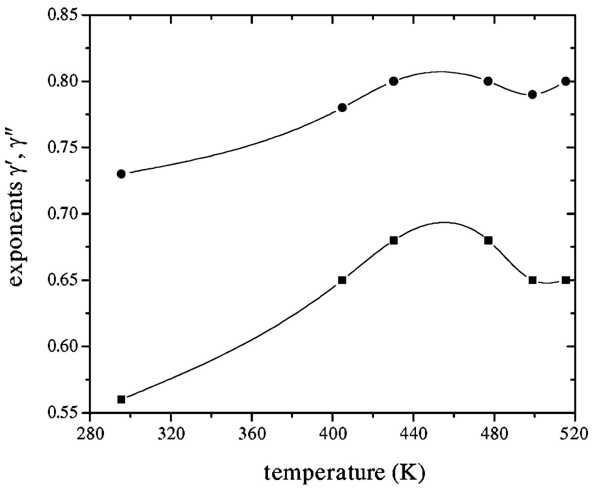

Figure 9 A plot of the dielectric constant (■) and dielectric loss (•) exponents against temperature for the Microwave treated Ilmenite samples. The solid line is a spline fit to the data. T_p from this plot is estimated to be 460 K.

loss follows the frequency dependence of Equation 5, with the γ'' exponents varying between 0.72 and 0.82 in the low frequency region. Such relatively high values of γ'' have been observed in ferroelectrics with good ionic conductivity [16, and references therein], which has been referred to as low frequency dielectric dispersion (LFDD) (Figs 7and 8).

Fig. 9 shows the exponents γ' and γ'' plotted against the temperature. It is clear that the dispersion of $\varepsilon''$is stronger (γ'' values lie between 0.72 and 0.82) than that of ε'(where γ' values vary from 0.56 to 0.68). Shantha and Varma [16] attributed this stronger response to the influence of dc conductivity on ε''. Note also the existence of a peak temperature in Fig. 9, estimated to be around 460 K (Fig. 9).

Fig. 10 shows a plot of ε'' against temperature fitted to Equation 6. The results were fitted by treating ε_0, A, ω_0 and T_p as parameters. ε_0 is the room temperature value of the dielectric loss at a particular frequency which controls the initial vertical displacement of the curve. The parameter ω_0 (which was fixed for a particular frequency) controls the width of the curve peaks, while A is related to the amplitude of the peaks. The values of ω_0, A, ε_0 and T_p respectively for the three frequencies are: 0.150, 257 ± 25, 4.13 ± 0.11, 463 ± 0.5 K (10^{-2} Hz), 0.189, 248 ± 18, 0.59 ± 0.07, 465 ± 5 K (10^3 Hz) and 0.190, 161 ± 16, −0.11 ± 0.06, 464 ± 5 K (10^5 Hz). The peak temperature (T_p) was extracted from a least squares fit to the experimental data. As can be seen from the fitted values, T_p is essentially independent of frequency and in good agreement with the peak temperature shown in the γ' and γ'' plots of Fig. 9. The successful fitting of Equation 6 to the data shows that the variation of the loss with temperature could be qualitatively described by such a peak function. There is need for more experimental data to be fitted to this function in order to obtain more quantitative information which could be used to test its validity to model dielectric data, especially in ferroelectric systems (Fig. 10).

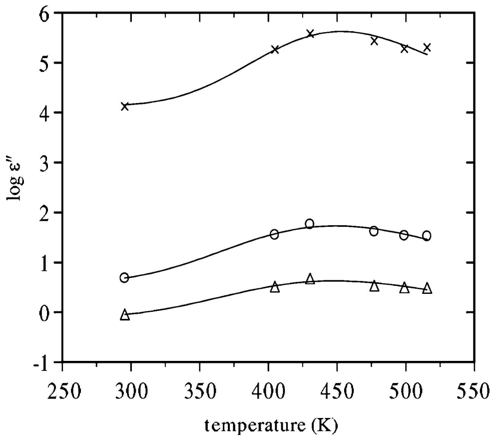

Figure 10 A plot of the dielectric loss against temperature for the Microwave treated Ilmenite samples at three chosen frequencies (10^{-2} (×), 10^3 (○) and 10^5 Hz ( )). The solid line is a fit of the data to Equation 6 with $T_p = 464 \pm 5$ K.

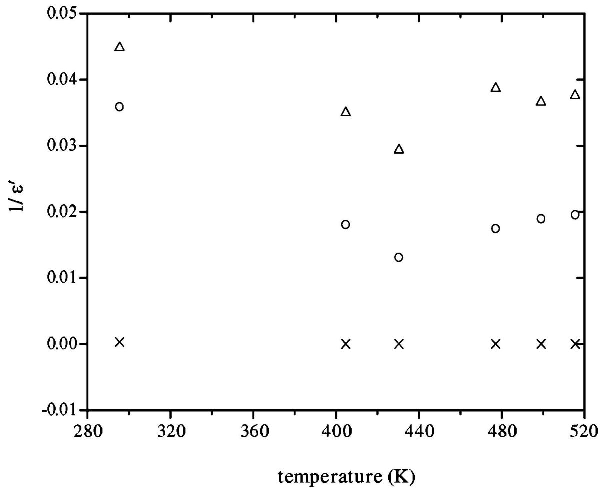

Figure 11 A plot of the reciprocal dielectric constant against temperature for the Microwave treated Ilmenite samples at three chosen frequencies (10^{-2} (×), 10^3 (○) and 10^5 Hz ( )).

Fig. 11 shows a plot designed to test the Curie-Weiss law:

$$\frac{1}{\varepsilon' - 1} = \frac{T - T_c}{C},$$

where T_c is the temperature close to the Curie point and C is a constant with the dimensions of temperature [17]. From the results in Fig. 11, it appears that the Curie-Weiss law is only obeyed at particular frequencies, implying that the phenomena might be related to some form of relaxation mechanism. In our samples, the linear behaviour at 10^3 Hz is evidence that the Curie-Weiss law holds better at this frequency. In Fig. 12, the results at 10^3 Hz are fitted to the Curie-Weiss law. T_c is assumed to be close enough to T_p so the latter is used in the plot.

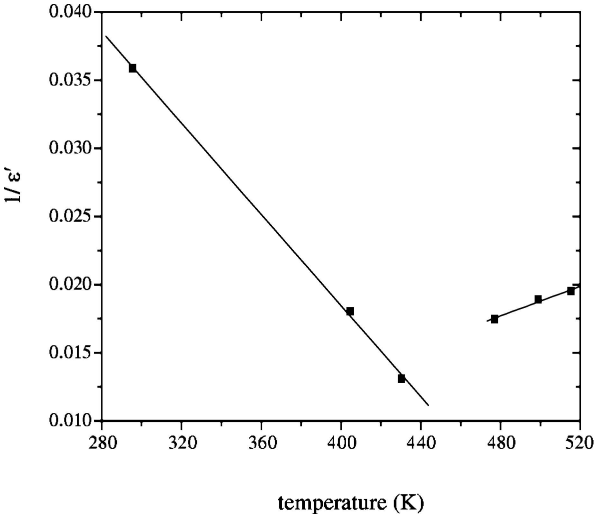

Figure 12 A plot of the reciprocal dielectric constant against temperature for the Microwave treated Ilmenite samples at 10^3 Hz (■) below and above $T_\text{p} = 464 \pm 5$ K. The solid line is a linear fit of the data to Curie-Weiss law given in the text with $T_\text{p} = T_\text{c} = 464 \pm 5$ K.

In addition, $\varepsilon' \gg 1 : \varepsilon' - 1 \approx \varepsilon'$. The results in Fig. 12 indicate that the Curie Weiss law is obeyed below and above T_p, but with different C constants (C_L below T_p and C_H above T_p). From Fig. 12, $C_\text{L} = -(5.98 \pm 0.17) \times 10^3$ K and $C_\text{H} = (1.84 \pm 0.28) \times 10^4$ K. These values of C are close to the value obtained in the mineral lawsonite [18]. Sondergeld *et al.* [18] indicated that low values of C are typical for order-disorder ferroelectrics where phase transitions are of dynamic order-disorder type as opposed to those of a displacive nature (Figs 11and 12).

4. Concluding remarks

The above measurements show that irradiating samples of ilmenite with microwaves does lead to a change in the electrical properties. The increase in conductivity with temperature may be attributed to the presence of hopping charge carriers which acquire more energy to hop from one site to another as the temperature increases due to dielectric heating. However, it appears that further increase in temperature leads to the formation of a less conducting phase, or that it affects the relative proportions of the charged species responsible for conductivity (Fe^{2+} and Fe^{3+}), which is probably why the conductivity decreases at higher temperatures as in Fig. 3 and the negative activation energy observed in Fig. 4.

Heating of ilmenite under some given conditions has always led to either oxidation or reduction. Oxidation leads to the formation of Fe^{3+} through hematite, which increases the conductivity. However, the presence of a conductivity (dielectric) peak in our samples seems to indicate that both oxidation (low temperature) and reduction (at higher temperatures) might have occurred in the temperature range covered in the experiment.

The presence of the pronounced peaks in the conductivity and dielectric constant results around 460 K is indicative of some significant changes occurring within the sample. Phenomenon such as the dielectric peak has been observed in systems which exhibit ferroelectric behaviour. The similarities in structure between these systems and ours seem to imply that the dielectric peak behaviour observed in the present study could also be linked to a ferroelectric transition.

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