Dielectric Properties of BaTiO$_3$ Ceramics Prepared from Powders with Bimodal Distribution

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Abstract: BaTiO$_3$ (BT) powders having bimodal distribution were synthesized successfully through a simple classical solid-state reaction route using cheap BaCO$_3$ and TiO$_2$ as starting materials. These powders were further processed in the form of green pellets to obtain dense BT ceramics having densities of ~ 94~96 % after sintering in air at 1350 and 1400 °C/4 h in air. The room temperature dielectric constant ($\varepsilon_{RT}$) of ~ 500 at 1 KHz frequency was increased to $\geq 0000$ at a Curie temperature ($T_C$) ~ 26 °C, showing a very sharp transition from a polar tetragonal to a non-polar cubic structure. The dielectric loss factor (tan$\delta$) was ~ 5 %. SEM studies revealed the presence of dense microstructures having a distribution of smaller grains (size: 2~3 µm) surrounded by larger grains ($\geq 5 \mu m$). The ferroelectric hysteresis loop measurements on these samples gave values of spontaneous polarization ($P_s$) of ~ 2.0 μC/cm$^2$, a coercive field ($E_C$) of ~ 5 kV/cm, and a dielectric strength ($E_b$) of ~ 3.0 kV/cm. DC-resistivity as high as $1.5\times10^9 \ \Omega \cdot$cm was obtained in these samples. All these results are quite comparable with reported ferroelectric/dielectric data and are discussed elaborately in this paper.

Keywords: BaTiO$_3$, sintering, stoichiometry, microstructure, dielectric-ferroelectric properties

Introduction

BaTiO$_3$ is a ubiquitous electronic ceramic that is very widely used in the manufacture of disc and multi-layer capacitors, thermistors, and electro-optic devices [1,2]. For reliable and reproducible manufacture of these components, careful control of both the composition and microstructure during chemical processing is essential. Conventionally, BaTiO$_3$ powder is synthesized by using a classical solid-state reaction, namely a calcination process of milled BaCO$_3$ and TiO$_2$ at temperatures ranging from 800 to 1200 °C in air. The resultant BT powders are always obtained in the form of aggregates of sub-micrometer crystallites, which can be further disintegrated easily through a grinding operation to obtain sub-micrometer-sized crystallites [3]. Therefore, a simple solid-state route toward the synthesis of BT powders is an alternative to the more expensive wet chemical routes [4]. Undoubtedly, wet chemical methods do produce highly pure, homogeneous, and ultrafine powders with controlled chemistry and geometry [4]. However, the BT powders obtained from the sol-gel, chemical co-precipitation, and hydrothermal methods [4] require heat-treatment ($T \geq 00 \ ^{\circ}C$) in air to convert the metastable cubic phase to the tetragonal ferroelectric polymorph upon cooling to the room temperature [4]. It has been reported [3] that the hydrothermal method directly crystallizes the tetragonal powders under highly alkaline conditions at a lower temperature ($240 \ ^{\circ}C$) in the presence of Cl$^-$ ions. However, in the absence of halide ions, a metastable cubic polymorph is obtained, which further requires heat treatment (exceeding 1000 °C) to stabilize the tetragonal form upon cooling [3]. The disadvantage associated with the hydrothermal method is that the contamination from alkali ions in the BT powders adversely affect the properties of the BT ceramics [5]. There is an enormous amount of literature available [6,7] on the properties of BT ceramics and the effect that
the Ba/Ti ratio has on the microstructure evolution and dielectric/ferroelectric properties of BT ceramics prepared using various methods. In the case of fine-grained undoped BT ceramics, a higher room temperature dielectric constant (\(\varepsilon_{\text{max}}\)) is reported, which is explained in terms of an internal stress below the Curie temperature and a higher domain density [8]. There are also many reports in the literature describing studies of BT ceramics where the dielectric/ferroelectric properties were found to be dependent on the Ba/Ti ratios, which affect the sintering kinetics and microstructure evolution [4,9]. Therefore, it is worth studying the effect of the microstructure on the dielectric/ferroelectric properties in undoped BT ceramics prepared from powders while keeping the Ba/Ti ratio at ~ 0 through a simple solid state reaction route and varying the sintering temperatures, and then further studying the effects of these parameters on the properties of these ceramics. The advantage of choosing this particular composition lies in the fact that the second phase formation reported in the case of a Ti-rich or Ba-rich composition [7] is avoided. Therefore, the main objective of this present investigation was to use a simpler solid state reaction route to generate BT powders having a Ba/Ti ratio of ~ and to study the evolution of the microstructure after sintering the pellets at two different temperatures (1350 and 1400 °C) while keeping the soaking time constant under identical conditions in air and then to study their dielectric/ferroelectric properties.

**Experimental**

BaCO\(_3\) (Aldrich chemical, USA, 99.9 % pure), TiO\(_2\) (Loba Chemie, 98.9 %), and distilled water were used as starting materials for the preparation of the BT powders. The oven-dried BaCO\(_3\) and TiO\(_2\) powders were weighed very accurately in the required molar ratio (\(\sim\)) and then mixed to form a slurry with the aid of distilled water as a mixing agent. The slurry was taken into a plastic jar containing ceramic balls and then the mixture was ball-milled for 10 h. The ball-milled slurry was then dried in an oven at 100 °C. The oven-dried powder was calcined at 1150 °C for 6 h in air. The calcined powder was ground in an agate mortar and then used for further characterization. The crystalline phase analyses of the calcined powders and sintered pellet powders were performed using an X-ray diffractometer (Philips PW-1710 with Cu-K\(_\alpha\) radiation using ‘Ni’ filter) in the range of 2\(\theta\) = 20–\(\sim\)80° at a scan speed of 4°/min. A scanning electron microscope (SEM Leica, Stereoscan 440 M/s Leica Cambridge Ltd., UK) was used to estimate the particle size, morphology, and nature of the agglomerates in the calcined powders and the microstructure, grain sizes, shape, grain growth, and voids in the fractured surfaces of the sintered pellets. The pellets (diameter: 20 mm; thickness: ~ ~ gm) of this well-dried powder were prepared using a hydraulic press (Carver, USA) under a constant pressure (5000 psi). The pellets were sintered at two different temperatures (1350 and 1400 °C) for 4 hrs in air. All of the sintered pellets were lapped to a uniform thickness of 0.6 mm by using the 400-mesh carborundum powder. The circular electrical contacts of known diameter were prepared by applying silver paint to both sides of the sintered pellets. All pellets were cured at a temperature of 600 °C for 30 min to remove any organic binder present in the silver paint and to obtain suitable electrical contacts. Lapped disks were used for the capacitance measurements. The capacitance was measured using an impedance bridge (Systronics, Ahmedabad) at 1 kHz frequency. The spontaneous polarization (\(P_s\)), coercive field (\(E_c\)), and breakdown voltage (\(E_b\)) were obtained from the ferroelectric hysteresis-loop observed at 50 Hz on an oscilloscope (515A Tektronix, Inc., Portland, Oregon, USA) with the aid of a simple standard Sawyer-Tower circuit.

**Results and Discussion**

This paper describes our efforts to make use of a simple solid state reaction in the preparation of bimodal barium titanate powders and to examine the effect of the sintering temperature on the microstructure and dielectric/ferroelectric properties while keeping the Ba/Ti ratio at ~ during the synthesis. Previously, Erkalfa and co-workers [6] and Lee and coworkers [7] reported in-depth studies on the effects of the Ba/Ti ratio on the microstructure evolution and dielectric/ferroelectric properties of BT ceramics. Their important findings are summarized below:

In Ti-excess samples, with a Ba/Ti ratio of 0.97, the room temperature dielectric constant decreased to 1100 because of the formation of a liquid phase at higher temperature during sintering; a value of \(\varepsilon_{\text{max}}\) of 300 was obtained. On the other hand, for Ba-excess samples having a Ba/Ti ratio of 1.03, a second phase, Ba\(_2\)TiO\(_4\), was formed that increased the stress in the material, which enhanced the room temperature dielectric constant to 1800, but broadened the transition at the Curie temperature, and the value of \(\varepsilon_{\text{max}}\) decreased to 4500. However, in Ti-rich compositions, the BT ceramics gave similar properties (after sintering at 1350 °C for 2 hrs) to those of stoichiometric BT ceramics having Ba/Ti ratios of 1.0, i.e., \(\varepsilon_{\text{RT}}\sim\sim 500\), and the transition is sharp with \(\varepsilon_{\text{max}}\sim 500\) at the Curie temperature. Therefore, we selected a stoichiometric composition of BT for the present study, but chose two sintering temperatures (1350 and
Figure 1. XRD patterns of a ball-milled mixture of BaCO$_3$ and TiO$_2$ and of the mixture calcined at 1150 °C/6 h.

Figure 2. SEM image of the powder mixture calcined at 1150 °C/6 h.

1400 °C) to improve the densification and microstructure/properties in the resulting ceramics; no dedensification effects are reported for these undoped compositions in the literature [10].

Figure 1 shows the XRD patterns of the ball-milled mixture of BaCO$_3$ and TiO$_2$ and the material calcined at 1150 °C/6 h. The ball-milled mixture clearly shows all of the reflections corresponding to both BaCO$_3$ [11] and TiO$_2$ [12]. Furthermore, the calcined material shows all of the reflections corresponding to a cubic/tetragonal BaTiO$_3$ phase [13]. No additional peaks due to any impurity phases are observed in the XRD pattern of the calcined material. Thus, this XRD study confirmed the formation of a pure Ba-TiO$_3$ phase during the calcination stage.

Figure 2 displays an SEM image of the powder mixture calcined at 1150 °C/6 h. We observe the formation of a bimodal distribution of many spherical grains of smaller size (0.25–0.35 µm) with a few larger grains (1.5–3.0 µm). The average green density of all of the BaTiO$_3$ pellets was between 64 and 65 % of the theoretical density (6.017 gm/cc). The bimodal distribution helps to increase the green density through the better packing of bimodal particles. The sintered density values for all of the samples were in the range of 94 to 96 % of the theoretical density. Figure 3 depicts the XRD patterns of powders of pellets sintered at 1350 and 1400 °C for 4 hr.

Figure 3. XRD patterns of BT pellets sintered at 1350 and 1400 °C for 4 h.

Figure 4. SEM images of the fractured surfaces of the pellets sintered at 1350 and 1400 °C for 4 h.
in air. Both patterns clearly display all of the reflections corresponding to only the tetragonal phase of BaTiO$_3$ [14]. Better tetragonality [splitting of the (200) peak into two peaks, (002) and (200)] is observed in the material sintered at higher temperature.

Figure 4 display SEM images of the fractured surfaces of the pellets sintered at 1350 and 1400 °C for 4 hrs. The material sintered at 1400 °C exhibits a more well-defined and uniform compact microstructure when compared with the 1350-°C-sintered sample. The grain sizes appear to be in the range 3-10 μm. Furthermore, we observe that small grains surrounded the large grains and no segregation of a Ba-rich or Ti-rich second phase occurred at the grain boundaries. It has been reported that dedensification occurs above 1335 °C in Ba- or Ti-excess samples because of pores trapped within the grains and at the grain boundaries [10]. The stoichiometric composition did not lead to any dedensification effect [10]. However, a small amount of porosity is evident in our sample, due to the presence of some voids in the material sintered at 1350 °C. The inferior microstructure and the small amount of porosity in this sample lowered its dielectric performance parameters.

Figure 5 displays the temperature dependence of the dielectric constant and the dielectric loss for the pellets sintered 1350 and 1400 °C for 4 h. The room temperature dielectric constant ($\varepsilon_{RT}$) was $\sim$ 500 (for the 1400-°C-sintered sample), with dielectric loss ($\tan\delta$) of $\sim$ 0.02; these values are better than those reported for ceramics having a Ba/Ti ratio of $\sim$ 7. The temperature dependence of the dielectric constant and the loss factor experiments revealed that the Curie temperatures (Tc) of both samples were $\sim$ 26 °C, with the maximum dielectric constant ($\varepsilon_{max}$) reaching $\geq$ 0000 in the 1400 °C-sintered compact. Although the room temperature dielectric constant is comparable with the reported value, the value of $\varepsilon_{max}$ $\geq$ 0000 is much higher than that reported (8000) for the same Ba/Ti ratio [7]. The dielectric loss value ($\tan\delta$) was found to be $\sim$ 0.025, which is in close agreement with the reported data [7].

**Hysteresis Loop Measurements**

Well-defined ferroelectric hysteresis loops were exhibited by all of the samples under high electric fields in the Sawyer-Tower circuits. The spontaneous polarization (Ps) value obtained in present study was $\sim$ 2.0 μC/cm$^2$ for the 1400 °C-sintered compact with a Ba/Ti ratio of $\sim$ 1.0 kV/cm is reported [15]. The coercive field (Ec) values obtained for our samples ($\sim$ 2.0 - 5 kV/cm) were lower than the reported values for ceramic samples having the same composition [7]. However, for single crystals, the lowest value of Ec of $\sim$ 5.0 kV/cm is reported [15]. The lower Ps and Ec values in our samples, relative to those reported for single crystals of BT, may be due to the polycrystalline nature of the samples [15]. A high electric strength (E$\beta$) of $\sim$ 0 - 20 kV/cm has been reported for the ceramic samples [15], but our samples had values of E$\beta$ of $\sim$ 5.0 kV/cm.

The lower electric strength (E$\beta$) for our ceramics may be due to the lower densification and microstructure developed during the sintering process. The DC resistivity of the sintered pellets was $\sim$ 28×10$^9$ Ω-cm. From all of these observations, we note that better properties were obtained for the BT ceramics when keeping the Ba/Ti ratio at $\sim$ and increasing the sintering temperature to 1400 °C.

**Conclusions**

A simple solid state reaction provided a bimodal distribution of BT powders after calcination of BaCO$_3$ and TiO$_2$ in air. These BT powders exhibited a higher green density because of their better packing and their compact, dense microstructures resulted in better dielectric/ferroelectric properties when maintaining the Ba/Ti ratio at $\sim$
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References

11. ASTM card No. 5-0378.
12. ASTM card No. 4-0477.
13. JCPDS File No. 31-0174 (27582).
14. ASTM card No. 5-0626.