Studies on electrical properties of $SrBi_4Ti_{4-3x}Fe_{4x}O_{15}$

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Abstract. The system $SrBi_4Ti_{4-3x}Fe_{4x}O_{15}$ belonging to bismuth layer structured ferroelectric (BLSF) materials with $x = 0$, $0\cdot1$ and $0\cdot2$ has been prepared through solid-state double sintering method. Increase of iron content in $SrBi_4Ti_4O_{15}$ resulted in densification of the samples. The normal puckering observed in the sample has been found to decrease and the lattice distortion increased. Dielectric measurements indicate the ferroelectric transition temperature of the samples to be 530°C, 560°C and 606°C. The increase of transition temperature with increasing iron content is correlated with lattice distortion. Conductivity measurements show two slopes and the activation energies have been found to increase with the iron content. Impedance spectroscopy measurements confirm insulating behaviour at lower temperatures. With increase in temperature the samples become conducting and show relaxational effects. The Cole–Cole plots at higher temperatures are found to be semi-circles. The relaxation times decrease with the increase of iron content.

Keywords. Layer structure compounds; ferroelectrics; piezoelectrics; impedance; dielectric properties.

1. Introduction

$SrBi_4Ti_4O_{15}$ belongs to bismuth layer structured ferroelectrics (BLSF) having four perovskite like layers in between those of bismuth oxide (Bi_2O_2) layers. These compounds have a general formula

$$(Bi_2O_2)^{2+} (A_{m-1} B_m O_{3m+1})^{2-},$$

where A is mono, di, trivalent ions or a mixture of them, and B is a small sized cation with higher valence. These compounds are known to be high temperature piezoelectric materials with large coercivity, high temperature stability, low dielectric loss and high anisotropy. They have added advantage of being lead-free unlike PZT, PLZT etc (Aurivillius 1949a, b, 1950). The cubo-octahedral A sites and octahedral B sites of perovskite layers in these compounds can be substituted by various aliovalent ions (Smolenski *et al* 1961; Subba Rao 1962a, b). The $Bi_2O_2^{2+}$ layers are very strong and cannot be easily disturbed. The number of layers can either be even or odd. Early studies indicate that the even and odd layer compounds exhibit varied physical behaviour. The compounds crystallize either in pseudo orthorhombic or tetragonal structure, they transform to different polar groups up on cooling. The odd layer compounds show single first-order phase transition whereas, many even layered compounds show two transitions, which are about 200°C apart. The lower tran-

sitions appear to be first-order and upper transition, which is Curie point, is second-order. Because of large polarizations and high Curie temperatures, large lattice distortions are expected in these compounds. The compounds synthesized in the present study have Sr^{2+} at A site, Ti^{4+} or Fe^{3+} at B site and the value of n is four. The compounds under study can be considered to form solid solution with the end members $Bi_4Ti_3O_{12}$ and $SrTi_{1-3x}Fe_xO_3$. The compounds can also be represented as

$$Bi_2O_3\ 4[(Sr_{1/4}Bi_{2/4}\square_{1/4})\ (Ti_{(4-3x)/4}\ Fe_{4x/4})O_3].$$
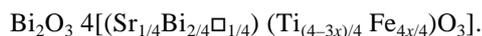
$Sr_{1/4}Bi_{2/4}\square_{1/4}$ are the ions occupying A site, $Ti_{(4-3x)/4}\ Fe_{4x/4}$ are the ions at the B site in the perovskite like ABO_3 structure. $\square$ is unoccupancy (Chan Da Ren and Guo Yanyi 1982; Chan Da Ren 1986). The aim of this communication is to understand the effect of the lattice distortion on electrical properties of the compounds $SrBi_4Ti_{4-3x}Fe_{4x}O_{15}$ with $x = 0$ (SBT), $x = 0\cdot1$ (SBFT1) and $x = 0\cdot2$ (SBFT2).

2. Experimental

The polycrystalline samples in the series $SrBi_4Ti_{4-3x}Fe_{4x}O_{15}$ were prepared by employing solid state reactive sintering. The initial compounds $SrCO_3$, Bi_2O_3, TiO_2, and Fe_2O_3 of AR-grade with 99·99% purity were mixed in appropriate stoichiometric ratios. The mixture was thoroughly ground and the particle size of the starting materials was of the order of few microns. The mixture was stacked in a crucible and sintered isothermally in air at 850°C for

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150 min and then furnace cooled. The material so formed was crushed and powdered by repeated grinding. Pellets were made by pressing them in the form of cylinders at a pressure of 10 Mpa. Samples were final sintered at 1100°C for SBT ($x = 0$), 1070°C for SBFT1 ($x = 0.1$) and 1050°C for SBFT2 ($x = 0.2$) for 2 h. The entire sintering protocol was carried out in a microprocessor-controlled furnace. The pellets were hard discs having a diameter of 1.2 cm and a thickness of 1–2 mm.

2.1 X-ray diffraction

X-ray diffractograms of the powder samples were taken using Cu-K$_a$ radiation at a scanning speed of 1°/min (figures 1a and b). Formation of a single-phase material was confirmed by unambiguously indexing of all the recorded peaks. The lattice constants *a*, *b* and *c* were

Figure 1. X-ray diffractogram of a. SBFT1 and b. SBFT2.

evaluated. The relevant parameters are summarized in table 1. Using this data X-ray densities were computed, and compared with those experimentally determined. The experimental densities of the samples were found to be above 95% of the X-ray density. The density of the samples was found to increase with the increase of iron content. The porosity of the present samples was about 5%. The (b/a) ratios were found to decrease and c/a ratio also decreased with increase of iron content.

2.2 Poling procedure

Samples were poled electrically prior to the dielectric measurements. The poling was done at 150°C under a d.c. field of 20 KV/cm and cooled to room temperature rapidly in the presence of the field. Poling above 150°C was not possible due to increased conductivity of the sample.

2.3 Electrical measurements

The dielectric and impedance measurements were made in the frequency range of 100 Hz–10 MHz from room temperature to 600°C. The large faces of the pellets were initially coated with silver paint and dried at 110°C. Data was collected in steps by using a HP-4192A impedance analyzer interfaced to a computer. The acquisition of data at still higher temperatures was restricted by the enhanced conductivity of the samples. The dielectric constant was determined by measuring the capacitance of the electrically poled sample, at fixed frequencies of 10 kHz, 50 kHz and 100 kHz, with increasing the temperature in steps up to 600°C.

3. Results and discussion

Figures 2–4 present the variation of dielectric constant (a) and loss tangent (b) as a function of temperature at three different frequencies. The dielectric constant and tan *d* remain constant in all these samples up to about 400°C. The room temperature dielectric constant is found to increase with the increase of iron content. Pure SBT sample shows a kink around 450°C and a peak at 530°C. The loss tangent values in all these samples are about 10^{-3} at room temperature. The loss variation is similar to that of dielectric constant variation as a function of tempera-
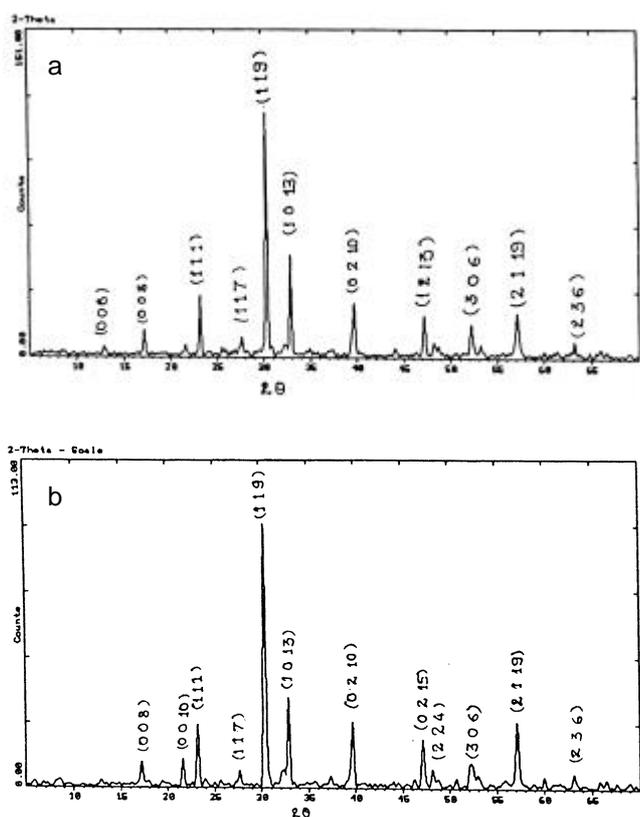
Table 1. Structural parameters of $SrBi_4Ti_{4-3x}Fe_{4x}O_{15}$.

| Compound | Sintering temperatures (°C) | Density (g/cm^3) | | (b/a) | (c/a) | Distortion (Δz) (nm) |
		Experimental	Theoretical			
SBT ($x = 0$)	1100	7.13	7.46	1.004	7.561	1.960
SBFT1 ($x = 0.1$)	1070	7.16	7.47	1.003	7.555	1.996
SBFT2 ($x = 0.2$)	1050	7.23	7.52	1.002	7.550	2.052

ture. The peaks observed in tan δ are much broader. The values of dielectric constant and loss at the peak temperature decrease with the increase of frequency. In SBFT (x 0), the low temperature kink observed in SBT, has become a shoulder peak at 400°C. From the dielectric data transition temperatures are 560°C for SBFT1 and 606°C for SBFT2. No peaks could be recorded in tan d measurements. As the iron content is increased, the peaks in dielectric constant versus temperature curves move to higher temperature and become broader. The capacitance and hence dielectric constant values decrease

with increase of iron content. The pertinent data on dielectric properties are given in table 2.

Figure 5 presents the variation of d.c. conductivity as a function of inverse of temperature on semi-log scale for SBT, SBFT1 and SBFT2. The conductivity ($s_{d.c.}$) of the samples vary about eight orders and show three distinct regions. The first one below 250°C, the second between 250–450°C and the third beyond 450°C. The activation energies increase with increase of iron content. Some results from conductivity measurements are presented in table 3.
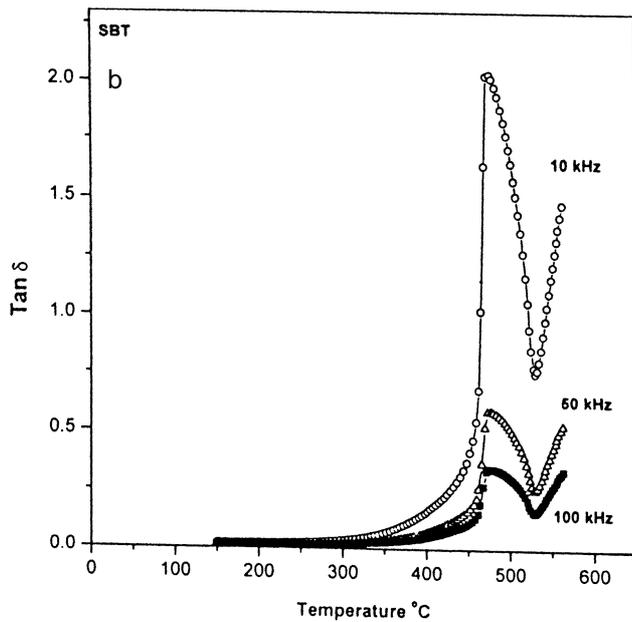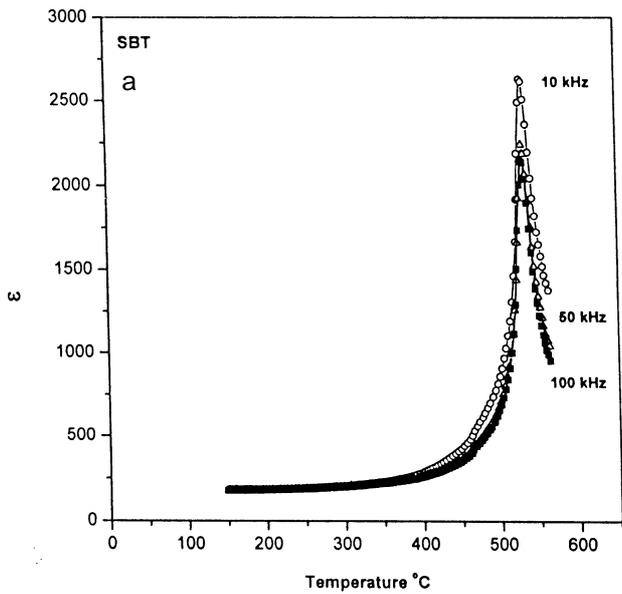

Figure 2. a. Variation of dielectric permittivity with temperature at frequencies mentioned for SBT and b. variation of dielectric loss with temperature at frequencies mentioned for SBT.
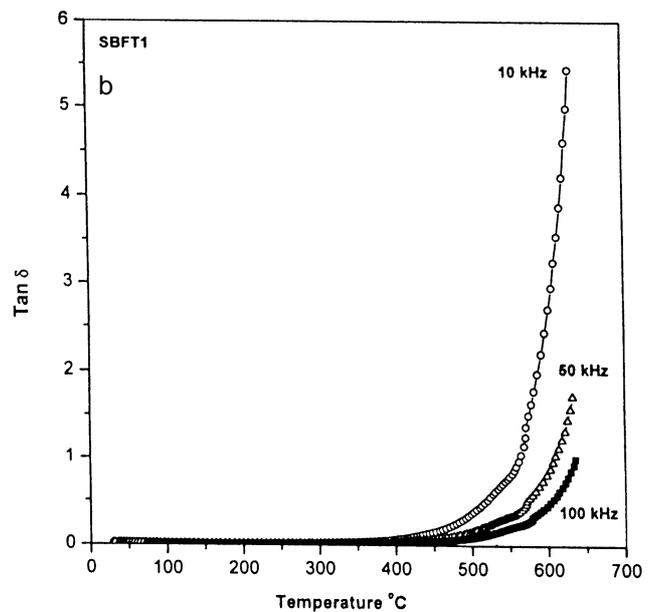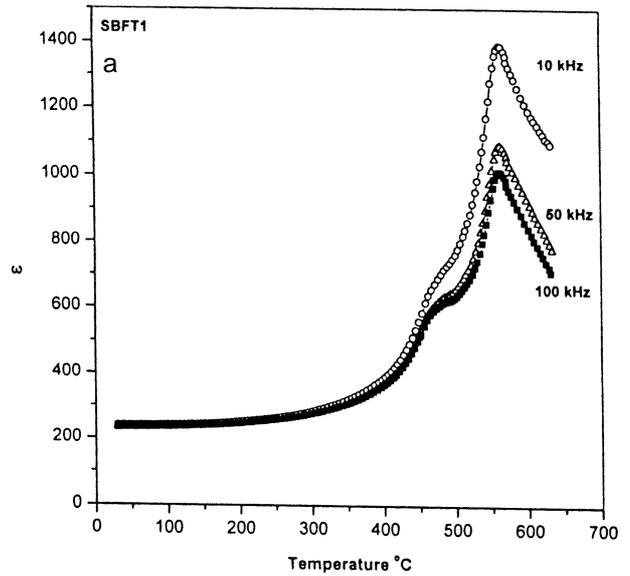
Figure 3. a. Variation of dielectric permittivity with temperature at frequencies mentioned for SBFT1 and b. variation of dielectric loss with temperature at frequencies mentioned for SBFT1.

The present class of compounds have four perovskite layers interleaved between $(Bi_2O_2)^{2+}$ layers. There are two crystallographically defined positions for the bismuth ions. The bismuth in bismuth oxide-layer has five near neighbours arranged in a pyramid. The decrease of b/a ratio from unity would indicate the distortion of square pyramidal shape in bismuth oxide layer. The bismuth ions in perovskite layers contribute strongly to spontaneous polarization (Newnham 1968). The deviation of a/c ratio

indicates the distortion of octahedra (Newnham 1971). It has been shown that (Subba Rao 1962b) the atoms in the perovskite layers can be replaced but atoms/ions in Bi_2O_2 layers cannot be substituted. As mentioned earlier these compounds consist of four perovskite (ABO_3) layers forming TiO_6 octahedra. The polarization would involve the displacement of highly charged B site cations away from the centre of coordination octahedra (Subba Rao 1962a, b). The replacement of Ti^{4+} with Fe^{3+} ions in the present study increases the polarization and therefore may increase the Curie temperature as observed in the present measurements. Incorporation of Fe ions into the B sites of the perovskite layers changes the distortion of octahedra. It has been reported (Abraham *et al* 1968) that the atomic displacement (Δz) of certain atoms from their equilibrium positions can be correlated with Curie temperature as per the relation

$$T_c = (2 \cdot 00 \pm 0 \cdot 09) \times 10^4 \, (\Delta z)^2.$$

T_c is expressed in degree Kelvin and (Δz) in Å units, here Δz refers to displacement of Ti/Fe (B site ions) from octahedral centre. The calculated Δz values are tabulated in table 1. Δz values increase with increase of iron content, Δz and c/a parameters characterize distortion of octahedra of perovskite layers. From the principle of minimum strain energy in phase transition, the oxygen octahedra within the materials of even layered compounds exhibit zig–zag distortion as indicated by (a/c) ratio (Newnham
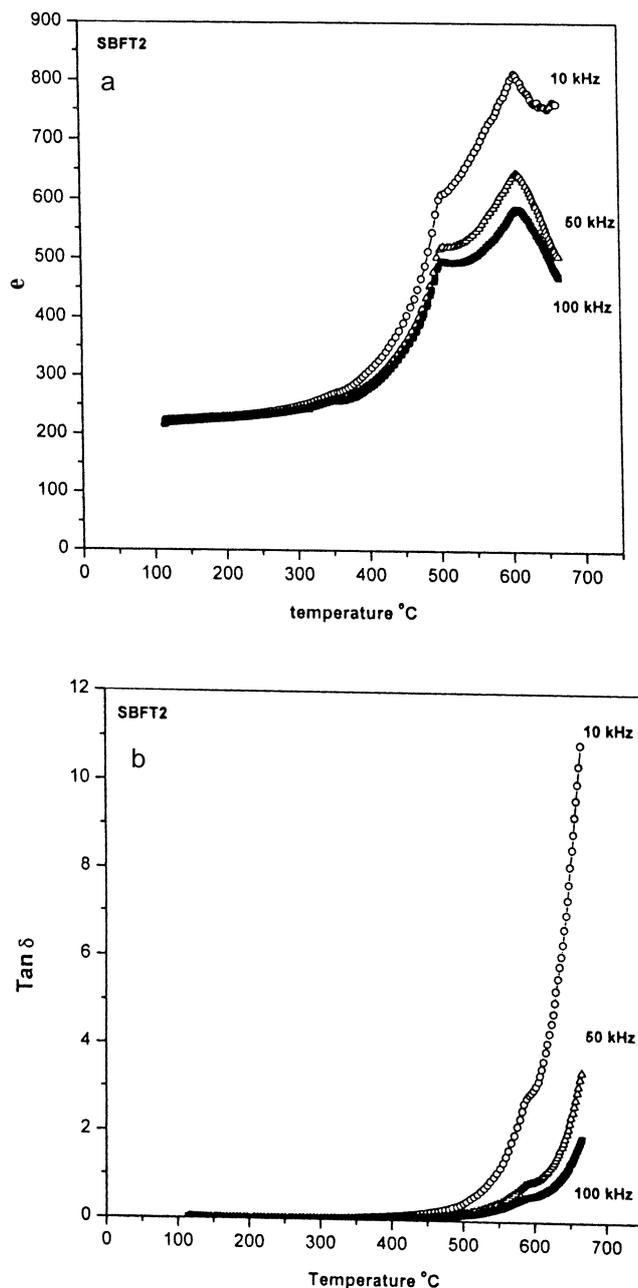

Figure 4. a. Variation of dielectric permittivity with temperature at frequencies mentioned for SBFT2 and b. variation of dielectric loss with temperature at frequencies mentioned for SBFT2.
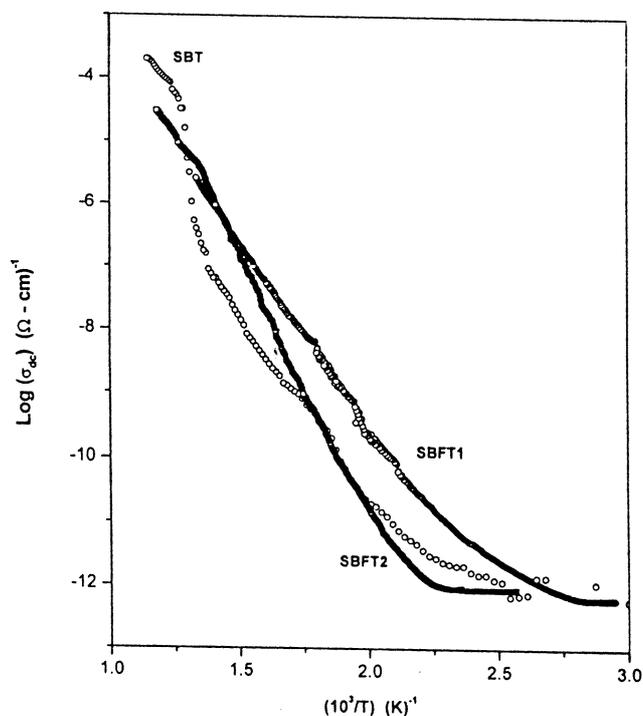

Figure 5. D.c. conductivity vs inverses of temperature of SBT, SBFT1 and SBFT2.

1968; Chan Da Ren 1986). The angle of this distortion changes with the increase of iron concentration. In the present samples Fe^{3+} incorporation (substituting for Ti^{4+} in B sites of perovskite ABO_3 layers) causes the movement of Fe^{3+} ions towards positive ions of A sites from the octahedra, thereby effecting (b/a) ratios and polarization as observed in the present measurements. Large variation of d.c. conductivity with temperature (8 orders) in the range from room temperature to 550°C is an indication of presence of long range conducting charge species in the samples. Beyond 550°C, the samples become highly conducting. The conductivity in the iron-substituted samples is also independent of temperature up to certain temperature, beyond which the conductivity increases with temperature. At high temperatures the charges are set free in the sample and conductivity increases (Rama Sastry *et al* 1998). This idea is also supported by observation of larger activation for conduction in Fe substituted samples. Impedance measurements as a function of temperature undertaken in these samples show a peak in imaginary

Table 2. Pertinent dielectric data of SrBi$_4$Ti$_{4-3x}$Fe$_{4x}$O$_{15}$.

Compound	Transition temperature (°C)	Kink temperature (°C)	Dielectric constant						Loss (at room temperature)		
			10 kHz		50 kHz		100 kHz				
			RT	T_c	RT	T_c	RT	T_c	10 kHz	50 kHz	100 kHz
SBT ($x = 0$)	530	450	169	2634	158	2238	157	2129	0·0082	0·0067	0·0055
SBFT1 ($x = 0·1$)	560	475	180	1388	177	1087	177	1005	0·0112	0·0104	0·0099
SBFT2 ($x = 0·2$)	606	500	203	818	199	649	197	587	0·0164	0·0196	0·0205

RT: Room temperature ≈ 30°C

Table 3. D.c. conductivity and activation energies for conduction.

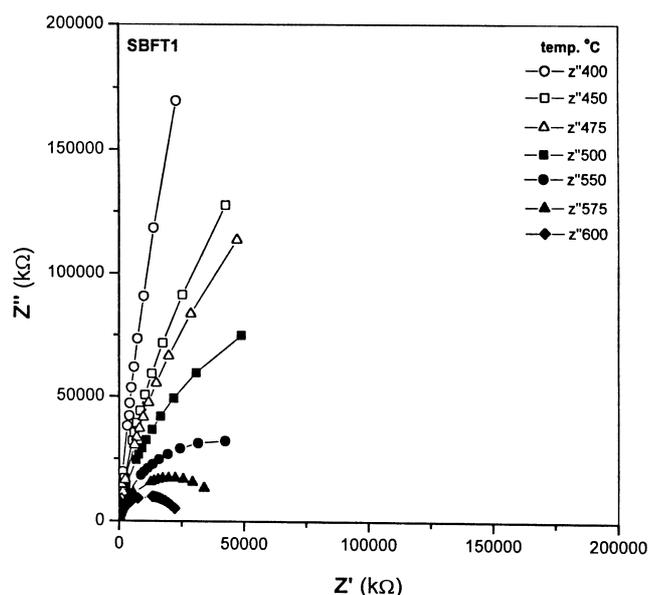| Compound | Conductivity (Ω-cm)$^{-1}$ | | | | Activation energy (eV) | |
	100°C	200°C	300°C	400°C	(250–450°C)	(450–600°C)
SBT ($x = 0$)	$6·00 \times 10^{-13}$	$6·54 \times 10^{-12}$	$7·20 \times 10^{-10}$	$1·78 \times 10^{-8}$	0·80	1·09
SBFT1 ($x = 0·1$)	$9·62 \times 10^{-13}$	$6·23 \times 10^{-11}$	$9·77 \times 10^{-9}$	$2·95 \times 10^{-7}$	0·82	1·16
SBFT2 ($x = 0·2$)	$8·68 \times 10^{-13}$	$3·40 \times 10^{-12}$	$1·24 \times 10^{-9}$	$2·40 \times 10^{-7}$	0·97	1·26

Figure 6. Complex impedance plane plots of SBFT1 at different temperatures.
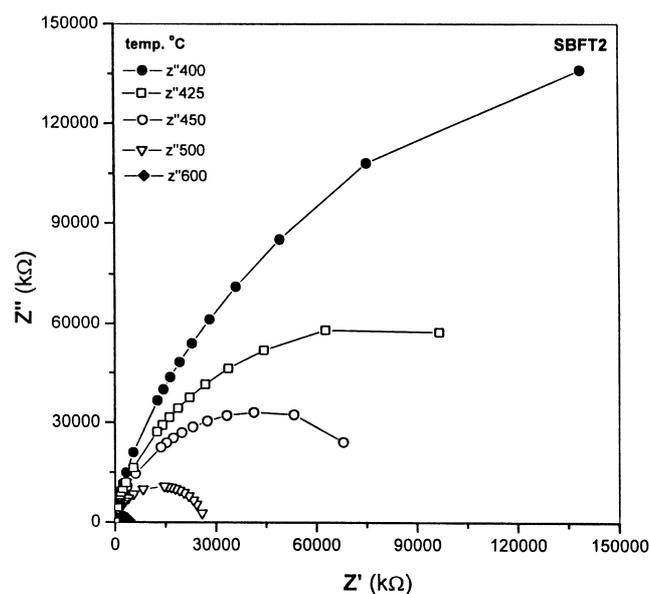

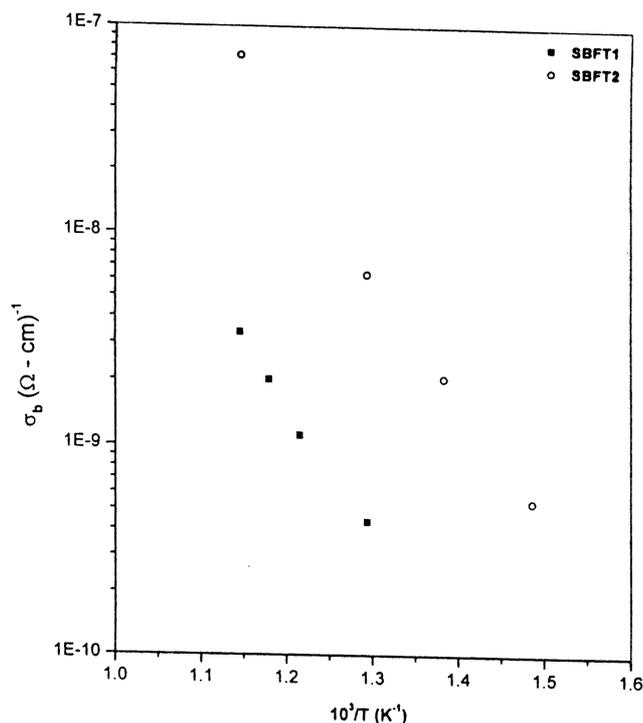**Figure 7.** Complex impedance plane plots of SBFT2 at different temperatures.

Figure 8. Arrhenius plots for the bulk conductivity of SBFT1 and SBFT2.

Figure 9. Relaxation time versus inverse of temperature of SBFT1 and SBFT2.

part of the impedance beyond 400°C. The peaks shift to higher frequencies at higher temperatures. SBFT1 samples show maximum impedance at the peak. The imaginary part of the impedance (Z'') when plotted as a function of real part of impedance (Z') give Cole–Cole plots. These Cole–Cole plots characterize the relaxing species in the samples. The Cole–Cole plots of a sample with single relaxation give Debye relation and semi-circles with centres on *x*-axis (Johnscher 1981; Bunget and Popescu 1984; James *et al* 1996). The shapes of the Cole–Cole plots obtained in the present study depends on temperature and are shown in figures 6 and 7. At lower temperatures (< 400°C), the Cole–Cole plots of SBFT1 are more or less straight lines with large slopes. As the temperature is increased the line curves and beyond 550°C the curve becomes almost semi-circular. The intercept of this semicircle with real axis gives bulk resistance of the sample (James *et al* 1996). Using these values of the resistance bulk conductivity is calculated and plotted in figure 8. This calculated bulk conductivity increases with the increase in temperature. SBFT2 samples also show similar behaviour from the peak position of Cole–Cole plots. The relaxation times are obtained and plotted in figure 9, as a function of inverse of temperature. The slope of Arrhenius gives the activation energy for relaxation. These values are 1·18 eV for SBFT1 and 1·23 eV for SBFT2. These energies are nearly equal to activation energies of conduction in these samples (1·16 eV for SBFT1 and 1·26 eV for SBFT2 samples), hence the relaxation species may be
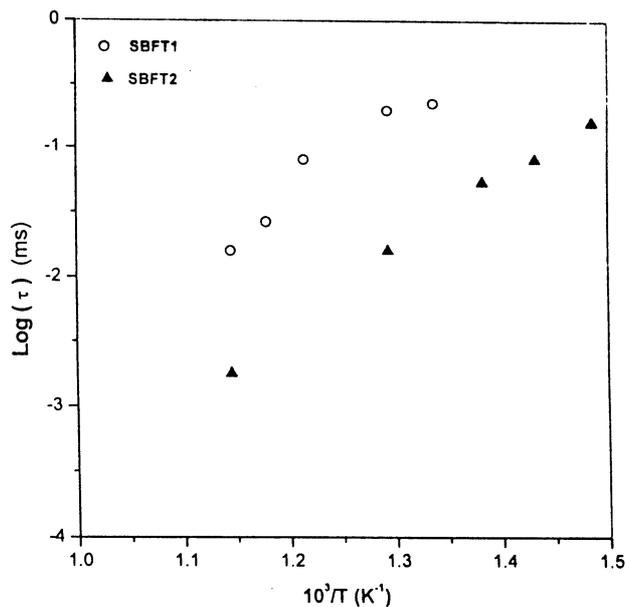
defect–ion complexes, the possibilities are $Fe^{3+}-V_0$ or $Ti^{3+}-V_0$ (Warren *et al* 1996) complexes.

4. Conclusions

(I) SBT, SBFT1 and SBFT2 samples have been synthesized and found to form single-phase materials. The density obtained is about 95% of theoretical density.
(II) The ferroelectric Curie temperature T_c increases with the increase of iron content. This is interpreted in terms of distortion introduced due to iron incorporation.
(III) The samples show large variation of d.c. conductivity with temperature.
(IV) Bulk resistance, relaxation times and activation energy for relaxations are obtained from impedance study.

Acknowledgements

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