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Impedance spectroscopy study of polycrystalline $Bi_6Fe_2Ti_3O_{18}$

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Abstract. **The electrical properties of polycrystalline $Bi_6Fe_2Ti_3O_{18}$ are investigated by impedance spectroscopy in the temperature range 30–550°C. The imaginary part of impedance as a function of frequency shows Debye like relaxation. Impedance data are presented in the Nyquist plot which is used to identify an equivalent circuit and the fundamental circuit parameters are determined at different temperatures. The grain and grain-boundary contributions are estimated. The results of bulk a.c. conductivity as a function of temperature and frequency are presented. The activation energies for the a.c. conductivity are calculated. The polaron hopping frequencies are estimated from the a.c. conductivity data.**

Keywords. **BLSF; equivalent circuit; ferroelectric; impedance; polaron hopping.**

1. Introduction

The general formula for layered oxide compounds of the Aurivillius family is $Bi_2M_{n-1}R_nO_{3n+3}$. In these compounds the cubo-octahedral site (M) is occupied by divalent or trivalent rare earth ions and R is occupied by Fe and Ti ions. The integer n represents the number of layers in the compounds. These compounds have received much interest because of their unusual dielectric and magnetoelectric properties (Aurivillius 1949, 1950; Wood and Austin 1974; Deverin 1978; Singh *et al* 1994; Singh 1996; James 1997; Srinivas *et al* 1999). Wood and Austin (1974) have indicated the possible applications of these materials as modulators, switches, phase inverters, rectifiers etc.

The compound with Bi in place of M and Fe/Ti in place of R were found to be interesting because of dielectric anomalies at higher temperatures and also ME (Wood and Austin 1974; Singh 1996) interactions at room temperature. From our laboratory we have synthesized and reported data on physical properties of $Bi_5FeTi_3O_{15}$, $Bi_6Fe_2Ti_3O_{18}$, $Bi_7Fe_3Ti_3O_{21}$, $Bi_8Fe_4Ti_3O_{24}$, $Bi_9Fe_5Ti_3O_{27}$ and related isotropic materials. The compounds with n = 1,2,3,4 and 5 have been reported to show simultaneous existence of ferroelectric and magnetic properties at higher temperatures. The dielectric and magnetoelectric measurements on $Bi_6Fe_2Ti_3O_{18}$ compounds have been reported (Deverin 1978; Singh *et al* 1994). The impedance measurement on a number of BLSFM compounds such as $LaBi_4FeTi_3O_{15}$, $SmBi_5Fe_2Ti_3O_{18}$, $SrBi_4FeTi_3O_{15}$ and $SrBi_4Fe_2Ti_3O_{18}$ have been reported (James *et al* 1994; Prasad *et al* 1998). The electrical conduction mechanism of $SmBi_5Fe_2Ti_3O_{18}$ showed relaxor like behaviour (Prasad *et al* 1998). These have attracted our attention to the electrical properties of $Bi_6Fe_2Ti_3O_{18}$. A.c. impedance methods are widely used to characterize electrical materials. Data may be analysed in terms of four possible complex formalisms, the impedance, Z^*, the electric modulus, M^*, the admittance, A^* (or y^*) and the permittivity, e^* (Macdonald 1987). These are interrelated as

$$M^* = jwC_0\, Z^*, \tag{1}$$

$$e^* = (M^*)^{-1}, \tag{2}$$

$$A^* = (Z^*)^{-1}, \tag{3}$$

$$A^* = jwC_0\, e^*, \tag{4}$$

where w is the angular frequency $2pf$, C_0 the vacuum capacitance of the measuring cell and electrodes with an air gap in place of the sample, $C_0 = e_0/k$, where e_0 represents the permittivity of free space ($8{\cdot}854 \times 10^{-14}$ f/m) and $k = l/a$ the cell constant where l is the thickness and a the area of the sample.

In order to analyse and interpret experimental data, it is essential to have a model equivalent circuit that provides a realistic representation of the electrical properties. This is chosen based on (i) intuition as to what kind of impedance are expected to be present in the sample and whether they are connected in series or in parallel, (ii) examination of the experimental data to see whether the response is consistent with the proposed circuit, (iii) inspection of the resistance and capacitance values that are obtained in order to check that they are realistic and that their temperature dependence, if any, is reasonable with a series circuit. It is desired to separate each of the parallel RC elements and measure their component R and C values. This is best achieved using a combination of the impedance and modulus formalisms since each

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parallel *RC* element gives rise to a semicircle in the complex plane (Z'' vs Z'; M'' vs M').

In practice it is usually possible to find more than one equivalent circuit that fits, numerically, a given data set but only one of these is likely to provide a realistic representation of the electrical makeup of the sample. In the present materials, it is clear that both inter- and intra-granular impedance are present in the ceramics, and the electrical properties are determined in general by a combination of such impedances. Each of these components may be represented by a parallel *RC* element, and the simplest appropriate equivalent circuit is an array of parallel *RC* elements.

In view of the technological importance of these BLSFM ceramics, the present studies were undertaken to understand the electrical properties under varying frequencies and temperatures. By means of the impedance spectroscopy, the frequency response of the material under an alternating current was studied. This work presents impedance data in the complex impedance plane plot i.e. the Nyquist diagram at different temperatures. Each type of plot can be represented by equivalent circuits, which give important inputs for device applications. The grain and grain boundary contribution have to be separated. The a.c. conductivity data of the sample is to be studied to estimate the activation energies for conduction process (Johnscher 1981).

2. Experimental

Polycrystalline samples of $Bi_6Fe_2Ti_3O_{18}$ were prepared by high temperature solid-state reaction method using high purity AR grade Bi_2O_3, Fe_2O_3 and TiO_2 powders in required stoichiometry. The powders were mixed thoroughly and calcined in air at 850°C for 2 h. The pellets were finally calcined at 1000°C for 4 h. Polyvinyl alcohol was used as binder. The formation of the compounds was checked by X-ray diffraction technique. The sintered pellets were polished with fine emery paper in order to make both the surfaces flat and parallel. The pellets were then painted with silver for better contact. The samples were subjected to electrical poling at 30 kV/cm.

Electrical measurements were taken by means of complex impedance spectroscopy, in the 1 kHz–1 MHz frequency range, using a Hewlett-Packard HP4192A impedance analyser controlled by a personal computer. These measurements were performed in air atmosphere from 303 K–823 K with samples placed in an appropriate sample holder with a two-electrode configuration.

3. Results

Figure 1 shows the variation of the real part of impedance (Z') with frequency at different temperatures. As can be seen, the curves display decrease in value of Z' with frequency at all the temperatures. The magnitude of Z' decreases with temperature which indicates increase in the a.c. conductivity. The Z' values merge above 100 kHz at all temperatures.

Figure 2 shows the variation of the imaginary part of impedance (Z'') with frequency at different temperatures. The Z'' values reach a maxima peak with frequency for the temperatures above 325°C. For temperatures below 325°C, the peak was beyond the range of frequency of measurement. The peak in Z'' shifts to lower frequencies with increasing temperature indicating decreasing relaxation in the system. The relaxation times were calculated from the frequency at which Z″ maxima are observed. The maximum was found to increase with temperature indicating increasing loss in the sample.

Figure 3 shows the result of Z' as a function of temperature at different frequencies. The Z' maxima shifts to higher temperatures with increasing frequency. This indicates relaxation process in the sample, which increases with temperature. Similar observations were reported where BLSF samples are found to show similar relaxor like behaviour (James *et al* 1994; Singh *et al* 1994; Prasad *et al* 1998; Srinivas *et al* 1999).

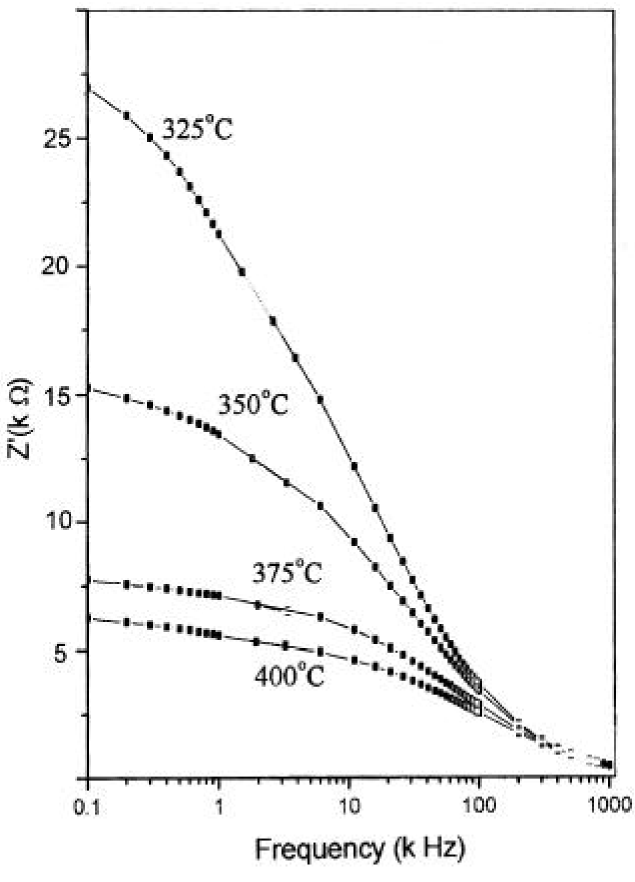

Figure 1. Variation of real part of impedance of $Bi_6Fe_2Ti_3O_{18}$ with frequency at different temperatures.

The Nyquist diagram obtained at different temperatures are displayed in figure 4, each point corresponding to a different frequency. The complex plane plots show increasingly resolved semicircles with increasing temperature. The peak maxima of the plot decreases with increasing temperature. The frequency for the maximum shifts to higher values with increasing temperature. From the peak maxima the relaxation times of the ceramic are calculated.

Figures 5a and b show typical complex impedance plot of $Bi_6Fe_2Ti_3O_{18}$ at 325°C and 400°C, respectively. As a first approximation, these complex impedance plots can be represented by the equivalent circuit models shown in the inset of the figures. Each semicircle is represented by a parallel resistance–capacitance circuit corresponding equivalent to the individual component of the material i.e. bulk and grain boundary. The resistances of each element are directly obtained from the intercept on the *x*-axis i.e. the real part of impedance. The capacitance can be calculated using the equation

$$wt = 1 \text{ i.e. } wRC = 1,$$

where w is the frequency at the maximum of the semicircle for the component. The calculated values of R and C for each component at elevated temperatures are as shown in these figures. At 325°C, only one broad unresolved semicircle is observed and this is resolved into two semicircles intercepting each other on the *x*-axis. The high frequency semicircle represents the material bulk electrical properties. The second semicircle, at low frequency indicates the electrical behaviour of grain boundary. A series resistor is added to account for the high frequency intersection of the first semicircle with the Z' axis. At 400°C, both bulk and grain boundary effects are more prominent (figure 5b). At this temperature the two semicircles represent the dielectric behaviour observed. The corresponding equivalent circuit is also shown in the figure. Above 400°C, a broad semicircle was observed in the low frequency region. As temperature is increased further, the two semicircles are increasingly resolved.

Figures 6 and 7 show the a.c. conductivity plots of $Bi_6Fe_2Ti_3O_{18}$ as function of frequency and temperature, respectively. The a.c. conductivity as a function of frequency shows slope change at a frequency (w_p) called hopping frequency of the polarons. The hopping frequency is found to shift to higher frequencies with increasing temperature. It is observed that the a.c. conductivity with frequency show flattening with temperature. Figure 7 shows the Arrhenius plot of a.c. conductivity at different

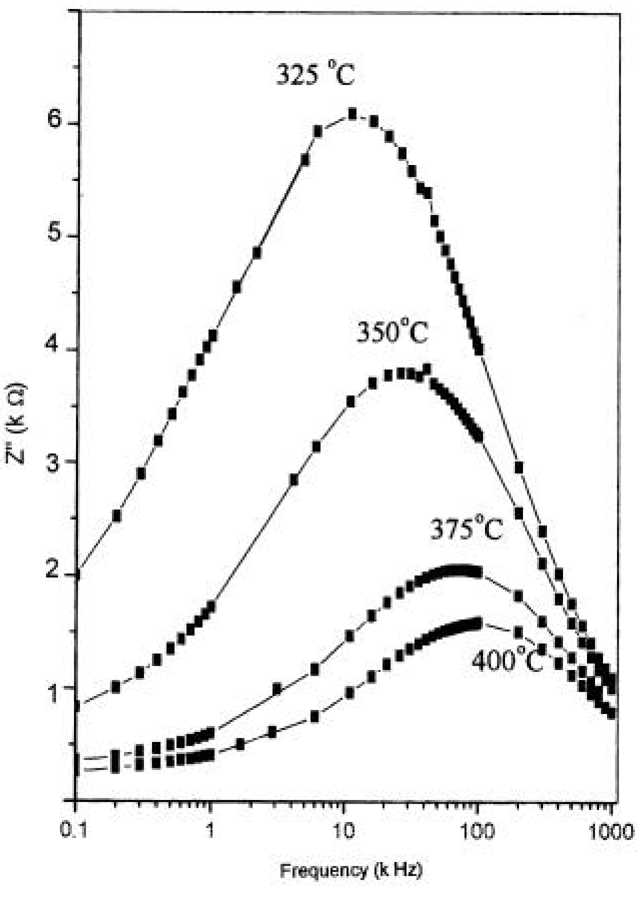

Figure 2. Variation of imaginary part of impedance of $Bi_6Fe_2Ti_3O_{18}$ with frequency at different temperatures.

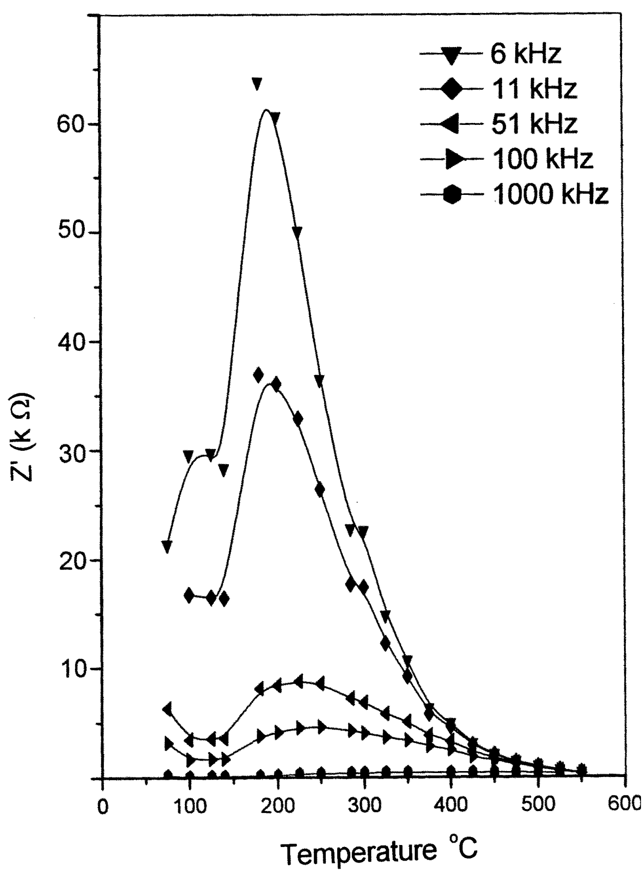

Figure 3. Z' of $Bi_6Fe_2Ti_3O_{18}$ as a function of temperature at different frequencies.

frequencies. The activation energies are calculated from the slopes of Arrhenius plots. The activation energies calculated were in the range of 0·7–0·96 eV as given in table 1.

Figure 8 shows that the relaxation times vary linearly with inverse of temperature. The relaxation times vary from 10^{-6} to 10^{-4} s. The activation energy for a.c. conductivity is found to be 0·94 eV.

4. Discussion

The variation of real part of impedance when plotted against frequency (figure 1) gives information about the relaxation process in the sample. It is observed that there is single relaxation process and shows increasing a.c. conductivity with temperature and frequency. The real part of impedance merge at higher frequencies for all the temperatures indicating release of space charges. The single relaxation process can also be observed in Z'' vs frequency plot at different temperatures (figure 2).

One way to determine the specific relaxation frequency is to use the semicircles obtained from plotting the cole–cole diagrams. An alternative approach is to determine the relaxation frequencies unlike the Z'' vs log f plots. In this study the latter has been used to determine the relaxation frequency (f_r). The peak frequency is used to determine the relaxation frequency. At that frequency (f_r) the relation $2pf_rC_b = 1$ (C_b, bulk capacitance). From the plots one can see single relaxation. Additional peaks would suggest additional relaxation processes in action. The height of plots of Z'' against log f are proportional to the resistance according to the equation (Von Hipple 1954)

$$Z'' = R\,[wt/(1 + w^2\,t^2)].$$

The peak heights are proportional to R in the Z'' vs frequency plots and to C^{-1} in the M'' peak. Hence the power of combined, impedance and modulus spectroscopy is that Z'' plot highlights the phenomenon with the largest resistance whereas M'' picks out those of the smallest capacitance. The frequency explicit plots of the imaginary parts of impedance and electric modulus indicate departures from the ideal Debye behaviour. In the ideal case the Z'' and M'' peaks should coincide on the frequency scale. The width of the Z'' vs log f plot at half height is

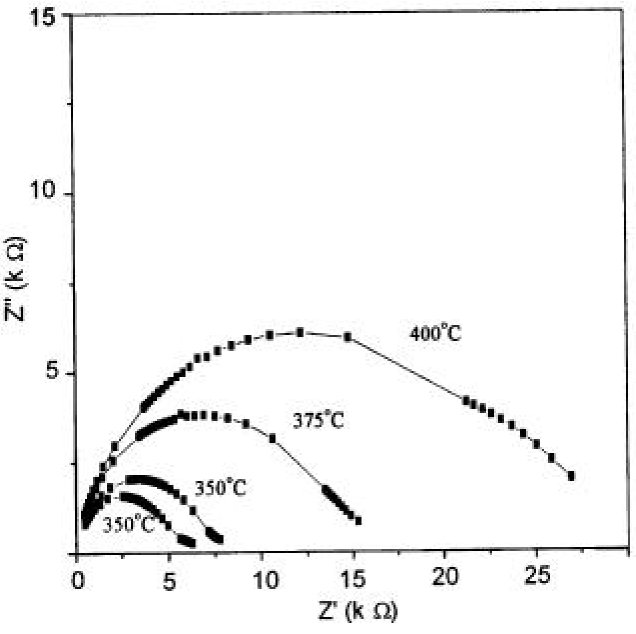

Figure 4. Nyquist diagram for $Bi_6Fe_2Ti_3O_{18}$ at different temperatures.

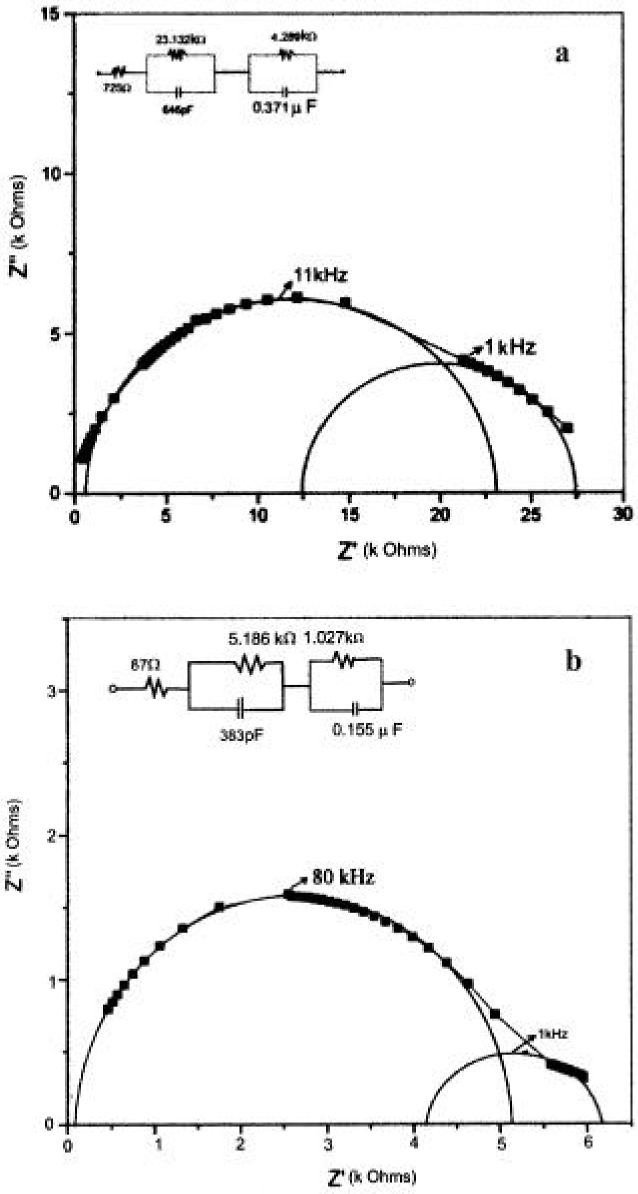

Figure 5. a–b. Complex impedance plots of $Bi_6Fe_2Ti_3O_{18}$ at 325°C and 400°C, respectively.

> 1·14 decades (the full width at half maximum in the ideal theoretical case should be 1·14 decades). The electrical behaviour of space charges depends on frequency. A Debye like peak in the frequency dependence of the Z'' usually indicates the presence of space charges. The peaks shift to lower frequencies with increasing temperature indicating the dependence of space charges on temperature and frequency. The relaxor like behaviour in the ceramic is also observed in Z' vs temperature plot at different frequencies (figure 3). Such relaxor like behaviour in BLSF ceramics has been reported in literature (Prasad 2000; Prasad *et al* 2001).

The impedance data in figure 4 can be fitted into two semicircles indicating the presence of two relaxation processes. Figures 5a and b show the complex impedance plane plots measured at 325°C and 400°C, respectively. Each curve is composed of two semicircles, a large one and a small one. The large one at high frequencies indicates the effect of the grain and the small one at low frequencies reflects the grain boundary effect. Each semicircle is represented by a parallel *RC* circuit that corresponds to individual components of the material. The intercepts of the semicircle on the real axis give the resistance of the corresponding component contributing towards the impedance of the sample. The values of the grain resistance or bulk resistance (R_b) and grain boundary resistance are calculated to be R_b = 23·132 kΩ and R_{gb} = 4·289 kΩ at 325°C and R_b = 5·186 kΩ and R_{gb} = 1·027 kΩ at 400°C.

The capacitance of each component can be calculated using the formula

$$wt = 2p\, f_{max}\, RC = 1,$$

where f_{max} is the frequency of the maximum of semicircles, $w = 2p\, f_{max}$ and t the relaxation time. f_{max} = 11 kHz at 325°C and f_{max} = 80 kHz at 400°C for the first semicircle and 1 kHz for 325°C and 400°C for the grain boundary.

The calculated values of C_b = 646 pf and C_{gb} = 37100 pf at 325°C and C_b = 383 pf and C_{gb} = 15500 pf at 400°C. A series resistor (R_s) is added corresponding to the high

Table 1. A.c. conductivity activation energies at different frequencies.

Temperature range (°C)	A.c. conductivity activation energy (eV)				
	6 kHz	11 kHz	51 kHz	100 kHz	1000 kHz
175–325	0·41	0·39	0·32	0·31	0·30
400–525	0·73	0·7	0·66	0·50	0·46

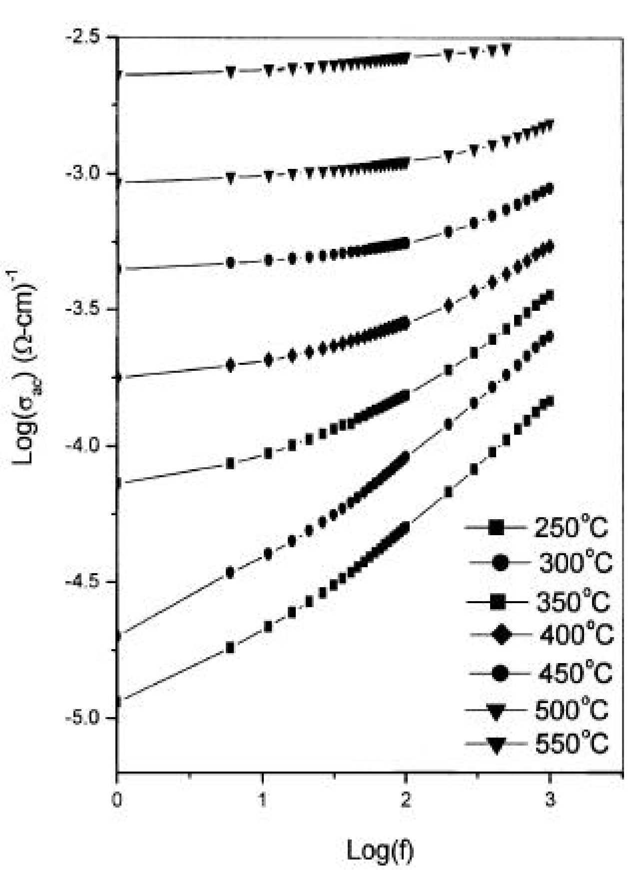

Figure 6. A.c. conductivity plot of $Bi_6Fe_2Ti_3O_{18}$ as a function of frequency.

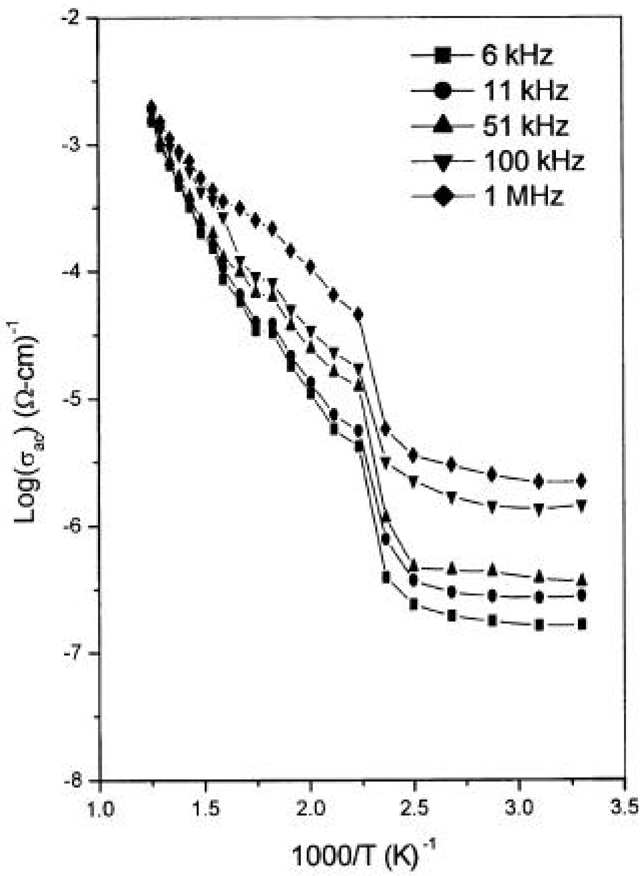

Figure 7. Arrhenius plot of a.c. conductivity of $Bi_6Fe_2Ti_3O_{18}$ at different frequencies.

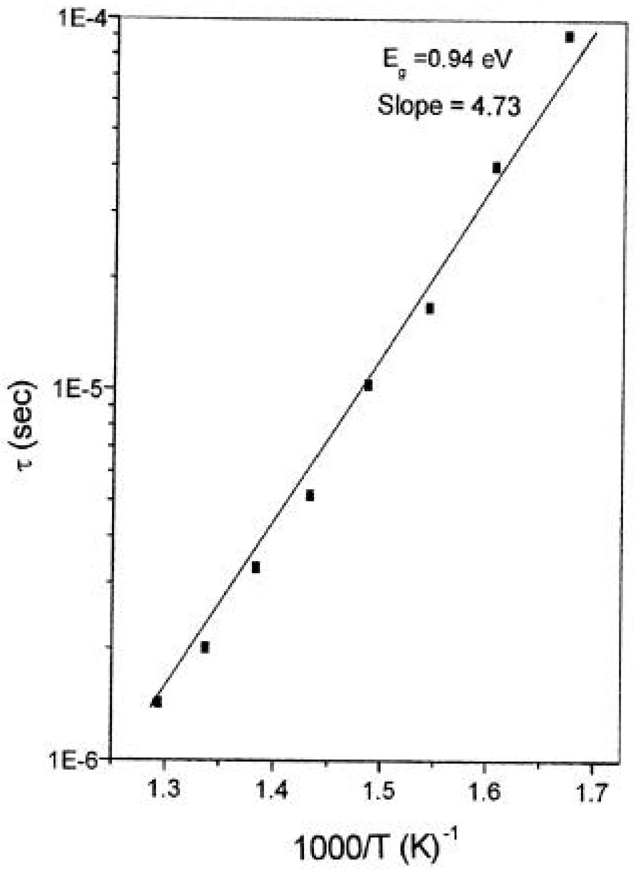

Figure 8. Inverse of relaxation time of $Bi_6Fe_2Ti_3O_{18}$ as a function of temperature.

frequency intersection of the first semicircle (R_s = 725 Ω at 325°C and R_s = 87 Ω at 400°C). These values along with the equivalent circuit are mentioned in the inset of figure 5. In addition to these two semicircles a third semicircle is observed in certain material indicating the electrode–grain interfaces which serve as traps for space charges. This third semicircle was not observed in our material.

The decreasing grain boundary resistance of the ceramic with increasing temperature can also be seen in log (a.c. conductivity) vs log (frequency) plot at different temperatures. The temperature at which the grain resistance dominates over grain boundary resistance, there is a change in the slope of a.c. conductivity with frequency. The frequency at which the slope change is observed corresponds to polaron hopping of charged species. The polaron hopping frequency is observed to shift to lower frequencies with increasing temperature indicating increasing conductivity with temperature. With increasing temperature the charged species that are accumulated at grain boundaries have sufficient energy to jump over the barrier, thereby increasing the conductivity. Thus the grain boundary resistance decreases beyond this frequency and temperature (figure 6). From the Arrhenius plot of a.c. conductivity vs frequency the activation energies are calculated. The activation energy value corresponds to the energy required for the polaron to jump over the grain boundaries. The energy required for jumping over the barrier decreases with both frequency and temperature. This can be seen from the Arrhenius plot of a.c. conductivity at different frequencies (figure 7). The activation energies of a.c. conductivity at different frequencies are summarized in table 1. It is observed that the activation energies are lower than the d.c. conductivity, this is mainly because the a.c. conductivity is due to small polaron mechanism, which is both frequency and temperature dependent as explained above. The polarons tend to relax at frequencies below the hopping frequency. From these hopping frequencies of polarons, the relaxation times are evaluated. The relaxation times of the polarons decrease with increasing temperature. As the temperature increases, the polarons have sufficient thermal energy to get activated and jump over the barrier (figure 8). From the slope of the plot (figure 8), the activation energy for the polaron conduction is estimated. It is clear that the a.c. conductivity in $Bi_6Fe_2Ti_3O_{18}$ is governed by the polaron hopping mechanism and the conductivity is influenced by both frequency and temperature.

5. Conclusions

The impedance spectroscopic data of polycrystalline $Bi_6Fe_2Ti_3O_{18}$ show a semi circle in the high frequency region corresponding to the grain properties of the ceramic pellets, followed by a second more depressed semicircle attributed to the grain boundary. The electrical properties of polycrystalline $Bi_6Fe_2Ti_3O_{18}$ can be described as a parallel *RC* circuit in which *R* represents the bulk resistance and *C* the bulk capacitance. The bulk electrical conductivity of $Bi_6Fe_2Ti_3O_{18}$ follows an Arrhenius law with activation energy of 1·15 eV.

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