

## Grain growth behaviour and mechanical properties of BZT ceramics under various sintering conditions

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### Abstract

Barium zirconium titanate ceramics ( $\text{Ba}(\text{Zr}_{0.07}\text{Ti}_{0.93})\text{O}_3$ ) doped with 3wt%  $\text{B}_2\text{O}_3$  were prepared via a solid-state sintering method. The samples were sintered at 1050-1250 °C for 2 h. Effects of sintering temperature on many properties were investigated. The sintering temperature enhanced grain growth, density and mechanical properties. The optimum properties were observed for the temperature of 1200 °C, indicating that the sintering was completed at this temperature. The mechanical properties of the ceramics were found to relate with their densification.

*Keywords:* Grain growth, Mechanical properties, BZT ceramics

### INTRODUCTION

Barium zirconium titanate (BZT) is one of the most studied lead-free materials (Tanmoy *et al*, 2006; Pengpat *et al*, 2006; Jarupoom *et al*, 2008; Kantha *et al*, 2009). This material exhibits high dielectric, ferroelectric, and piezoelectric properties which is of interest as a candidate to replace the lead-based materials. BZT can be formed by the substitution of Zr ions at the Ti site of  $\text{BaTiO}_3$  lattices. This substitution significantly produced changes in the structural and electrical properties of  $\text{BaTiO}_3$  (Pengpat *et al*, 2006), including a relaxor ferroelectric and diffuse phase transition behaviour (Tanmoy *et al*, 2006; Pengpat *et al*, 2006). In recent years, many authors have focused on improving the electrical properties by doping or adding sintering aid reagents into the lead-free ceramics for using in many devices such as sensors, actuators, and multilayer capacitors. For multilayer capacitor applications, many works have focused on decreasing the sintering temperature as well as improving the dielectric properties by adding sintering aids into lead-free ceramics. Among the most frequently used sintering aids, including LiF,  $\text{Bi}_2\text{O}_3$ , and  $\text{Li}_2\text{O}:\text{B}_2\text{O}_3$  is of great interest as it has effects on the improvement of the densification in the lead-free ceramics (Valant and Suvorov, 2004; Prakash *et al*, 2000). To our knowledge, microstructure and mechanical properties of  $\text{B}_2\text{O}_3$  doped BZT ceramics have not been widely investigated. In the present work, BZT ceramics in a composition of  $\text{Ba}(\text{Zr}_{0.07}\text{Ti}_{0.93})\text{O}_3$

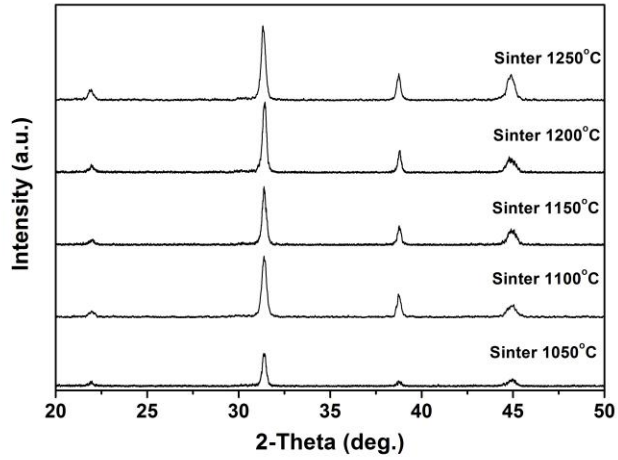
doped with  $B_2O_3$  were synthesized via a solid-state reaction. Effects of the heat treatment on grain growth behavior and mechanical properties were related.

## EXPERIMENTAL PROCEDURE

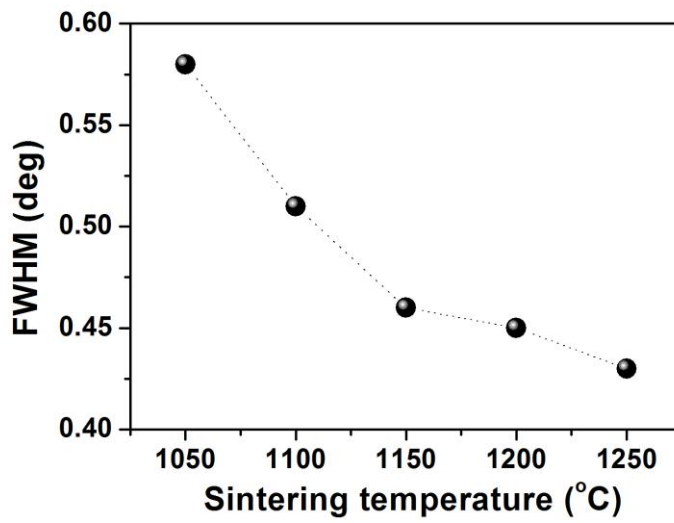
In this work,  $Ba(Zr_{0.07}Ti_{0.93})O_3$  (BZT) powder and ceramics were synthesized by a solid-state reaction method. Metal oxide powders of  $BaCO_3$ ,  $ZrO_2$  and  $TiO_2$  with high purity were used as raw materials. The metal oxide powders were weighed based on the formula of  $Ba(Zr_{0.07}Ti_{0.93})O_3$ . The weighed batch was mixed and then ball-milled in alcohol for 24 h using zirconia balls milling media. The obtained powder was calcined at  $1200\text{ }^\circ\text{C}$  for 2 h. To investigate the effect of boron oxide on the properties of the BZT ceramics, boron oxide ( $B_2O_3$ ) powder was added with concentrations ranging between 1 and 3 wt% and mixed with 3 wt% polyvinyl alcohol (PVA) binder by the ball milling method in ethanol for 24 h. The resulted powders were pressed into disc-shape pellets with 10 mm in diameter. The pellets were sintered at temperatures ranging from  $1150\text{ }^\circ\text{C}$  to  $1450\text{ }^\circ\text{C}$  for 2 h. Phase formation of the obtained ceramics was investigated by X-ray diffraction technique (XRD). The bulk density of the sintered samples was determined using the Archimedes method. Microstructural study of the sintered ceramics was performed under a scanning electron microscope (SEM). The mechanical properties of the ceramics were determined by Knoop hardness tester.

## RESULTS AND DISCUSSION

The XRD patterns of the samples sintered at various temperatures are illustrated in Figure 1(a). All samples exhibit a perovskite phase which has a good consistency with that of the previous works (Jiwei *et al*, 2004). The increase in sintering temperature results in a decrease in width of the diffraction peaks (full width at half maximum, FWHM). For example, FWHM values of (200) XRD peak as a function of sintering temperature was calculated as seen in Figure 1(b). The FWHM was found to decrease with increasing the sintering temperature. This result indicates a high degree of crystallinity in the high sintering temperature samples. Therefore, better properties should be observed in the higher sintering temperature samples.

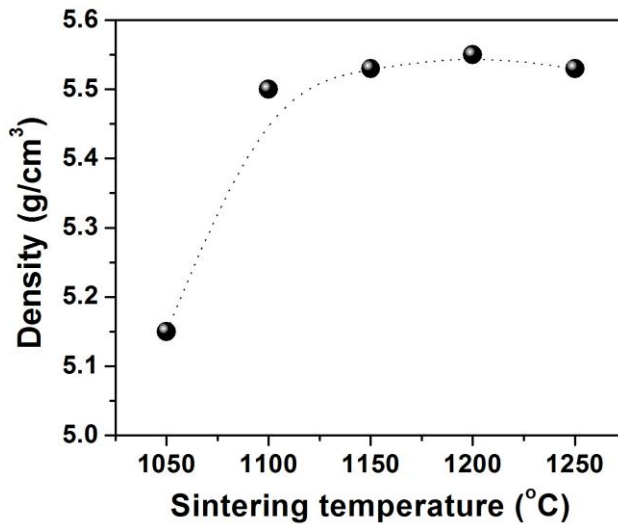


(a)



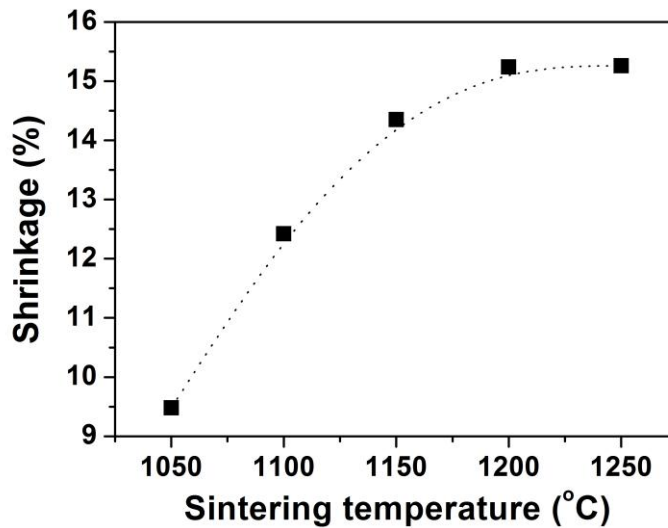
(b)

**Figure 1** (a) XRD patterns of 3wt% B<sub>2</sub>O<sub>3</sub> doped BZT ceramics and (b) FWHM as a function of sintering temperature.



**Figure 2** Density as a function of sintering temperature of  $B_2O_3$  doped BZT ceramics.

Value of density as a function of sintering temperature of the ceramics is shown in Figure 2. Raising the sintering temperature to 1250 °C brings about a significant increase in the measured density of samples. The maximum density of 5.55 g/cm<sup>3</sup> is observed for the 1200 °C sample. However, the 1250 °C sample shows a slightly drop in their density. The density values in this work are slightly lower than that reported by Zheng and et al. (2009) who prepared BZT doped with CuO, due to they use different addition and sintering temperature. The shrinkage profile which is shown in Figure3 exhibits an increase from 9.48% for the 1050 °C sample to 15.26% for the 1250 °C sample. These results suggest that the sintering completed at 1200 °C.



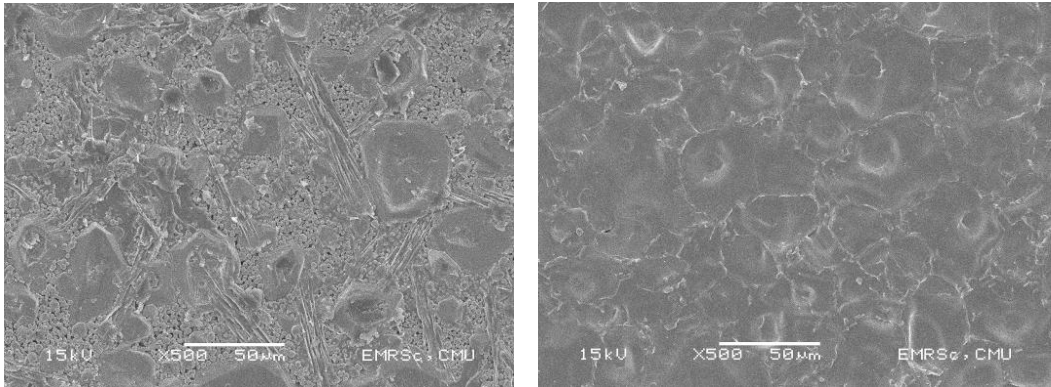
**Figure 3** Shrinkage as a function of sintering temperature of  $B_2O_3$  doped BZT ceramics.

Figure 4 shows SEM micrographs of the BZT ceramics. For the 1050 °C sample, heterogeneous in microstructure with small grain is observed. This evidence was also reported by Wei and et al. (2009) where their BZT ceramic was sintered at short soaking time. Therefore, the present result implies that the sintering was not completed at the sintering condition. However, higher homogeneity with courser grain is found for the higher sintering temperature samples. The average grain size as a function of sintering temperature is shown in Figure 5. The grain size becomes much larger at higher sintering temperature. The grain size increases from 9.5  $\mu m$  for the 1050 °C sample to 18.9  $\mu m$  for the 1250 °C sample. The change in the grain size with sintering temperature can be described by the Arrhenius equation as

$$r^n - r_0^n = k_0 \exp(-\Delta H / RT) \quad (1)$$

where  $r_0$  is the initial grain size,  $n$  is a grain growth exponent,  $k_0$  is a constant,  $R$  is the gas constant,  $T$  is temperature in Kelvin and  $\Delta H$  is the activation energy. A plot of  $\ln(r^n - r_0^n)$  versus reciprocal temperature is shown in Figure 6. For  $n = 2$ , a linear relationship between  $\ln(r^n - r_0^n)$  and  $(1/T)$  is noted. Generally, a large gain growth exponent implies a small grain growth rate. However, this value is lower than some lead based ceramics

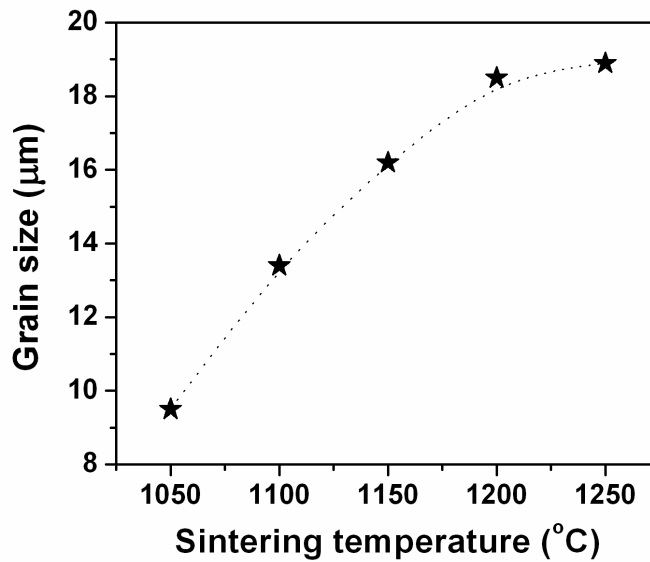
system (Wagner *et al*, 2005) In addition from the slope of the curve in Figure 6, the activation energy has been determined to be about 129 kJ/mol.



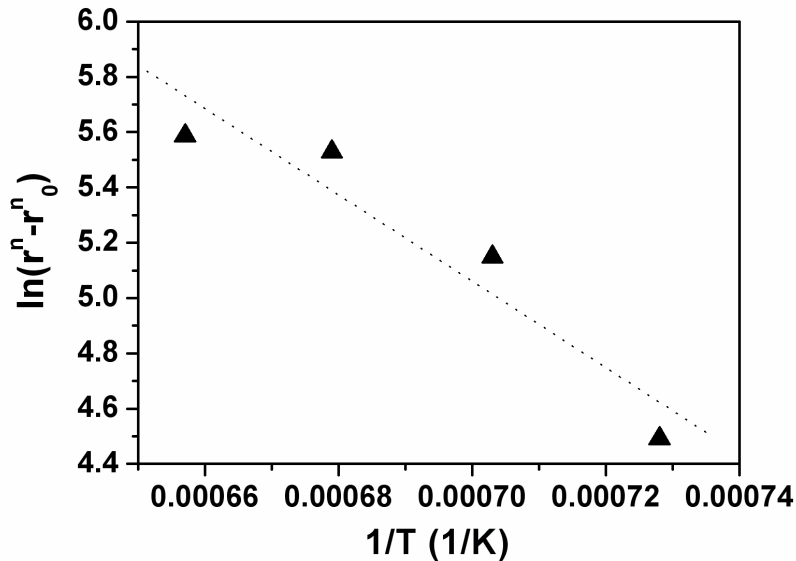
(a)

(b)

**Figure 4** SEM micrographs of B<sub>2</sub>O<sub>3</sub> doped BZT ceramics sintered at: (a) 1050 °C and (b) 1200 °C.



**Figure 5** Grain size as a function of sintering temperature of B<sub>2</sub>O<sub>3</sub> doped BZT ceramics.



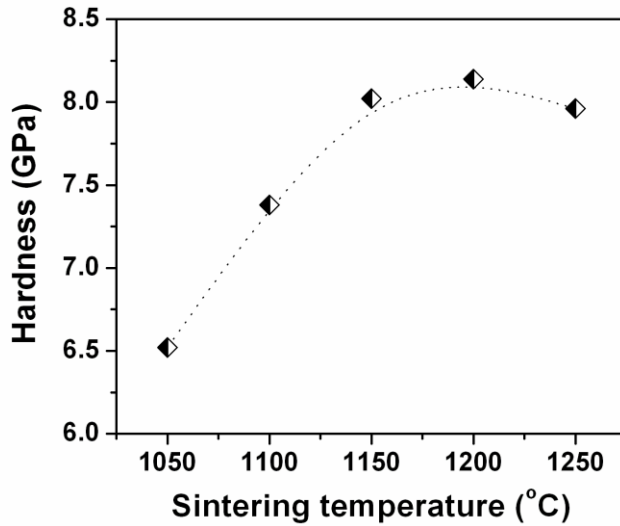
**Figure 6** A plot of  $\ln(r^n - r_0^n)$  as a function of  $1/T$  of  $B_2O_3$  doped BZT ceramics.

It is important for some applications that the ceramics are resistant to microcracking or fracture toughness when subjected to large applied electric fields. Therefore, mechanical properties such as hardness and Young's modulus were determined (Meyers and Chawla, 2002). It is also the first time for mechanical property characterization in this material to our knowledge. Figure 7 shows the Knoop hardness values for all samples. Knoop hardness data indicates that sintering temperature improved the hardness of the samples. The Knoop hardness value increases from 6.52 GPa for the 1050 °C sample to 8.14 GPa for the 1200 °C sample, and then decreases to 7.96 GPa for the 1250 °C sample. Generally for ceramic materials, the grain size and hardness are related to the Hall–Petch equation: (Meyers and Chawla, 2002)

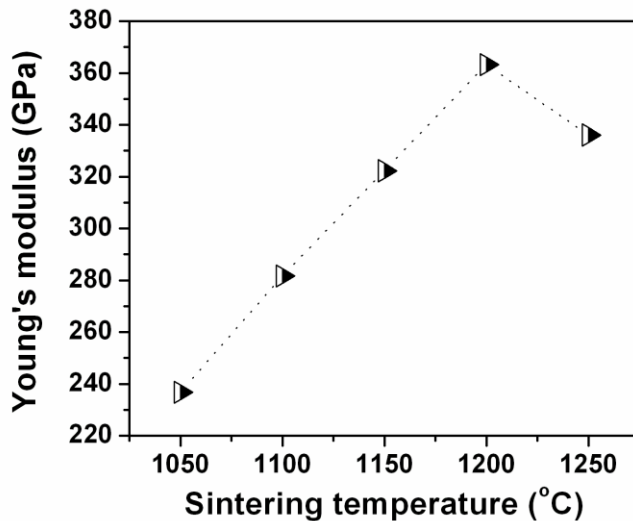
$$H = H_0 + kd^{\frac{1}{2}} \quad (2)$$

where  $H$  is hardness,  $d$  is grain size, and  $H_0$  and  $k$  are constants. However, our results indicate that the  $B_2O_3$  doped BZT ceramics do not obey the Hall–Petch equation. Because of the samples sintered at higher temperature shows the increase in grain size, the grain size may not be a main reason for the incensement of hardness. In this work, however, it is believed

that densification behavior should be a reason for the improvement in the mechanical properties, i.e. the higher density samples give higher measured hardness (see also Figure 2).



**Figure 7** Hardness as a function of sintering temperature of  $B_2O_3$  doped BZT ceramics



**Figure 8** Young's modulus as a function of sintering temperature of  $B_2O_3$  doped BZT ceramics.



Figure 8 shows the values of Young's modulus of the ceramics, sintered at various sintering temperatures. Trend of Young's modulus data is consistent with the hardness measurement. It should be noted that, the present BZT ceramics exhibit higher mechanical properties, compared to BaTiO<sub>3</sub> ceramics (Jiansirisomboon and Watcharapasorn, 2008). Based on these results, sintering temperature is an important processing parameter to control the properties of B<sub>2</sub>O<sub>3</sub> doped BZT ceramics and the optimum sintering temperature in this work is 1200 °C.

## CONCLUSIONS

In this work, B<sub>2</sub>O<sub>3</sub> doped BZT ceramics were prepared by solid state reaction technique under various sintering temperature conditions. The sintering temperature promoted the increase in grain size. The optimum of density and mechanical properties was observed for the samples sintered at 1200 °C. The results indicated that sintering temperature is an important parameter to obtain the optimum properties of the ceramics.

## ACKNOWLEDGEMENTS

This work was supported by The Royal Golden Jubilee Ph.D. Program, National Nanotechnology Center (NANOTEC), NSTDA, Thailand, Faculty of Science and Graduate School, Chiang Mai University and Faculty of Science, Naresuan University.

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