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Effect of Sintering Temperature on the Hysteresis Properties of Barium Titanate Ceramic

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ABSTRACT

In this work, barium titanate ($BaTiO_3$ or BT) ceramic has been prepared by a conventional mixed oxide method with sintering temperature at 1250-1450 ºC. The samples were characterized the phase formation by using X-ray diffraction analysis (XRD), the density by using Archimedes method, the microstructure by scanning electron microscope (SEM) and the hysteresis properties by using modified Sawer-Tower circuit. The hysteresis parameters such as saturation polarization (P_s), remanent polarization (P_r) and coercive field (E_c) were measured as a function of sintering temperatures. The results show that the saturation polarization (P_s) increases with increasing sintering temperature, whereas the remanent polarization (P_r) and the coercive field (E_c) decrease, a characteristic of the enhanced ferroelectric interaction for BT ceramic.

Keywords: barium titanate, sintering, hysteresis properties.

INTRODUCTION

Lead-based ceramics, such as lead zirconate titanate (PZT), lead magnesium niobate (PMN) and lead titanate (PT), have been widely investigated and used for transducers, piezoelectric actuators, surface acoustic wave (SAW) filters and sensors because of their excellent electrical properties (Jaffe *et al*., 1971; Moulson and Herbert, 2003; Uchino, 2000). However, high volatilization of PbO and its toxicity can contaminate the environment and damage human health. With the raise of environmental consciousness, therefore, it is the present tendency to develop excellent lead-free materials replacing Pb-based ferroelectric ceramics.

Barium titanate ($BaTiO_3$; BT) ceramic is an attractive material and has been extensively exploited both for academic science and for technological utilizations over the past decades (Haertling, 1999; Moulson and Herbert, 2003). Owing to its high dielectric constant, large mechanical-quality factor, large pyroelectric coefficient, non-toxic handling and low cost of manufacturing, compared to several lead-based ferroelectrics, BT-based ceramics have been strong candidates for several electronic applications including ultrasonic transducers, actuators and sensors (Haertling, 1999; Moulson and Herbert, 2003; Swartz, 1990; Uchino, 1998). However, these excellent electrical properties of BT ceramics are affected by many physical features such as grain size, crystalline structure, purity, density and etc. These physical features can be controlled directly by parameters of preparation processing especially sintering conditions. The sintering process promotes not only the densification but also grain growth which strongly results in dielectric and hysteresis properties. Therefore, there have been many studies investigating the influence of the sintering conditions on the electrical properties of BT ceramics. Ying and Hsieh (Ying and Hsieh, 2007) studied the sintering behavior and dielectric properties of nanocrystalline barium titanate. Their work reported that specific control on sintering condition is required for the $BaTiO_3$ ceramic to achieve desired microstructure, crystalline phase and dielectric properties of BT samples. Moreover, the influence of sintering processes on PTCR properties of BT ceramics was also investigated by Mukherjee et al. (Mukherjee *et al.*, 2002).

So far, there have been no systematic studies on the influence of sintering condition on hysteresis properties of BT ceramic. It is well known that BT ceramic exhibit high coercive force regardless of their grain sizes (Kumar *et al.*, 1992), which mentioned earlier that strongly affected by sintering conditions. Therefore, the main purpose of this work is to investigate the effect of sintering temperature on hysteresis properties of BT ceramic prepared by conventional mixed-oxide method. The saturation polarization (P_s), remanent polarization (P_r) and coercive field (E_c) of BT ceramics under various sintering temperatures will also be reported.

METHODOLOGY

Ceramics with molar formula $BaTiO_3$ were prepared by a conventional mixed-oxide method. The starting materials were $BaCO_3$ and TiO_2. Stoichiometric quantities were weighted, ground, homogenized and ball-milled in ethanol for 24 h. The powders were calcined at T = 1300 °C for 2 h. After that, the calcined BT powders were mixed with 3% polyvinylalcohol (PVA) and pressed into disk samples of 15 mm diameter and 1 mm thickness. The BT pellets were then sintered between 1250 to 1450 °C for 2 h in air.

Densities of sintered BT ceramics were measured by Archimedes method and X-ray diffraction (XRD using CuK_α radiation) was employed to identify the phases formed. The microstructure evolution was observed using a scanning electron microscope (SEM). The average grain size (diameter) was determined from the number of grains in the fixed area using a mean linear intercept method. For electrical measurements, silver paste was fired on both sides of the polished samples at 550 ºC for 30 min as the electrodes. The polarization (P) was measured as a function of electric field (E), using a ferroelectric tester system (Radiant Technologies, Inc., RT66A). The ferroelectric hysteresis (*P*-*E*) loop was recorded at room temperature (25 ºC). The parameters obtained from the loops were the saturation polarization (P_s), the remanent polarization (P_r) and the coercive field (E_c), which are defined as the points where the loops reach the maximum polarization, cross the zero field and cross the zero polarization, respectively.

RESULTS AND DISCUSSION

The phase formation of the sintered BT ceramics is revealed by XRD as shown in Figure 1. The results indicated that the single phase of perovskite $BaTiO_3$ (yield of 100% within the limitations of the XRD technique) was found in all samples with no evidence of the second phase of Ba_2TiO_4, $BaTi_2O_5$ and $BaTi_3O_7$

compositions (Berbenni *et al*., 2001; Lee *et al*., 2001; Maison *et al*., 2003). The strongest reflections in the majority of XRD trace indicate the formation of the perovskite phase of barium titanate ($BaTiO_3$) which could be matched with JCPDS file no. 5-0626, in agreement with other works (Chaisan *et al*., 2004; Chaisan *et al*., 2005). To a first approximation, this phase has a tetragonal perovskite structure in space group *P4/mm* (no. 99) with cell parameters a = 399.4 pm and c = 403.8 pm (2002).

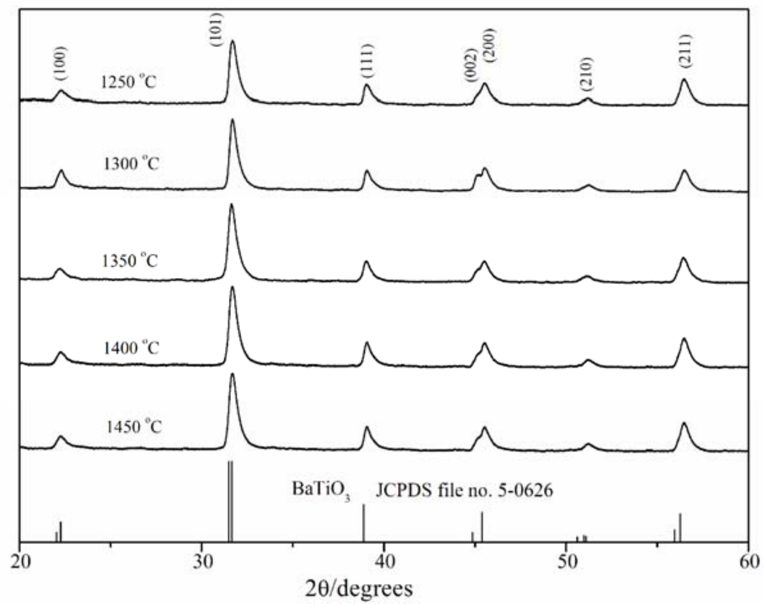

Figure 1 X-ray diffraction pattern of BT ceramics sintered at various temperatures.

The optimum sintering temperature was determined by monitoring the bulk densities obtained for a dwell time of 2 h with heating/cooling rates of 5 °C/min at a range of temperatures from 1250-1450 °C. The theoretical density of tetragonal phase of BT ceramics, which was used for the relative density calculation in the sintered samples, was estimated from the lattice parameter data to be ~ 6.012 g/cm^3 (JCPDS file no. 5-0626). Density data of all BT ceramics sintered at various temperatures are given in Figure 2. In general, it is observed that a density of about 76-98 % of the maximum value for BT can be achieved in this study. The density value continuously increases with increasing sintering temperature up to 1400 °C and slightly drops after increasing temperature to 1450 °C. The maximum density (~ 5.88 g/cm^3) was obtained by the sintering conditions of 1400 °C for 2 h. The observed fall-off in density at 1450 °C is probably due to the dominant effect of grain coarsening mechanism and weight loss during firing at high sintering temperature as suggested by other workers (Rohrer, 2005; Valdivieso *et al*., 1996).

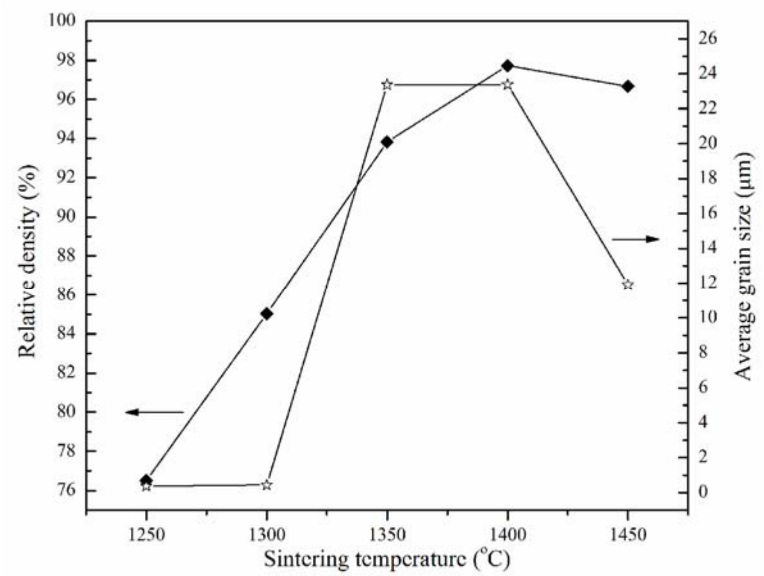

Figure 2 The relative density and average grain size of sintered BT ceramics as a function of sintering temperatures.

The microstructure of BT ceramics with the various sintering temperatures was revealed by SEM. Micrographs of BT samples sintered at 1300, 1350, 1400 and 1450 °C are shown in Figure 3(a-d), respectively. From the Figure 3(a), it can be seen that the BT ceramic sintered at 1300 °C consisted of fine grain (~0.5 μm) with poor density. After the sintering temperature was increased to 1350 °C, the grain size of BT ceramic was enlarged to be ~10-50 μm. The variation of average grain size of BT ceramic versus sintering temperature was also plotted in Figure 2. It is clearly seen that the sample sintered at 1400 °C exhibits a single phase perovskite $BaTiO_3$ as confirmed by phase analysis using X-ray diffraction (Figure 1), together with a dense and refined microstructure (Figure 3(c)) and agrees with the measured density of ~98% theoretical density. Moreover, the BT samples with high densification also show abnormal grains of size around ~50 μm due to the recrystallization during firing and variation of stoichiometric compositions (Hur *et al.*, 1998; Jaffe *et al.*, 1971). However, even though the average grain size of BT ceramic significantly increased from 0.5 μm at 1250 °C to 50 μm at 1400 °C, the full width of half maximum (FWHM) value of XRD peaks remain unchanged due to the overlap of two strongest peaks which cannot recognized by bare eyes. Additionally, 180° domain can be observed in the micrographs of BT ceramics sintered at 1350 and 1400 °C and the domain width of sample is determined to be around 0.5 μm (Jaffe *et al.*, 1971; Lee *et al.*, 2001).

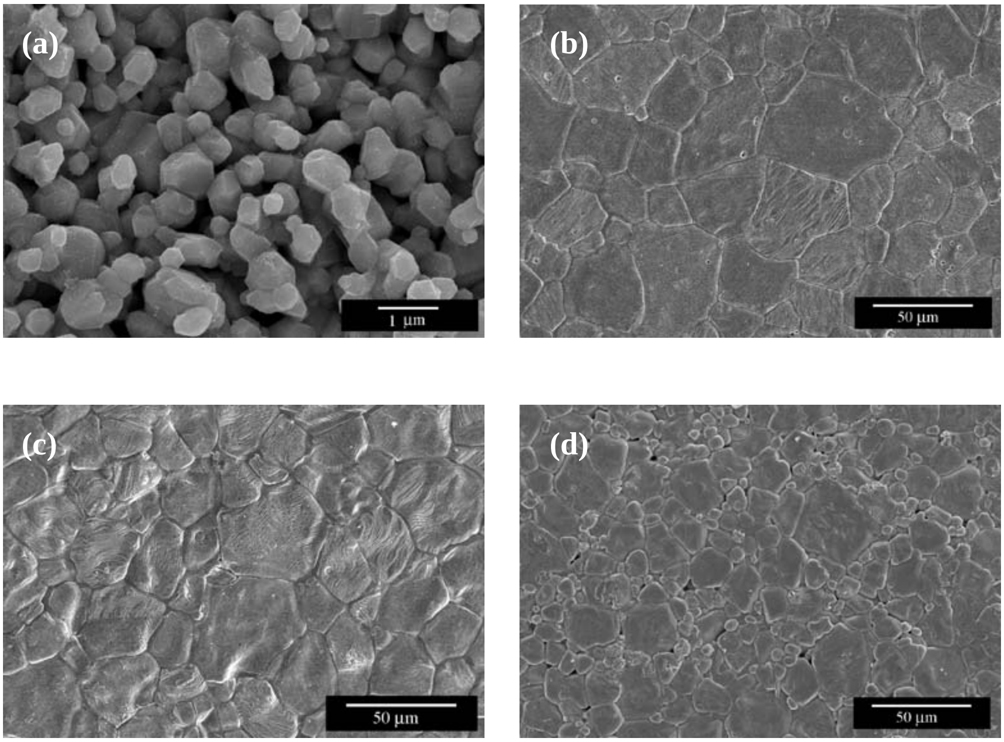

Figure 3 Microstructure of BT ceramics sintered at various temperatures: (a) 1300 °C, (b) 1350 °C, (c) 1400 °C and (d) 1450 °C.

Figure 4 shows the polarization versus electric field (*P-E*) hysteresis loops of BT ceramics sintered at 1250, 1400 and 1450 °C for 2 h. The *P-E* hysteresis loops of all conditions are clearly observed. It can be seen that all ceramics exhibit the typical ferroelectric hysteresis loops at room temperature. This indicated that all BT ceramics sintered at various temperatures are spontaneous polarized, a characteristic of typical ferroelectric materials (Xu, 1991). For the BT ceramic sintered at 1250 °C, the saturation polarization (P_S) is 10.7 μC/cm^2, the remanent polarization (P_r) is 6.0 μC/cm^2 and the coercive electric field (E_C) is 9.8 kV/cm. After increasing the sintering temperature, the value of P_S continuously increases whereas P_r and E_C values decrease as illustrated in Table 1. An examination of the hysteresis curves led to the conclusion that the coercive force decreased as the sintering temperature rose, as a result of the greater grain growth of the ceramic samples during sintering at higher temperatures. In fact, it is clear that increasing the sintering temperature produced progressive grain growth (0.37 μm at 1250 °C to 23.4 μm at 1400 °C). Moreover, the decrease of P_r and E_C values might be ascribed to the increase of the bulk density that diminishes the leakage current enhancing the polarization in process (Chang *et al*., 2007; Kosec *et al*., 2004). Additionally, since the results showed that the hysteresis parameters of BT ceramic are really affected by sintering temperatures, therefore the interested studies such as AFM, TEM and dielectric measurement concerning to ferroelectric interaction of BT ceramic would need to be considered in further work.

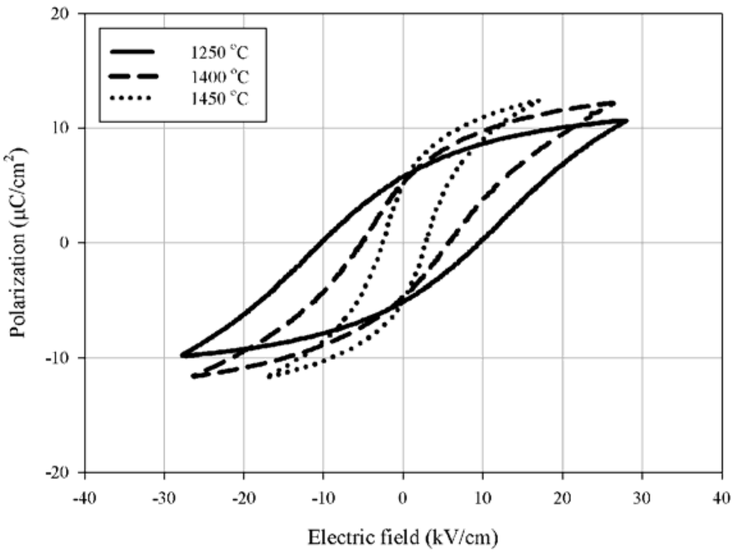

Figure 4 Hysteresis loops of BT ceramics at various sintering temperatures.

Table 1 Hysteresis properties of BT ceramics sintered at various temperatures.

Sintering temperature (°C)	P_S **(μC/cm²)**	P_r **(μC/cm²)**	E_C **(kV/cm)**
1250	10.7	6.0	9.8
1300	10.9	5.7	7.4
1350	11.5	5.5	6.5
1400	12.4	5.4	6.0
1450	12.5	5.0	2.8

CONCLUSION

The effect of sintering temperature on the phase formation, microstructure and hysteresis properties of BT ceramics were investigated in this study. From the results, it can be summarized that barium titanate ($BaTiO_3$) ceramics have been successfully synthesized by conventional mixed-oxide method. The phase structure in all samples is pure perovskite phase. As increased sintering temperature, the density of BT ceramics continuously increases and fall-off after sintered at 1450 °C due to the effect of grain coarsening mechanism at high sintering temperature.

Moreover, the abnormal grain growth was found in the BT samples with high sintering temperature (>1350 °C). The hysteresis properties such as saturation polarization (P_S), remanent polarization (P_r) and coercieve field (E_C) as a function of sintering temperature of all BT ceramics are also revealed. It was found that P_S value increases with increasing sintering temperature, whereas P_r and E_C values decrease which refer to the enhancement of ferroelectric interaction for BT ceramic.

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