Defence Science Journal, Vol. 57, No. 1, January 2007, pp. 29-34

Synthesis and Characterisation of Strontium Bismuth Titanate Ceramics via High-energy Mechanical Milling

Gagan Anand[1], A.R. James[2], T. Radha Krishna[3], and P. Sarah[4]

[1]*St. Martin's Engineering College, Hyderabad-501 014*
[2]*Defence Metallurgical Research Laboratory, Hyderabad-500 058*
[3]*JNTU College of Engineering, Hyderabad-500072*
[4]*CVR College of Engineering, Vastunagar, A.P.-501 510*

ABSTRACT

The processing conditions, microstructure, and dielectric properties of strontium bismuth titanate (SBT) were systematically studied. The specimen was synthesised by a mechano-chemical processing route using a planetary ball mill. It is important that the action is vigorous enough to break up loose aggregates and a fine particle size is obtained. The specimen was calcined at 800 °C for 4 h. The calcined samples were subjected to cold isostatic pressing (CIP) process and finally sintered at 1200 °C for 2 h. A relative density ≈ 90 per cent of the theoretical density was obtained. Pellets having a diameter of 1cm and thickness of 1 mm were prepared from the sintered compacts for electrical measurements. X-ray diffraction showed that a single phase with the layered perovskite structure of SBT was formed. Morphological studies were carried out by SEM analysis. Frequency dependence of impedance can provide additional insight into mechanisms controlling the electrical response. Resonance studies were made on poled sample in the frequency range 100 kHz – 20 MHz using an impedance analyser (HP-4294A) interfaced to a computer at room temperature. Dielectric measurements in the frequency range 100 Hz–1 MHz were made using an impedance analyser (HP-4192A) interfaced to a computer and the measurements were carried out from room temperature to 550 °C. The ferroelectric hysteresis loop was measured using a standard ferroelectric analyser based on Sawyer-tower circuit. Elastic compliance (s_{33}, s_{11}) coupling factor (k_{33}, k_{31})were also obtained. These materials can be utilised in practical applications as substitutes for lead titanate and lead zirconate titanate (PZT)-based ceramics, where high temperature applications are foreseen.

Keywords: Strontium bismuth titanate, synthesis, characterisation, resonance, dielectric measurement, SBT, perovskite, mechano-chemical processing

1. INTRODUCTION

The materials with the generic formula $Bi_2M_{n-1}R_nO_{3n+3}$ (where M=Ca^{2+}, Sr^{2+}, Ba^{2+}, and Pb^{2+} and R=Ti^{4+}, Nb^{5+}, etc), (n=1, 2, 3, 4, 5) belong to a large family of layered structure compounds[1]. With n=4 and M site being occupied by Bi^{3+}_2 and Sr^{2+} and R with Ti^{4+}, one can synthesise the compound $Bi_4SrTi_4O_{15}$. The compound is tetragonal with slight orthorhombic distortion. Their a and b axes lie along $(110)_c$ where the suffix denotes the cubic perovskite subcell so that $a \approx b \approx 2ac \approx 0.54$ nm. The c axis is inherently long. The pseudo-structure of strontium bismuth titanate (SBT) can be seen

Revised 16 September 2006

in Fig. 1. These layered perovskite compounds are ferroelectric with high curie temperatures[2].

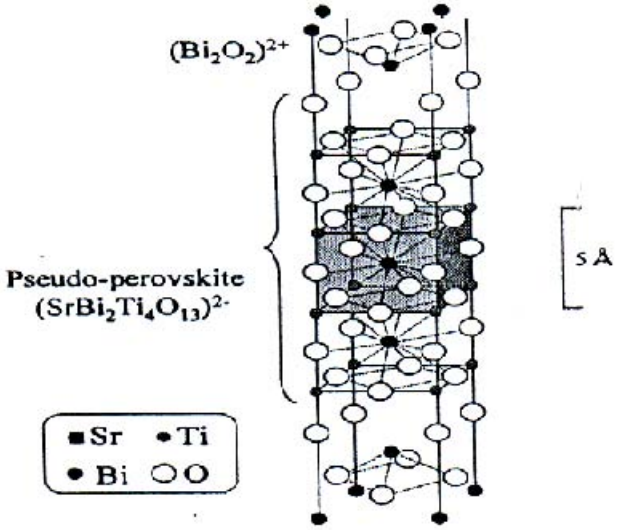

Figure 1. Lattice structure of strontium bismuth titanate.

The ionic polarisation makes an important contribution to the permanent dipole in the ferroelectric state. The structural consequence of this polarisation is to distort the octahedral coordination, and thereby lower the crystal symmetry. For the present system, the molecular formula[3] can also be written as

$$Bi_2O_3\ \ 4(Bi_{2/4}Sr_{1/4}TiO_3)$$

The latter part has an 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 vacancy. The number of Bi^{3+} ions in the perovskite layer is twice as much as that of the Sr^{2+} ions. Chen and Guo[4] reported piezoelectric properties of a number of compounds by replacing the cations having similar structural configurations. According to them, the Bi^{3+} ion has an important effect on the bond strength of Ti^{4+}-O^{2-} (along an axis) in the compound $Bi_4SrTi_4O_{15}$. 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 $Bi_4SrTi_4O_{15}$ either under high temperature or under one-dimensional stress. Such compounds are important for many applications involving piezoelectric properties of ceramics.

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 polarisation 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[5].

It was felt that different preparation methods give compounds with different electrical conductivities. 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 variations in the concentration of the free-charge carriers. When the crystal shifts from paraelectric to the ferroelectric phase, it has been found that the electrical conductivity appreciably restricts the utilisation of several properties of ferroelectrics. For example, polarised 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. The synthesis of SBT by a mechano-chemical route has been carried out with an aim to study the differences between normally synthesised SBT ceramics and mechano-chemical processed samples.

2. EXPERIMENTAL

2.1 Sample Preparation

The polycrystalline samples of $Bi_4SrTi_4O_{15}$ were prepared by reactive sintering. The standard ceramic fabrication procedure was followed for the preparation. The initial compounds $SrCO_3$, Bi_2O_3, TiO_2 (Sigma Aldrich, 99.9 % pure, 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 using a planetary ball mill for 5 h. The particle size of the initial materials ranged from 1 μm to 2 μm. The mixture was stacked in a crucible and calcined isothermally in air at 800 °C for 4 h and then cooled. The calcined samples were subjected to cold isostatic press (CIP) for compaction and finally sintered at

1200 °C for 2 h and then allowed to furnace cool. Pellets of dia 1 cm and thickness 1mm were made. The entire sintering was done in a microprocessor-based furnace. The densified pellets were used for all measurements.

2.2 Characterisation and Measurements

The density of the pellets was found to be 90 per cent of the x-ray density. The single-phase formation was confirmed by XRD. SEM image of the SBT is shown in Fig. 2. The electric poling was done placing the silver-coated sample in an oil bath in between two electrodes to which an electric field of 15 kV/cm was applied. The sample was heated in the presence of an external field to 100 °C. The field was retained during cooling as well. The dielectric measurements were made on electrically poled samples with an impedance analyser (HP-4192A) at different frequencies from room temperature to 550 °C.

These measurements were carried out on silver-coated pellets by placing these in between two stainless steel blocks, which in turn were connected to the leads. The resonance measurements were carried out in the frequency range 100 Hz–1 MHz at room temperature using HP-4294A interfaced to computer. The ferroelectric hysteresis loop measurements were done placing the silver-coated unpoled samples in a silicon oil bath in between two electrodes using a ferroelectric hysteresis loop analyser based on a modified Sawyer-tower circuit interfaced to computer. Resonance date were used to calculate elastic compliance [s_{33},s_{11}] coupling factor [k_{33},k_{31}] for SBT[6].

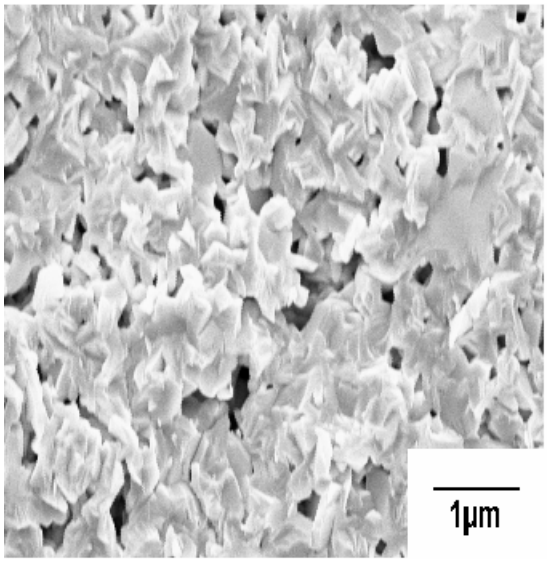

Figure 2. SEM of strontium bismuth titanate ceramics.

3. RESULTS AND DISCUSSION

Figure 3 represents the observed variation of dielectric constant with temperature as a function of frequency. A small peak was observed at 370 °C, apart from the dispersion a peak was observed at around 530 °C. It was found that the even- and odd-layered compounds behave differently[7]. Odd-layered crystals belong to orthorhombic space group B2cb, and show a single first-order transition. Many even-layered compounds such as SBT show two- phase transitions about 200° apart. The lower transition appears to be first-order with a large hysteresis. The upper transition is considered to be the Curie point and is of second-order.

The dielectric constant versus temperature curve obeyed a Curie-Weiss law.

$$\varepsilon = C/(T-T_c)$$

where ε is the dielectric constant, C the Curie constant and T_c the transition temperature. Upon

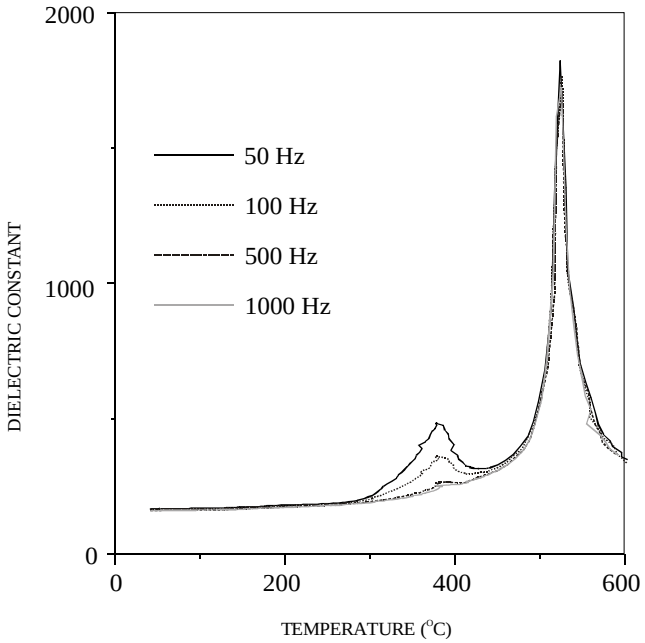

Figure 3. Variation of dielectric constant with temperature.

fitting to the Curie-Weiss law, T_c was found to be 528 ºC and the Curie constant 2.7 x 10-5 ºC. Figure 4 depicts the variation of tan δ as a function of both temperature and frequency. The value of tan δ increases appreciably before the dielectric transition. It decreases with increasing frequency at higher temperatures and the peak in tan δ becomes broader.

Hysteresis loop for the sintered SBT sample are shown in Fig. 5. The coercive field (E_c) values that resulted from these measurements were 12.6 kV/cm. The remnant polarisation obtained was 0.92 μC/cm^2. The maximum field applicable was limited on account of the power supply limitations.

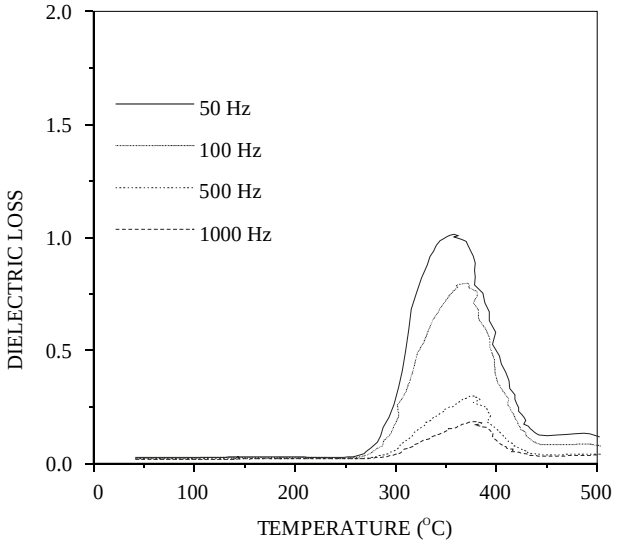

Figure 4. Variation of dielectric loss with temperature.

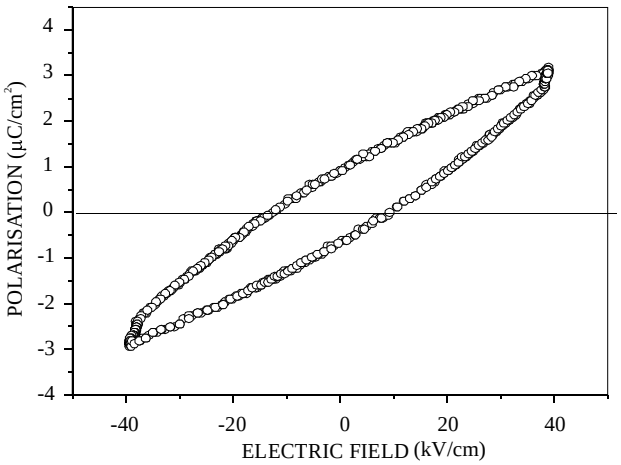

Figure 5. Polarization versus electric field hysteresis loop for $Bi_4SrTi_4O_{15}$.

Elastic compliance [s_{33},s_{11}] coupling factor [k_{33},k_{31}] were obtained for SBT as presented in Table 1 .

Table 1. Measured electromechanical coefficients

Constant	Strontium bismuth titanate
k_{33}	0.38
k_{31}	0.39
k_p	0.41
s_{33}^D	1.62×10^{-12} m^2/N
s_{33}^E	1.90×10^{-12} m^2/N
s_{11}^E	1.84×10^{-12} m^2/N
s_{11}^D	1.56×10^{-12} m^2/N
c_{33}^D	1.139×10^{11} N/m^2

4. CONCLUSION

Polycrystalline SBT was successfully synthesised using a planetary ball mill. X-ray diffraction revealed a single-phase formation. Structural, dielectric properties were characterised for strontium bismuth titanate (SBT) ceramics that contained four perovskite layers. The synthesis of $Bi_4SrTi_4O_{15}$ by a mechano-chemical route[8] has been reported earlier. Our studies revealed a significant reduction in processing temperature and time, thus mechano-chemical process is a more efficient processing route while still offering cost efficiency.

In addition, an enhancement was found in dielectric constant and lowering of dielectric loss in comparison with their previous work in which the properties of SBT *via* solid-state reaction route were presented[9]. Thus, mechano-chemical activation is seen to improve the synthesis, characteristics, and dielectric properties of the SBT.

ACKNOWLEDGMENTS

The authors thank Director, Defence Metallurgical Research Laboratory, Hyderabad, for providing experimental facilities; Dr K.C. James Raju, School of Physics, HCU, for resonance measurements; Department of Physics, MRL, Osmania University, for dielectric measurements; and Principal and Management of St Martin's Engineering College for their constant encouragement.

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Contributors

Mr Gagan Anand obtained MSc (Physics) from the Osmania University in 2000. He is working as Assistant Professor at the St. Martin's Engineering College, in the field of bismuth-layered structured ferroelectric materials since 2004.

Dr A.R. James obtained his PhD in Physics from the Osmania University. He then worked as a postdoctoral Fellow at the Max Planck Institute of Microstructure Physics in Germany, on the growth and characterisation of large area epitaxial, ferroelectric thin films. Thereafter, he was a postdoctoral Fellow at the Materials Research Lab, at the Pennsylvania State University, USA, from 1999-2001, wherein he worked on the development of ultra high strain piezoelectrics, for the Office of Naval Research, Washington DC, and frequency agile materials for microwave electronics under DARPA's FAME programme. He is currently working at the Defence Metallurgical Research Laboratory (DMRL), Hyderabad. His current interests are: Soft piezoelectric ceramics, thin films, and microwave ferroelectrics. He has about 50 publications in international journals and conference proceedings, and a patent to his credit.

Dr (Ms) P. Sarah has done her MSc from the Kanpur University and PhD (Physics) from the Osmania University. Presently, she is Head, Dept of Physics, CVR College of Engineering, Hyderabad. She has been guiding PhD, MSc and MPhil students. She has 25 research papers in international/national journals and conference proceedings to her credit.