Dielectric behavior of Ba_{0.95}Sr_{0.05}TiO_{3} ceramics sintered by microwave

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Abstract

Here we report detailed dielectric studies carried out on a Barium Strontium Titanate (BST) (95:5) composition. The material was synthesized by conventional ceramic method and microwave processing, and the later technique resulted in material with high density, improved microstructure and dielectric properties. The dielectric properties were studied as a function of frequency and temperature and well-defined ferroelectric behavior of first order transition was observed. It follows Curie-Weiss law above transition temperature (paraelectric region). Curie temperature is slightly higher for microwave sintered (MS) material.

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1. Introduction

In recent years, materials with a high dielectric constant ε' have been in demand for insulators in dynamic random access memory (DRAM), capacitors and various other applications [1,2]. Barium strontium titanate (BST) is a solid solution ferroelectric material that exhibits high ε' and Ba/Sr composition-dependent Curie temperature (Tc). It is a perovskite-based ferroelectric, and one of the most studied ferroelectric materials [3], exhibiting normal, first-order phase transition behavior. The Tc and lower symmetry transition temperatures can be modified through the use of isovalent and aliovalent substitutions [4]. The BST family of normal ferroelectrics are interesting candidates for field-induced piezoelectric transducers due to the large polarizations, large permittivities and large induced strains achievable. There are several reports available on the structure and electrical behavior study of these ceramics synthesized by conventional and other chemical processes. However, very limited literature is available on the microwave sintering of BST ceramics. Most of the studies on ferroelectric materials have been done for their structural, mechanical and positive temperature-coefficient of resistance (PTCR) characteristics only [5–10].

On the basis of cooperative thermic and electrodynamics effects ('microwave effect'), the application of microwave energy opens new and effective technological possibilities for materials science as well as in the field of preparative chemistry [11–13]. This technique requires less time and temperature to achieve the same quality of materials as sintered by conventional route. First of all the main interest was directed to comparative studies of microwave and conventional sintered bodies with respect to their microstructure development and dielectric behavior. Smaller grain sizes and more uniform microstructure are developed due to volumetric heating and rapid sintering in microwave processing [14]. Here we report detailed dielectric studies of Ba_{0.95}Sr_{0.05}TiO_{3} composition sintered by conventional and microwave methods.
2. Experimental procedure

The material powder with compositional formula \( \text{Ba}_{0.95}\text{Sr}_{0.05}\text{TiO}_3 \) was synthesized by conventional ceramic method using AR grade, BaCO\(_3\), SrCO\(_3\) and TiO\(_2\). The powder mixture was ball milled using zirconia balls and distilled water as wetting agent. The dried powder was calcined at 1050 °C for 4 h. The reacted powder was ball milled again and recalcined at 1100 °C for 4 h to obtain more homogeneous mixture. The powders were isostatically pressed in a rod form at a pressure of 200 MPa using Cold isostatic press (M/s Autoclave Engineers). Cold isostatic process gives homogeneous and better compaction of green rods. One set of rods was sintered at 1450 °C for 4 h in air atmosphere.

Another set of compacted rods was sintered using microwave oven (1.5 kW, 2.45 GHz single mode microwave applicator). The heating rate was kept in the range of 100 °C min\(^{-1}\) (by controlling the input power to microwave oven) for all synthesis procedures present. Density and microstructural information were obtained on microwave processed and conventionally processed samples by Archimedes principle and SEM, respectively. The single phase formation of the compounds was confirmed by X-ray diffraction technique.

For electrical characterization, sintered rods were ground and sliced to make specimens of 0.5 mm thickness and 10 mm dia. Both the faces of the sliced samples were platinum sputtered. Measurements of capacitance (\( C \)) and dissipation factor (\( \tan \delta \)) were carried out by HP 4284A LCR meter interfaced with PC, both as a function of frequency (100 Hz–1 MHz) and temperature (25–150 °C). Heating rate was maintained at 1 °C min\(^{-1}\) and data were recorded automatically.

Polarization switching was observed using an automatic PE loop tracer based on modified Sawyer–Tower circuit. Samples were immersed in a silicone oil bath to prevent electrical breakdown of the specimen.

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<th>Strucural and electrical parameters for conventionally and microwave sintered BST samples</th>
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3. Results and discussion

Samples prepared by conventional sintering (CS) and microwave sintering (MS) were subjected to XRD analysis in order to determine structure and lattice parameters. From the lattice parameters, X-ray density, \( d_s \), was calculated. Experimental density, \( d_{exp} \), was determined by water immersion method. The values of \( d_s \) and \( d_{exp} \) were used to calculate the percentage porosity using the relation, \% porosity = (\( d_s \) – \( d_{exp} \))/\( d_s \) × 100. These parameters are summarized in Table 1. Fired densities ~97% of theoretical were achieved with microwave process. All the specimens reveal a single phase formation with tetragonal structure. The lattice parameters are found to be slightly higher for MS samples, and the tetragonality (\( c/a \)) is slightly diminished due to the formation of core-shell structure in the microwave processed samples owing to its higher cooling rate after sintering. The Sr deficient core is surrounded by a Sr-enriched shell. Therefore, the value of lattice parameters are slightly increased in case of microwave processed samples. Other possible reason may be the strain developed during fast cooling of the samples in MS samples, which may result in the higher value of lattice parameters. Similar reports have been given for \( \text{Ba}_{0.7}\text{Pb}_{0.3}\text{TiO}_3 \) system by Chang et al [15]. The higher cooling rate in MS samples results in slightly higher values of lattice parameters and also suggesting that domain mobility is restricted due to the pinning of domain boundaries by crystal defects. Therefore, higher \( T_c \) results in case of MS samples. Higher \( T_c \) for MS samples may probably be accounted for by the formation of a core-shell (inhomogeneous composition of grains) structure [16]. Above all, microwave processing is vigorous because so much is not understood and the reaction kinetics of \( \text{BaTiO}_3 \) system follows altogether different reaction paths as compared with conventional one [5]. The unit cell volume was found to increase from 63.65 to 64.40 Å\(^3\) in MS samples. MS samples show higher density and less porosity.

The microstructures of the fractured surfaces of CS and MS specimens are shown in Fig. 1. The grain size is fairly uniform for all the samples with ranges between 6 and 20 μm and is significantly smaller in cases of MS processed specimens and when the sample is denser than the conventional one. The rapidity of microwave method also avoids undesirable grain growth and provides a finer and uniform microstructure (Fig. 1), which is an attractive feature for the processing of electroceramics [17].

Temperature dependence of \( \varepsilon' \) and loss tangent (\( \tan \delta \)) for CS and MS BST samples is shown in Figs. 2 and 3, respectively. In the case of CS sample the phase
transition is observed at 114 °C with \( \varepsilon'_{\text{peak}} \approx 6600 \), however, the transition is sharper for MS sample with higher \( \varepsilon'_{\text{peak}} \) values of 8200 and phase transition at 119 °C. The compositions investigated here displayed dielectric properties characteristic of normal ferroelectrics. The sharp maxima and lack of frequency dispersion in the dielectric behavior have been observed for MS sample at the transition temperature that may be ascribed to uniform distribution of fine grains. The peak width also decreased considerably for MS samples. No shift in the dielectric maxima has been observed with the increment in frequency. The tan \( \delta \) for both the samples also exhibited a peak at the transition temperature (Tc) as shown in Fig. 2b and Fig. 3b, thereby, indicating a well-defined phase transition in both the samples [18]. The frequency dependence of \( \varepsilon' \) for CS and MS processed samples measured at different temperatures shows (Fig. 5) slight decrease in \( \varepsilon' \) with increasing frequency in high temperature region.

In the vicinity of the transition temperature, the \( \varepsilon' \) follows the well known Curie–Weiss law:

\[
\varepsilon' \equiv \frac{C}{T - T_0}
\]

where \( C \) is the Curie–Weiss constant and \( T_0 \) is the Curie–Weiss temperature [19]. Fig. 4 shows the variation of the inverse \( \varepsilon' \) with temperature in the vicinity of the transition temperature for both the samples. Di-
Fig. 3. Temperature dependence of (a) dielectric constant ($\varepsilon'$) and (b) loss tangent (tan $\delta$) for MS BST sample.

Fig. 4. Temperature dependence of inverse $\varepsilon'$ ($1/\varepsilon'$) in the vicinity of the Curie temperature for CS and MS BST samples.

According to Fig. 5, the 'n' values are close to zero ($\approx 0.0078$) for BST ceramics in the vicinity of the phase transition temperature that is characteristic of ordered systems. The character of the dependencies does not essentially change above and below phase transition point, only the 'n' values change slightly. So it is difficult to characterize the presence of impurities by these curves. The plot of ac conductivity versus inverse temperature (In $\sigma_{ac}$ vs. 1/$T$, Fig. not shown) shows the change in slope exactly at the transition temperature of the materials as observed in dielectric studies. Such type of anomaly has been observed in many other ferroelectric ceramics. This is due to the difference in activation energy in the paraelectric and ferroelectric phases. The difference arises due to the grain boundary effect. The activation energy in paraelectric region for both the samples is included in Table 1 at 1 kHz. It is found that the activation energy is higher for MS sample.

The polarization versus electric field ($P$ vs. $E$) behavior was measured using an ac field of 25–30 kV cm$^{-1}$ at 50 Hz. Characteristic $P$–$E$ loops for BST synthesized by conventional and microwave sintering methods are shown in Fig. 6. The coercive field (Ec) and remnant polarization (Pr) were also determined and it is observed that the magnitude of Ec and Pr is slightly decreased in case of MS sample. It is to be noted that the

Fig. 5. Typical frequency dependence of dielectric constant ($\varepsilon'$) at different temperatures (above and below $T_c$) for MS BST sample.

Fig. 6. $P$–$E$ loops for CS and MS BST samples.
electrical breakdown is significantly improved in case of MS sample owing to its pore free and fine grain sizes.

4. Conclusions

The Tc is found to increase in case of MS sample, as the lattice parameters are little higher for microwave sintered (MS) samples. ε' is little higher for MS sample and the loss tangent is low. The phase transition observed for MS sample is quite sharp and almost no frequency dispersion at and beyond Curie temperature that shows fine grain sizes and pore free microstructures. Both the samples processed by CS and MS methods depict first order phase transition and represent ordered systems. It is also observed that the electrical breakdown strength is remarkably improved in case of MS sample.

References