

## Synthesis and Dielectric Properties of Bismuth Doped Barium Titanate (BaTiO<sub>3</sub>) Ceramics

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### ABSTRACT

The dielectric properties of bismuth doped barium titanate ceramics were investigated. The powders were prepared using the solid-state reaction method. The dielectric properties were characterized by means of LCR meter. XRD clearly revealed only a monophasic perovskite of tetragonal asymmetry for the reference BaTiO<sub>3</sub>, which was established to possess both a-a- and a-c-type 90° domains. Examination of dielectric constant revealed a significant increase with increasing sintering temperature. Furthermore, sintering temperature has been shown to produce a linear increasing in the density. Nevertheless, an increase in the sintering temperature did not show any evidence of a change in the transition temperature. The maximum transition temperature of this system was 135 °C with the relative permittivity of 3500 at 1 kHz. Above the Curie temperature the relative permittivity follows the Curie-Weiss law with the Curie constant  $C = 1.8 \times 10^5 \text{ }^\circ\text{C}$ .

*Keywords: BaTiO<sub>3</sub>, Ferroelectricity, Phase transitions*

### INTRODUCTION

Barium titanate (BT) has become one of the most important electroceramics since the discovery of its versatility in multilayer ceramic capacitors (MLCC), positive temperature coefficient of resistance (PTCR) thermistors, piezoelectric sensors, transducers, actuators and ferroelectric random access memories (FRAM) and electro-optic devices (Uchino, 2000; Haertling, 1999). Its dielectric maximum shifted towards room temperature by the compositional substitution and its dielectrics were sensitive to temperature, field strength and frequency, especially near the Curie temperature. BaTiO<sub>3</sub> has demonstrated its high dielectric maxima of  $\epsilon_r \approx 15000$  in the Y5V materials and of  $\epsilon_r \approx 3000$  in the X7R specification (Buchanan, 1991).

The importance of BT is not limited by the above mentioned utilities, but ceramics of this material are also of special interest for their direct applications in thermistors. Due to its high band gap (>3 eV), undoped BT ceramics is an excellent insulator. The room temperature resistivity, however, can be reduced to a much lower value by introducing small amounts of trivalent ions (such as Bi<sup>3+</sup>, La<sup>3+</sup>, Y<sup>3+</sup>, etc.) in the Ba-site or pentavalent ions (such as Nb<sup>5+</sup>, Ta<sup>5+</sup> etc.) in the Ti-site to produce n-type semiconductor (Lines and Glass, 1977; Buchanan, 1991). Many commercial BT-based multilayer capacitors contain a certain amount of bismuth because of its significant effect on lowering the sintering temperatures (Zhou *et al.*,

1999). Bismuth is also found to be able to enhance the magnitude of positive coefficients of resistance and dielectric properties (Moulson and Herbert, 1990).

The electrical properties of BT-based ceramics are very sensitive to both microstructure and defect chemistry of the materials, which are strongly influenced by processing parameters, such as chemical composition and sintering conditions. In this work, the effects of sintering temperatures, density, microstructural development,  $\text{Bi}_2\text{O}_3$  doping and dielectric properties of  $\text{BaTiO}_3$  ceramics have been studied.

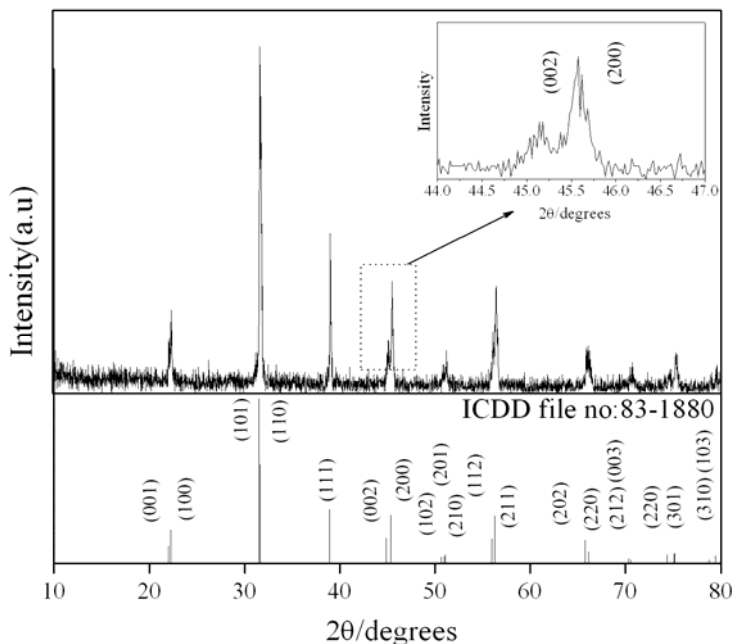
## EXPERIMENTAL PROCEDURE

$\text{BaTiO}_3$  ceramics were prepared by using the raw materials of  $\text{BaCO}_3$  and  $\text{TiO}_2$  with a molar ratio of 1.00:1.00. All chemicals used in this study were of high purity grade (at least 99.0% pure). The powders are doped by  $\text{Bi}_2\text{O}_3$  with an amount from 2 mol% of dopant ions. Generally, Bi is elements with a valency of +3 and the formulation was based on the assumption that  $\text{Bi}^{3+}$  would substitute  $\text{Ba}^{2+}$  on A-site. The starting materials were ball milled in a polyethylene jar using in alcohol for 24 h. followed by calcination at 1150 °C for 6 h. The calcined powders were remilled for 3 h. for reduced particle size. After grinding and sieving, the calcined powder was mixed with 5 wt % poly (vinyl alcohol) binder and uniaxially pressed into a pellet. Binder burnout occurred by slowly heating to 500 °C and holding at that temperature for 2 h. Sintering mechanism occurred between 1200–1350 °C with a dwell time of 4 h. Phases of both calcined and sintered products were identified by powder X-ray diffraction technique using  $\text{CuK}\alpha$  ( $\lambda = 1.54056 \text{ \AA}$ ) radiation. Scanning electron microscopy (SEM; JEOL JSM-840A) was employed in the observation of the ceramic morphology and the estimation of grain sizes. The densities of the sintered ceramics are measured by Archimedes method. The shrinkage of the ceramics was determined by measuring from the green body and the sintered samples, i.e., shrinkage = (diameter of pressed pellet – diameter of sintered pellet) /diameter of pressed pellet. Silver paint was pasted on the two major of surfaces to form electrodes. Each pellet used in the measurement of the temperature dependence of dielectric constant and dielectric loss. The temperature range in the measurement usually started from room temperature to 160 °C.

## RESULTS AND DISCUSSION

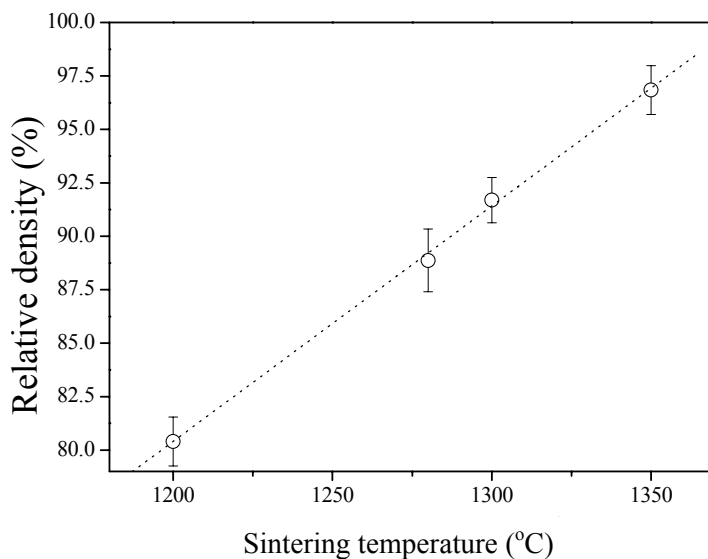
Figure 1 shows the XRD patterns of  $\text{Ba}_{0.8}\text{Bi}_{0.2}\text{TiO}_3$  ceramics. No evidence of the precursor phase  $\text{BaCO}_3$ ,  $\text{TiO}_2$  or  $\text{Bi}_2\text{O}_3$  was detected by XRD. In general, there are two phases of  $\text{BaTiO}_3$ , tetragonal phase and cubic phase. From the measurement, the strongest reflections apparent in the majority of the XRD patterns indicate the formation of two barium titanate phases. These can be matched with ICDD file numbers 31-174 and 83-1880 for cubic and tetragonal  $\text{BaTiO}_3$ , respectively. It is well known that tetragonal and cubic phases were identified by an analysis of the peaks (0 0 2 (tetragonal), 2 0 0 (tetragonal), 2 0 0 (cubic)) in the  $2\theta$  range 43-48 degree. The splitting of (0 0 2) and (2 0 0) peaks indicates the tetragonal phase, while the single (2 0 0) peak confirms the cubic phase. In our experimental results,

the XRD patterns indicate the formation of barium titanate phase, BaTiO<sub>3</sub>, which could be matched with ICDD file no. 83-1880. To a first approximation, this major phase has tetragonal structure with unit cell parameters  $a = 3.994 \text{ \AA}$  and  $c = 4.033 \text{ \AA}$ . It is also of interest that no existence of the aurivillius phases Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> reported by Zhou (Zhou *et al.*, 1999) and W. F. Su (Su and Lu, 2003).

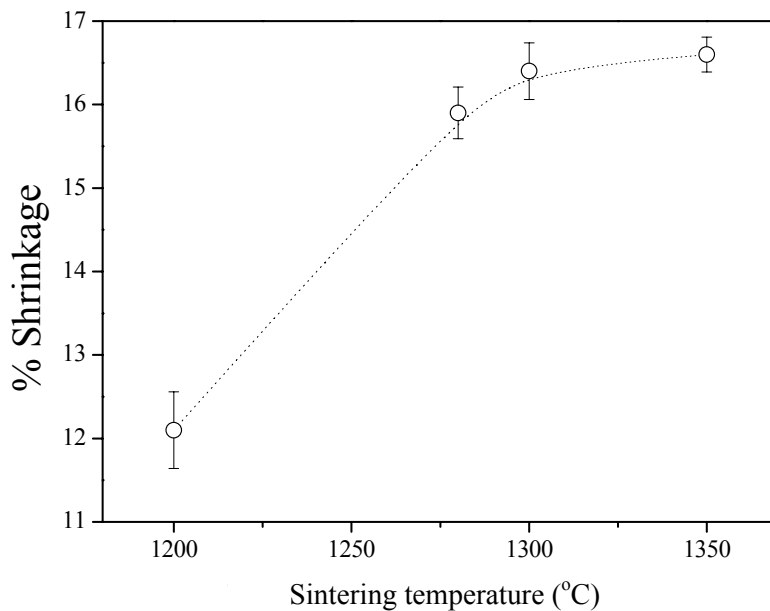


**Figure 1** Computerised XRD pattern of BaTiO<sub>3</sub> and a measured XRD pattern of Ba<sub>0.8</sub>Bi<sub>0.2</sub>TiO<sub>3</sub> ceramics.

It is observed that a density of about 80.4-96.4 % of the maximum value for Ba<sub>0.8</sub>Bi<sub>0.2</sub>TiO<sub>3</sub> can be achieved in this study (Figure 2). The density gradually increased with increasing sintering temperature. The maximum density was obtained in the samples sintered at 1350°C for 4 h. with heating/cooling rates of 5 °C/min. The change in dimension was gradually increased with sintering temperature at 1200 °C to 1280 °C and nearly constant above 1300 °C. It is seen that the linear shrinkage increased with sintering temperature (Figure 3).



**Figure 2** Dependence of relative density in Ba<sub>0.8</sub>Bi<sub>0.2</sub>TiO<sub>3</sub> ceramics sintered at various sintering temperatures.



**Figure 3** Percentage of shrinkage in Ba<sub>0.8</sub>Bi<sub>0.2</sub>TiO<sub>3</sub> ceramics sintered as a function of sintering temperature.

Dielectric properties observed at different sintering conditions are summarized in Table 1. The permittivity at a room temperature of Ba<sub>0.8</sub>Bi<sub>0.2</sub>TiO<sub>3</sub> ceramics at the sintering temperature of 1200 °C exhibited a approximately 350 (at 1 kHz). With increasing sintering temperature to 1350 °C, an increase of the permittivity (1 kHz) from an initial value of 350 to 1000 was clearly shown. The permittivity at 1 kHz as a function of temperature for Ba<sub>0.8</sub>Bi<sub>0.2</sub>TiO<sub>3</sub> ceramics under different sintering conditions is shown in Figure 4. In the relative permittivity versus temperature plots all samples displayed sharp peaks at a transition temperature of 135 °C. The sintering temperature was found to have a significant effect on the permittivity. The Ba<sub>0.8</sub>Bi<sub>0.2</sub>TiO<sub>3</sub> ceramics exhibited an increase in the permittivity with increased sintering temperatures. The results showed an increase in permittivity up to a maximum of 3400 at a sintering temperature of 1350 °C. Moreover an increase in the sintering temperature did not show any evidence of a change in transition temperature. In most ferroelectrics, the temperature dependence of the relative permittivity above the Curie temperature (in paraelectric phase regime) can be described accurately by a simple relationship called the Curie-Weiss law (Lines and Glass, 1977):

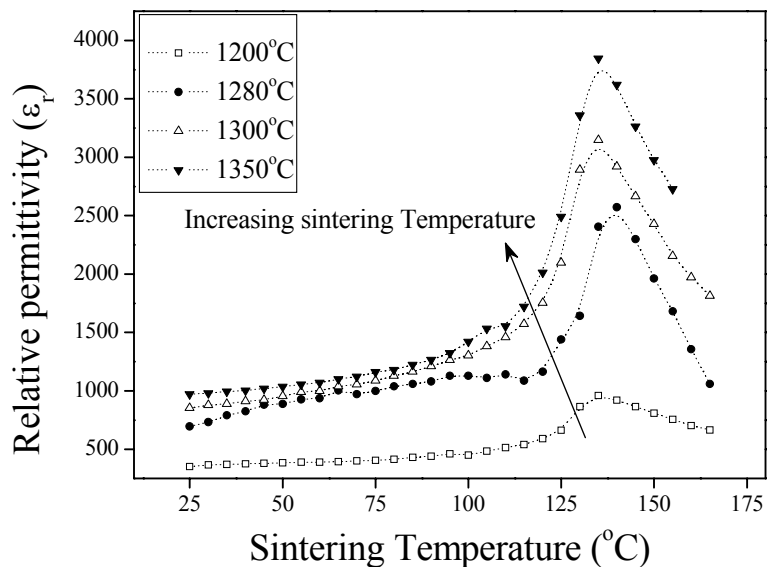
$$\epsilon = \epsilon_0 + \frac{C}{T - T_0} \tag{1}$$

where C is the Curie-Weiss constant and T<sub>0</sub> the Curie-Weiss temperature. Generally, in the case of a first-order phase transition, T<sub>0</sub><T<sub>c</sub>, while for the second-order phase transition T<sub>0</sub>=T<sub>c</sub>. Figure 5 shows the variation of inverse relative permittivity with temperature in the vicinity of transition temperature for Ba<sub>0.8</sub>Bi<sub>0.2</sub>TiO<sub>3</sub> ceramics sintered at 1350°C. The dielectric data show clearly first-order phase transition and excellent Curie-Weiss behavior. The Curie constant (C) obtained for this sample is 1.8x10<sup>5</sup> °C which is in good agreement with the reported value of pure BaTiO<sub>3</sub> (Moulson and Herbert, 1990).

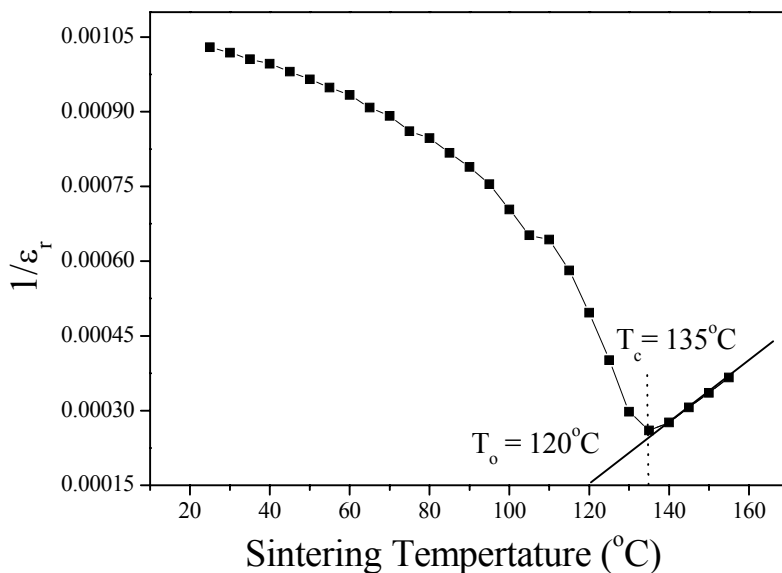
**Table 1** Dielectric properties measured at 1 kHz for Ba<sub>0.8</sub>Bi<sub>0.2</sub>TiO<sub>3</sub> ceramics fabricated at different sintering temperatures. Values at transition temperature were include for comprise purpose.

Sintering Temperature(°C)	Curie Temperature	ε <sub>r</sub> (room temperature)	tan (δ) ( room temperature)	ε <sub>r</sub> (transition temperature)*	tan (δ) (transition temperature)*
1200	135	350	0.02	960	0.02
1280	135	700	0.35	2500	0.18
1300	135	850	0.08	3150	0.04
1350	135	1000	0.03	3400	0.02

\* Depicted from Figure 4



**Figure 4** Temperature-dependent relative permittivity ( $\epsilon_r$ ) of  $\text{Ba}_{0.8}\text{Bi}_{0.2}\text{TiO}_3$  ceramic measured at 1 kHz.



**Figure 5** Temperature dependence of inverse of relative permittivity in the vicinity of transition temperature of  $\text{Ba}_{0.8}\text{Bi}_{0.2}\text{TiO}_3$  ceramic sintered at  $1350^\circ\text{C}$  measured at 1 kHz.

## CONCLUSIONS

Ba<sub>0.8</sub>Bi<sub>0.2</sub>TiO<sub>3</sub> ceramics were prepared by solid state reaction route. XRD results on Ba<sub>0.8</sub>Bi<sub>0.2</sub>TiO<sub>3</sub> revealed that the single-phase layered perovskites was formed without any detectable secondary phase. The dielectric constant increased with increasing sintering temperature, while the transition temperature point almost remained the same. The dielectric properties show the abrupt discontinuities in dielectric constant versus temperature plots; typical properties of first order transitions. Above the Curie temperature the relative permittivity follows Curie-Weiss law with Curie constant  $C = 1.8 \times 10^5$  °C.

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