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Grain-size effects on thermal properties of $BaTiO_3$ ceramics

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Abstract. **Dense nanocrystalline $BaTiO_3$ ceramics are successfully prepared by the high pressure assisted sintering. Microstructures are observed by scanning electronic microscopes. The grain sizes are estimated to be about 30 and 150 nm. In comparison, $BaTiO_3$ ceramics with the grain size of 600 nm and 1.5 μm are fabricated by conventional pressure-less sintering. The thermal properties of $BaTiO_3$ ceramics with different grain sizes are investigated by differential scanning calorimetry and thermal expansion. The results suggest that the enthalpy values for the tetragonal-cubic transition decreased and the thermal expansion values increased with decreasing grain size. Furthermore, the Curie temperature shifts to lower temperature with decreasing grain size.**

Keywords. **Nanocrystalline ceramics; thermal properties; size effect.**

1. Introduction

$BaTiO_3$ has been widely used in the electronic industry for its high dielectric constant and low losses above room temperature (Lines *et al* 1997). It is a typical ABO_3 perovskite-type material with a variety of crystal structure modifications. Depending on the transition temperature, $BaTiO_3$ have four kinds of crystal systems, that is, cubic, tetragonal, orthorhombic and rhombohedral. For single-crystal and polycrystalline $BaTiO_3$, the phase transition temperatures are about 125·5 and –90°C, respectively. Interestingly, during the tetragonal-cubic transition, there is abnormal volume shrinkage with increasing temperature, so the phase transition can be verified according to this phenomenon. Recently, the size dependence on the polarization (Arlt *et al* 1985; Maria *et al* 2006), dielectric properties (Arlt *et al* 1985, Zhao *et al* 2004; Deng *et al* 2006a; Maria *et al* 2006; Wang *et al* 2006), crystal structure (Deng *et al* 2006b; Frey and Payne 2006; Xiao *et al* 2008), hardness (Deng *et al* 2008) of $BaTiO_3$ ceramics has been widely studied in experimentally and theoretically (Lin *et al* 2006; Eliseev and Morozovska 2009). However, the research of thermal properties of $BaTiO_3$ ceramics is scanty, especially in dense nanocrystalline grain samples, which depends strongly on the microstructure.

In this paper, using the pressure assisted sintering (PAS) and conventional pressure-less sintering (PLS), dense $BaTiO_3$ ceramics with grain sizes of 30, 150, 600 nm and 1.5 μm were successfully prepared. The thermal properties of nanocrystalline $BaTiO_3$ ceramics compared with the different grain size specimens were discussed.

2. Experimental

In order to obtain dense nanocrystalline materials, very fine non-agglomerated powder with a narrow particle size distribution and an appropriate densification method to minimize the grain growth are required. In our experiment, the raw $BaTiO_3$ powder with the grain sizes of 10 and 100 nm were synthesized by chemical processing (Li *et al* 2002). Dense $BaTiO_3$ ceramics with grain sizes of 30 nm were obtained by PAS as described previously (Xiao *et al* 2008). A conventional PLS of the same raw $BaTiO_3$ powders was also conducted for comparison. The mixed granules with PVA binder were formed into rectangular bars by uniaxially pressing and then compacted by cold isostatic pressing (CIP) at 200 MPa. The compacts were fired in a furnace at 1200°C for 2 h in air.

The microstructure of the sample was observed by scanning electron microscope (SEM, XL30-FEG) on fresh fracture surface. The grain sizes of $BaTiO_3$ ceramics were determined with the linear intercept technique. The bulk density was determined using the Archimedes method. Differential scanning calorimetry (DSC, TA 2050DSC) measurements were made. The heating rate was 5°C/min. The dependence of phase transition behaviour on grain size was investigated for 15–20 mg specimens. Values for the enthalpy of transition were determined for the tetragonal-cubic transition. The thermal expansion curve was determined with a dilatometer (Theta Co., USA). The heating and cooling rates were 3°C/min.

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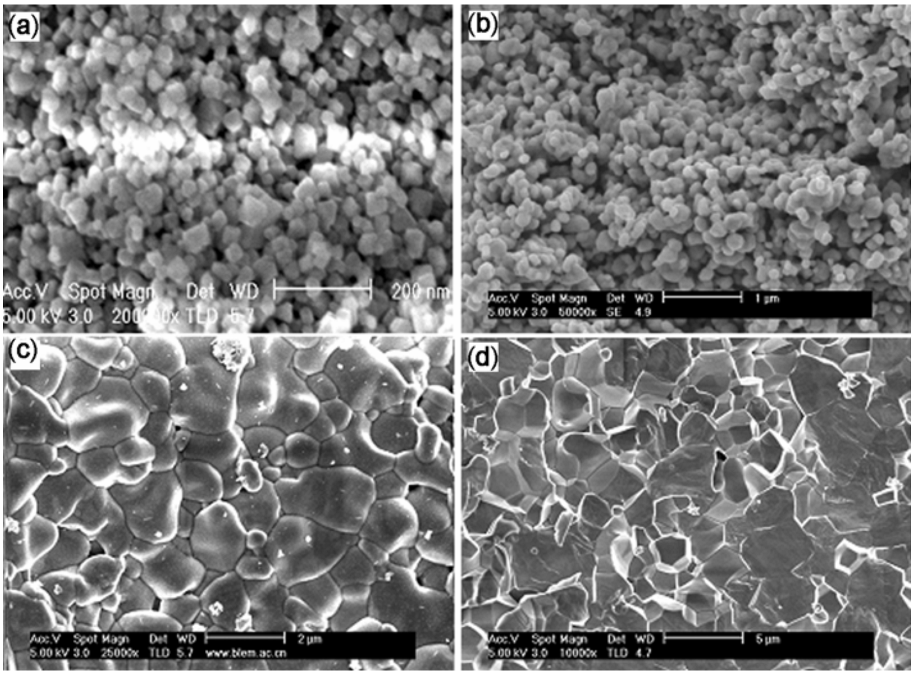

Figure 1. SEM photograph of $BaTiO_3$ ceramics with various grain sizes (**a**) 30 nm, (**b**) 150 nm, (**c**) 600 nm, (**d**) 1·5 μm.

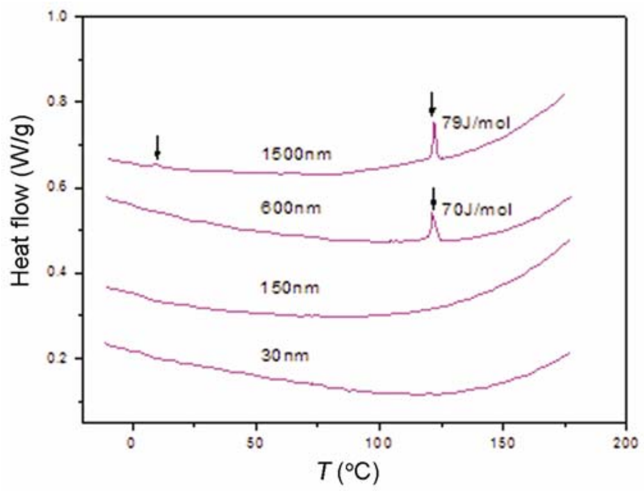

Figure 2. DSC data for of $BaTiO_3$ ceramics with various grain sizes.

3. Results and discussion

Figure 1 shows SEM images of $BaTiO_3$ ceramics sintered by PAS and PLS, respectively. Table 1 lists the processing conditions and the resultant properties of $BaTiO_3$ ceramics in this study. Average grain sizes of $BaTiO_3$ ceramics are approximately 30, 150, 600 nm and 1·5 μm prepared by PAS and PLS, which the raw $BaTiO_3$ powder were 10 and 100 nm, respectively. Smaller grain size can be obtained by PAS under lower temperature and shorter hold time.

Figure 2 gives differential scanning calorimetry data recorded for $BaTiO_3$ ceramics of various grain sizes with decreasing from 180 to –10°C. Endothermic features near 125 and 5°C for larger grain specimens are attributable to the first-order cubic-tetragonal and tetragonal-orthorhombic transformations, respectively. Clearly, there are marked changes which take place in the transition behaviour for $BaTiO_3$ ceramics with decreasing grain size. For 1·5 μm $BaTiO_3$ ceramics, there are two exothermic peaks associated with the first-order orthorhombic-tetragonal and tetragonal-cubic transformations at approximately 10 and 122°C, respectively. When the grain size decreased to 600 nm, only a exothermic peak associated with the tetragonal-cubic transformations exists at about 120°C. When the grain size further decreased to 150 and even 30 nm, the features associated with the two formerly independent transitions are lost. The enthalpy values for the tetragonal-cubic transition ranged from 79 J/mol for the 1·5 μm grain size to 70 J/mol for the 600 nm grain size, which compares closely with reported $BaTiO_3$ polycrystalline values. A reduction in transition enthalpy is reasonable for material exhibiting suppressed transition characteristics (Frey *et al* 2006). In addition, for 1·5 μm $BaTiO_3$ ceramics, the phase transition temperature for orthorhombic-tetragonal and tetragonal-cubic transformations were about 10 and 122°C, while the phase transition temperature for tetragonal-cubic transformations were about 120°C for 600 nm $BaTiO_3$ ceramics. The cubic-tetragonal transition shift to lower temperatures with decreasing grain size, as has been concluded previously based on dielectric constant data (Arlt *et al* 1985; Zhao *et al* 2004; Deng *et al* 2006a; Maria *et al* 2006; Wang *et al* 2006).

Table 1. Processing conditions and the resultant properties of $BaTiO_3$ ceramics.

Grain size (nm)	Sintering condition	Sintering temperature (°C)	Relative density (%)	Mean linear expansion coefficient ($^{-6}$/°C)
30	PAS	1000	96·2	7·31
150	PAS	1000	95·7	5·16
600	PLS	1200	97·7	3·27
1500	PLS	1200	98·1	2·28

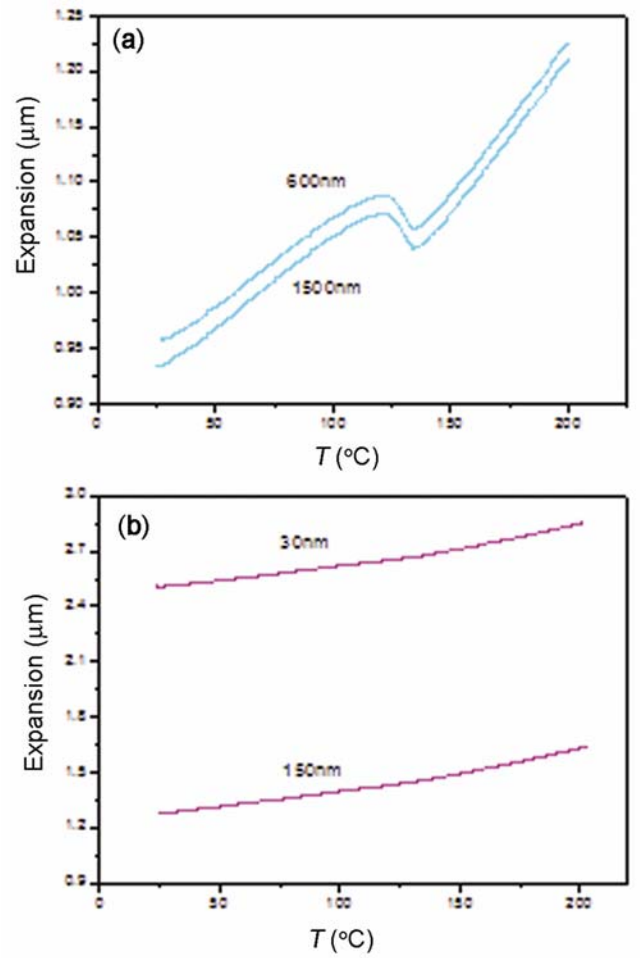

Figure 3. The thermal expansion curves of $BaTiO_3$ ceramics with various grain sizes. (**a**) 600 nm and 1·5 μm, (**b**) 150 and 30 nm.

The linear thermal expansion curves for $BaTiO_3$ ceramics of various grain sizes with increasing from room temperature to 200°C are shown in figure 3. With temperature increasing, there is clear shrinkage in 600 nm and 1·5 μm $BaTiO_3$ ceramics in figure 3(b). The abnormal volume changes associated with the phase transition between tetragonal and cubic as the transition taking place. The phase transition temperatures are both about between 123 and 136°C. In contrast, we can not see any change in 150 and 30 nm $BaTiO_3$ ceramics in figure 3(a). The features associated with the transition disappeared. This result is highly similar to those above reported of DSC data. The mean coefficients of linear thermal expansion are listed in table 1. From the table, it is clear seen that the value increased with decreasing grain size. As we all know, materials expand because an increase in temperature leads to greater thermal vibration of the atoms in a material, and hence to an increase in the average separation distance of adjacent atoms. Compared with the coarse-grained specimens, the presence of the large stress in fine-grained $BaTiO_3$ ceramics (Zhao *et al* 2004; Buessem *et al* 1966; Lin *et al* 2006) is one of the main factors. With increasing temperature, the stress gradually relieve, so that the linear thermal expansions of the fine-grained specimens are bigger than those of the coarse-grained specimens. Of course, the characters of nano-sized materials, such as high surface area and high degree of defects, may also play an important role.

4. Conclusions

Dense $BaTiO_3$ ceramics were successfully prepared by PAS and PLS. Microstructures are observed by scanning electronic microscopes. The grain sizes are estimated to be about 30, 150, 600 nm and 1·5 μm. The thermal properties of $BaTiO_3$ ceramics with different grain sizes were investigated by differential scanning calorimetry and thermal expansion method. The results suggest that the enthalpy values for the tetragonal-cubic transition decrease and the values for thermal expansion increase with decreasing grain size. Furthermore, the Curie temperature shifts up lower temperature with decreasing grain size. These differences of the thermal behaviour between $BaTiO_3$ ceramics are attributed to the variation of the resultant microstructure, especially the grain size of the ceramics.

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