

## Studies on electrical conduction in $\text{Bi}_4\text{SrTi}_4\text{O}_{15}$

A R JAMES, G S KUMAR, T BHIMASANKARAM and  
S V SURYANARAYANA

Department of Physics, Osmania University, Hyderabad 500 007, India

**Abstract.** The ferroelectric  $\text{Bi}_4\text{SrTi}_4\text{O}_{15}$  has been synthesized and a study of the electrical (AC) conductivity was made on both poled and unpoled samples in the frequency range from 100 Hz to 1 MHz and from room temperature to 550°C. In the case of unpoled samples the activation energy was found to be 0.54 eV and subsequent to poling it was lowered to 0.39 eV indicating an increased conductivity after poling. Further the conductivity increased with increasing frequency and temperature. DC conductivity measurements were also carried out. Dielectric measurements indicate a peak in the dielectric constant at 530°C.

**Keywords.** Ferroelectrics; electrical conductivity; poling; dielectric constant.

### 1. Introduction

The materials with the generic formula  $\text{Bi}_2\text{M}_{n-1}\text{R}_n\text{O}_{3n+3}$  (where  $\text{M} = \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}$  and  $\text{Pb}^{2+}$  and  $\text{R} = \text{Ti}^{4+}, \text{Nb}^{5+}$  etc. ( $n = 1, 2, 3, 4, 5$ )) belong to a large family of layered structure compounds (Auruwillius 1949). With  $n = 4$  and M site being occupied by  $\text{Bi}_2^{3+}$  and  $\text{Sr}^{2+}$  and R with  $\text{Ti}^{4+}$  one can synthesize the compound  $\text{Bi}_4\text{SrTi}_4\text{O}_{15}$ . The compound is tetragonal with slight orthorhombic distortion. Their a and b axes lie along  $\langle 110 \rangle_c$  where the suffix denotes the cubic perovskite subcell so that  $a \approx b \approx 2a_c \approx 0.54$  nm. The c axis is inherently long. These layered perovskite compounds are ferroelectric with high Curie temperatures (Subba Rao 1962). The ionic polarization makes an important contribution to the permanent dipole in the ferroelectric state. The structural consequence of this polarization is to distort the octahedral coordination, and thereby to lower the crystal symmetry. For the present system the molecular formula can also be written as (Chen Da Ren 1986),



The latter part has an  $\text{ABO}_3$  type perovskite structure but the ions in the A position are different. The occupancy of A site is 2/4 Bi, 1/4 Sr and 1/4  $\square$  vacancy. The number of  $\text{Bi}^{3+}$  ions in the perovskite layer is twice as much as that of the  $\text{Sr}^{2+}$  ions. Chen Da Ren and Guo Yan Yi (1982) reported piezoelectric properties of a number of compounds by replacing the cations having similar structural configurations. According to them the  $\text{Bi}^{3+}$  ion has an important effect on the bond strength of  $\text{Ti}^{4+} - \text{O}^{2-}$  (along a axis) in the compound  $\text{Bi}_4\text{SrTi}_4\text{O}_{15}$ . The low crystal symmetry and high coercive fields observed in these compounds, result in the high stability of the piezoelectric properties for ceramic materials of  $\text{Bi}_4\text{SrTi}_4\text{O}_{15}$  either under high temperature or under one dimensional stress. Such compounds are important for many applications involving piezoelectric properties of ceramics.  $\text{Bi}_4\text{SrTi}_4\text{O}_{15}$  has been tested recently for SAW device applications (Takenaka *et al* 1983).

It has been found that these ceramics with Bi-layer structure, owing to their very high coercive fields and lower symmetry may have an essentially weak point in that a satisfactorily large remanent polarization cannot be obtained by poling. To solve this problem, different methods of preparation of the compounds have been suggested viz. hot forging, hot rolling, hot extrusion and superplastic deformation. These methods give ceramics with grain orientations and different densities (Takenaka *et al* 1975). The present workers have felt that different preparation methods give compounds with different electrical conductivities. According to Gurevich (1971) the difference in the numerical values of the Curie constant determined by different authors, for ferroelectrics is far beyond the experimental errors and is due to the different electrical conductivities of the crystals. The conductivity appreciably affects the domain structure and its motion. The preparation of single domain crystals is dependent upon the competition between the rate of growth of the ferroelectric phase and variation in the concentration of the free charge carriers. When the crystal shifts from para to the ferroelectric phase, it has been found that the electrical conductivity appreciably restricts the utilization of several properties of ferroelectrics. For example, polarized ferroelectric ceramics should have piezoelectric properties up to the Curie point, but experimentally, many of the piezoelectric transducers suffer from the degradation of piezoelectric properties at temperatures much below this temperature. Due to the very strong increase in the electrical conductivity with rise in temperature it is not possible to polarize the ferroelectric ceramics near the Curie point and at the same time utilize the potentialities of the ferroelectric ceramics (Gurevich 1971). Therefore the study of electrical conductivity becomes an important aspect. The present workers have undertaken the study of conductivity of  $\text{Bi}_4\text{SrTi}_4\text{O}_{15}$  prepared by the double sintering method. The technique selected is that of the study of impedance by an impedance analyzer to analyze the AC conductivity. The DC conductivity has also been studied. The capacitance measurements have been made to assess its dielectric anomaly. The results are presented here.

## 2. Experimental

### 2.1 Sample preparation

The polycrystalline samples of  $\text{Bi}_4\text{SrTi}_4\text{O}_{15}$  were prepared by the method of reactive sintering. The standard ceramic fabrication procedure has been followed for the preparation. The initial compounds  $\text{SrCO}_3$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{TiO}_2$  (AR grade) were mixed in appropriate ratios as required by the balance equation for the synthesis of the desired compound. The mixture was thoroughly ground and the particle size of the initial materials ranged from 1–2  $\mu\text{m}$ . The mixture was stacked in a crucible and sintered isothermally in air at 850°C for 2 h and then cooled. Pellets having a diameter of 1 cm and thickness of 1–2 mm, were made by applying a pressure of 8 MPa. The pellets were subjected to thermal heating at 400°C for 2 h to eliminate the binder (polyvinylalcohol) and finally sintered at 1200°C for densification. The pellets were cooled slowly from 1200°C–1000°C and then allowed to furnace cool. The entire sintering was done in a microprocessor-based furnace. The densified pellets were used for all measurements. The density of the pellets was found to be 89% of the X-ray density.

## 2.2 Characterization and measurements

The single phase formation was confirmed by XRD. The electrical measurements in the frequency 100 Hz-1 MHz were made using an HP4192 A impedance analyzer interfaced to a computer in the temperature range from room temperature to 550°C. The larger faces of the pellets were initially coated with silver paint and dried at 100°C.

The DC conductivity data was evaluated by measuring the resistance in the sample under a DC bias using the two-probe method at various temperatures on a Keithley 610C electrometer.

Electrical (AC) conductivity (using the admittance method) measurements were carried out on the silver coated pellets by placing them in between two stainless steel blocks which in turn were connected to the leads. The frequency range used was 100 Hz-1 MHz and the measurements were carried out in the temperature range from room temperature to 550°C.

## 3. Results and discussions

### 3.1 Electrical conductivity

The specific conductivity in air was deduced from the admittance values and the results are shown in figure 1. The pellet used was an unpoled sample. At the initial temperatures above room temperature the admittance decreases up to about 150°C while at temperatures above this value, the conductivity increases with the rise in temperature as well as with frequency. The  $\log \sigma$  vs  $10^3/T$  plots shown in figure 1 indicate the behaviour of the sample with the frequency of the AC signal and the temperature. The activation energy from this plot comes out to be 0.542 eV (at 500 kHz). The conductivity increases with frequency (figure 2) and this dependence can be expressed as (Yootarou *et al* 1973)

$$\sigma' = A \cdot \omega^n, \quad (1)$$

where  $A$  is a constant,  $\omega$  the angular frequency and  $n$  a number (0.546 at 400°C). From the Arrhenius plots shown in figure 1 it is evident that in the low temperature region the conductivity variation at different frequencies is less dependent on temperature. The difference in frequency dependence of conductivity is more prominent at low temperatures. The activation energy as determined in the high temperature regions of the plots decreases with the increase in frequency.

The impedance data was also taken on the sample poled electrically. The electric poling was done placing the silver coated sample in an oil bath in between two electrodes to which an electric field of 10.6 kV/cm was applied. The sample was heated in the presence of an external field to 150°C and it was poled at this temperature in the presence of the field. The field was retained while cooling as well. The surface charges were removed by rubbing the sample with a shorted metal foil. The sample was then inserted in the sample holder and the impedance data collected. It was noticed that the poled samples showed higher conductivity values (figure 3) than the unpoled samples. The activation energy for a poled

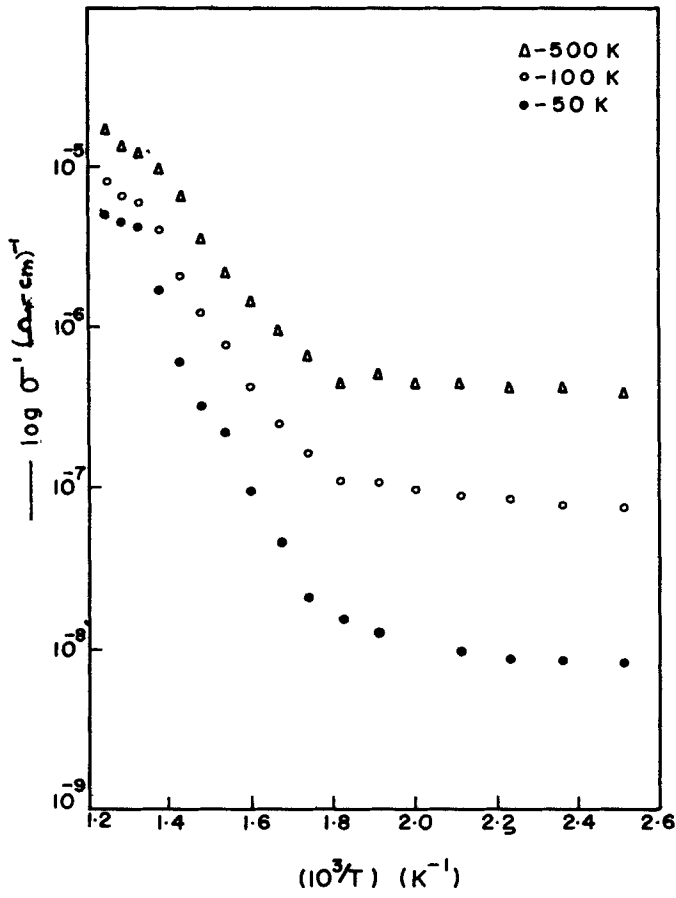


Figure 1. Variation of  $\log \sigma'$  with  $1/T$  for an unpoled sample.

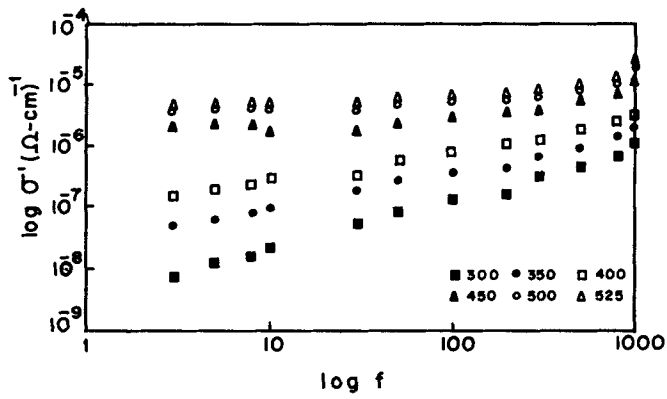
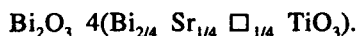


Figure 2. Variation of  $\log \sigma'$  with frequency.

sample in the high temperature region (0.39 eV) comes out to be less than that in the unpoled sample (0.54 eV). Further the activation energy as determined from the Arrhenius plots (figure 4) for DC measurements has been found to be 1.52 eV which is more than that for AC conduction in the same temperature region. The DC conductivity increases monotonously with temperature. As mentioned earlier for  $\text{Bi}_4\text{SrTi}_4\text{O}_{15}$ , the molecular formula can be written as



Therefore there is a vacancy in the A position, in the perovskite structure of  $\text{ABO}_3$  type, which will also contribute towards conductivity. The values of activation energies also suggest this. In the poled sample we get a higher AC conductivity and as the temperature is increased, there will be a depletion of polarized charges, contributing to higher conductivity values. This is obvious from the experiment which shows that above the transition temperature, the value of  $\sigma$  reaches the same values as those of the unpoled samples. The sample cannot be poled at higher

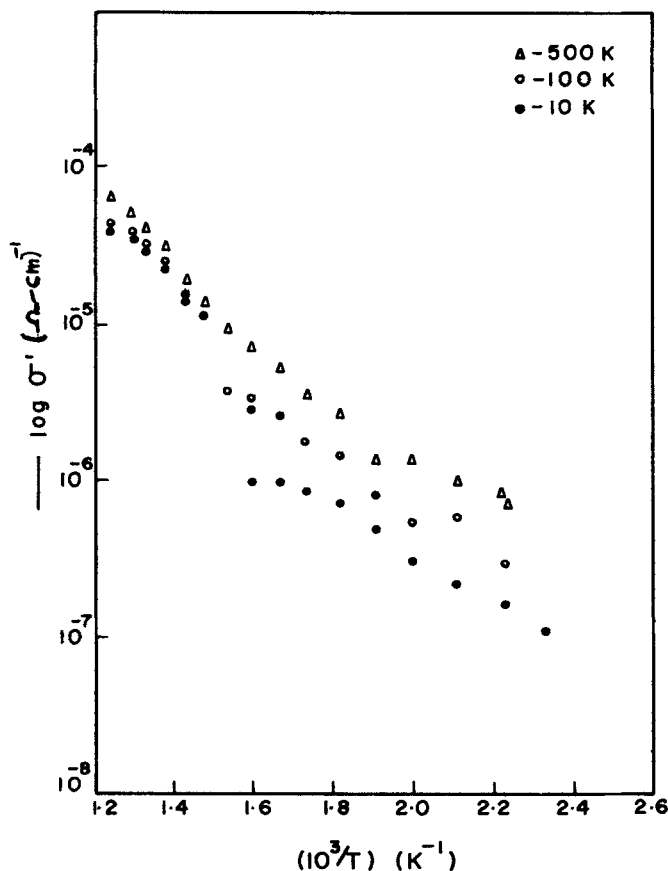


Figure 3. Variation of  $\log \sigma'$  with  $1/T$  for a poled sample.

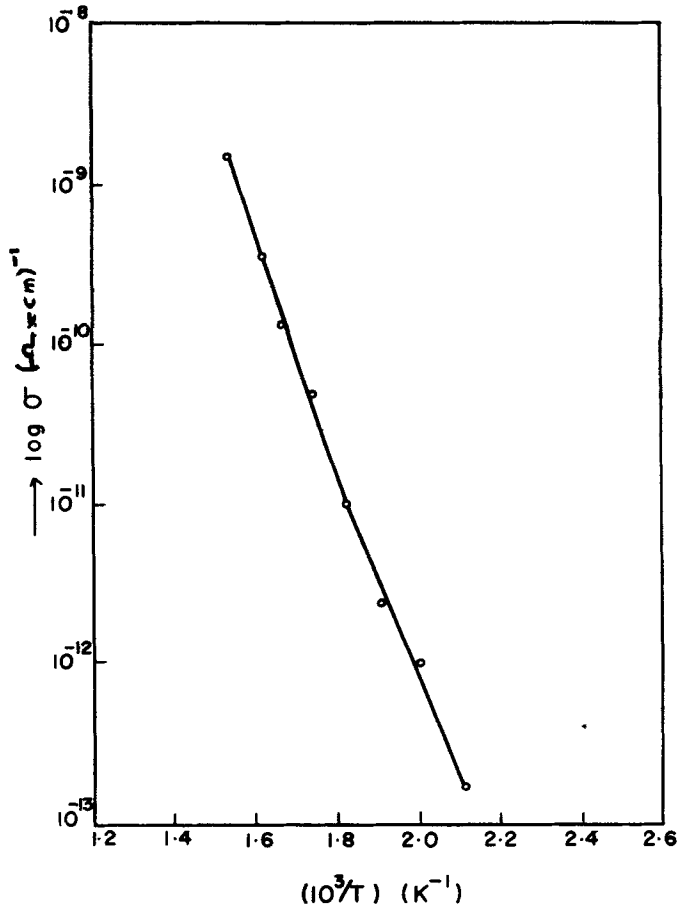


Figure 4. Variation of  $\log \sigma_{dc}$  with  $1/T$ .

temperatures on account of its high conductivity at those temperatures. Further the poling process in turn depends upon the density of the sample prepared.

### 3.2 Dielectric measurements

The capacitance measurements were made on electrically poled samples with an impedance analyzer at different frequencies and in the temperature range from room temperature to 600°C. Figure 5 represents the observed variation of dielectric constant with temperature as a function of frequency. It was found that at low frequencies the dielectric constant increased with temperature even beyond the  $T_c$ . This may be due to the fact that at lower frequencies the contribution of electrical conduction of the sample is more, leading to the masking of the dielectric peak at the transition temperature but at higher frequencies, apart from the dispersion a peak is observed at around 530°C. The values of permittivity are fitted into the Curie-Weiss law

$$\epsilon = C/(T-T_c),$$

where  $\epsilon$  is the dielectric constant,  $C$  the Curie constant and  $T_c$  the transition temperature.  $T_c$  has been found to be  $528^\circ\text{C}$  and the Curie constant comes out to be  $0.37 \times 10^4 (^\circ\text{C})$ . Figure 6 depicts the variation of  $\tan \delta$  as a function of both temperature and frequency. The value of  $\tan \delta$  increases appreciably before  $T_c$ . It decreases with increasing frequency at higher temperatures and the peak in  $\tan \delta$  becomes broader.

#### 4. Conclusions

The results of investigations on sintered pellets indicate that the poled and unpoled samples behave differently *vis-a-vis* their conductivities. It was found that the unpoled samples exhibit lower conductivity values under both AC and DC conditions,

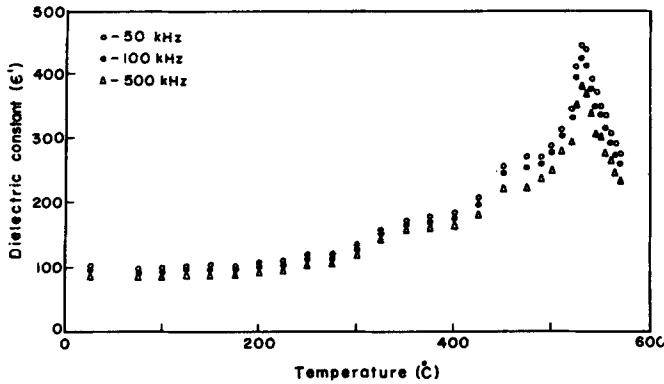


Figure 5. Variation of dielectric constant with temperature at different frequencies.

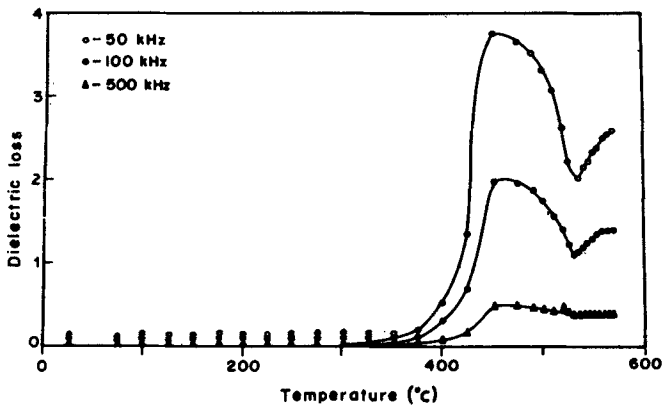


Figure 6. Variation of dielectric loss with temperature.

as compared to their poled counterparts. The converse was found to be true in the case of their activation energies. In so far as the dielectric transition is concerned, a peak was observed at 530°C which is well in agreement with the reported values. This piezoelectric ceramic is therefore suitable for use as a transducer material even at high temperatures on account of the fact that it has a high Curie temperature, low dielectric constant and a fairly stable behaviour at high temperatures.

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