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Microstructure and dielectric properties of ferroelectric barium strontium titanate ceramics prepared by hydrothermal method

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Abstract $Ba_xSr_{1-x}TiO_3$, nanoparticles with different Ba compositions were synthesized by a hydrothermal method. The mechanism of hydrothermal reactions was discussed based on DTA/TG, XRD and TEM characterizations. The result showed that perovskite structure was developed through the mutual diffusion between the intermediate phases and TiO_2 phase. The grain size of the $Ba_{0.77}Sr_{0.23}TiO_3$ (BST77) powders was about 20–40 nm. BST ceramics were made from the hydrothermal-derived BST powders and the dielectric properties of the BST ceramics were measured. Due to the small grain size and active surface energy of the BST powders prepared by hydrothermal method, the BST ceramics showed low sintering temperature. It was found that the BST77 ceramics sintered at 1280 °C showed dielectric constant peak dispersion which was believed to be caused by dimension domino effect.

Keywords BST ceramics · Hydrothermal method · Dielectric properties

1 Introduction

Barium strontium titanate, $Ba_xSr_{1-x}TiO_3$(BST), is a continuous solid solution of $BaTiO_3$ and $SrTiO_3$. Due to the high dielectric constant, low dielectric loss, low leakage current, low temperature coefficient for the dielectric constant and the composition-dependent Curie temperature (T_c), BST has been widely used in the fields such as integrated storage capacitors in gigabit dynamic random-access memory (DRAM), hydrogen gas sensors, pyroelectric sensors and as a dielectric layer in electroluminescent display devices [1–3].

Hydrothermal method is a commercial way to prepare powders. The powders prepared by hydrothermal method have the advantages of high purity, super fine, good fluidity, low agglomeration, narrow distributing of grain size and high activity of sintering. In this paper, BST nanoparticles with different Ba composition were synthesized by hydrothermal method and their formation mechanism of hydrothermal reaction was discussed. The dielectric properties of the BST ceramics derived from the hydrothermal-derived BST powders were measured.

2 Experimental procedure

$BaCl_2$, $Sr(NO_3)_2$ and $TiCl_4$ were used as starting materials. $TiCl_4$ was dissolved in the ethanol first and then $BaCl_2$ and $Sr(NO_3)_2$ were added in the $TiCl_4$ ethanol solution with continuously stirring. KOH solution was dripped into the mixed solution until it changed into gelatin. The gel was aged in air for 6–8 h. At last, the gel was hydrothermally treated in autoclave at 240 °C for 8 h. Three types of BST powders were prepared in this experiment, which were labeled as BST77, BST60 and BST50 relate to $Ba_xSr_{1-x}TiO_3$ with x=0.77, x=0.60, x=0.50 respectively. The as-prepared BST powders were used as source materials for the BST ceramics. The BST ceramics were prepared by dry press and were sintered at 1280 °C–1310 °C for 40 min.

A NET ZSCH STA499 DTA-TG thermal analyzer was used to analyze the reaction mechanism of the precursor. A M18 X-ray diffractometer (XRD) was applied to analysis to

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BST samples. The morphologies of the BST powders and BST ceramics were observed by JEM-200CX transmission electron microscope (TEM) and Phillip XL-20 scanning electron microscope (SEM). The dielectric properties of the BST ceramics were measured by LCR Meter 4225.

3 Results and discussions

3.1 DTA/TG analysis of the precursor

Figure 1 showed the DTA/TG result of the precursor. The curves showed that the thermal development of the precursor could be divided into three sections. The first section was below 200 °C, in this section, water in the networks of the gel was vaporized. The second section ranged from 200 to 600 °C. In this section, the endothermal peak was caused by the decompose of Ti^{4+} complex and the crystallize process of Ba^{2+} and Sr^{2+}. The third section was above 600 °C. A small quantity of organic impurity burning and some inorganic salt decomposition such as $BaCO_3$, $SrTiO_3$ leaded to precursor weight loss in this section. It was proposed from the analysis that perovskite structure of the BST developed through the mutual diffusion between the intermediate phase and TiO_2 phase.

To find out the mechanism of crystallization of the BST, XRD was used to analysis the phase of the BST77 powders. Figure 2 shows the XRD patterns of the BST77 precursors annealed at (a) 600 °C, (b) 700 °C and (c) 800 °C for 2 h. The powders were perovskite BST, but some intermediate phase of (Ba, Sr)CO_3 was detected in the BST powders annealed at 600 °C. No diffraction peak of (Ba, Sr)CO_3 was observed in the BST powders annealed at 700 °C. Figure 2(c) showed that the sample transformed into complete perovskite structure at 800 °C. It was indicated that perovskite structure developed through the mutual diffusion between the intermediate phase and TiO_2 phase [4–8].

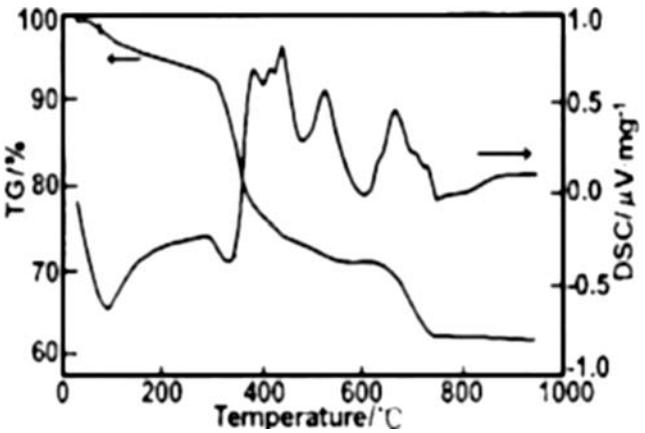

Fig. 1 DTA and TGA curves of BST precursor

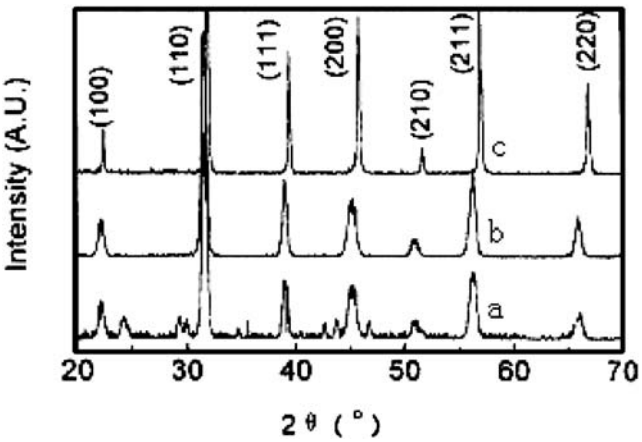

Fig. 2 XRD curves of BST77 gel annealing at (*a*) 600 °C (*b*) 700 °C and (*c*) 800 °C

3.2 Morphologies of BST powder

Figure 3 is the TEM micrographs of BST77 and BST50 powders prepared at 240 °C. Tetragonal nanosized grains was observed in the BST powders, which was closely related to the perovskite structure of the BST. The grain size of the BST ranged from 20 to 40 nm.

3.3 SEM observation of BST ceramic

Figure 4 shows the SEM micrograph of the BST77 ceramics sintered in (a)1280 °C and (b)1310 °C for 40 min. The grain size of BST ceramics sintered at 1280 °C was 3 μm, while the grain size increase to 5 μm with the increase of annealing temperature to 1310 °C. It was indicated that the crystals in the BST ceramics developed very well at the annealing temperature range of 1280–1310 °C. The crystal size of BST ceramics fabricated by traditional solid phase reaction method was larger than 10 μm [9]. In addition, the sintering temperature of BST material prepared by solid phase reaction method usually varied from 1380–1400 °C. However, the sintering temperature of BST powders synthe-

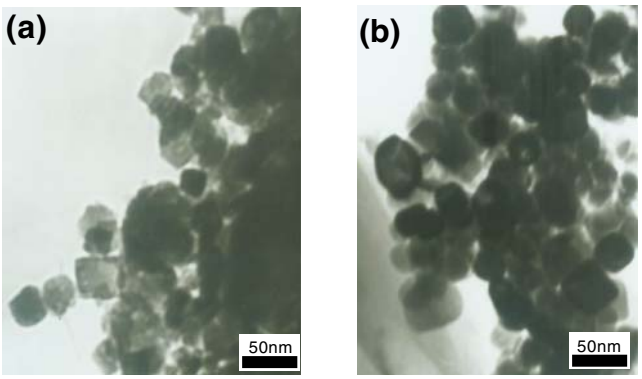

Fig. 3 TEM micrographs of (*a*)BST77 and (*b*)BST50 prepared at 240 °C

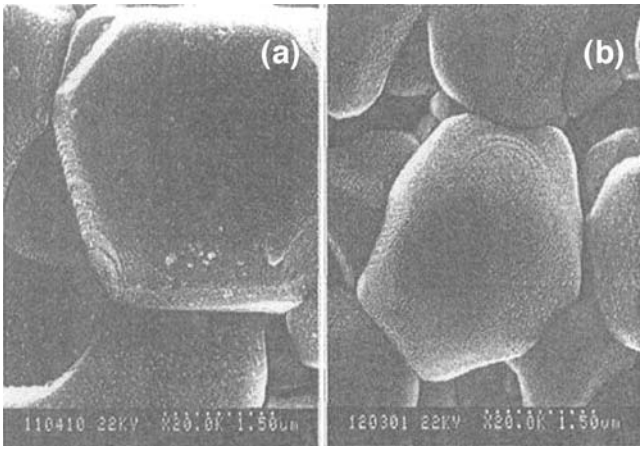

Fig. 4 SEM photograph of BST ceramics sintered at (**a**) 1310 °C and (**b**) 1280 °C for 40 min

sized by hydrothermal method was reduced to 1280 °C due to tiny particle size and high sintering activity.

3.4 Electrical properties of BST ceramics

Figures 5 and 6 show the dielectric constant vs. temperature of the BST77 ceramics sintered at 1280 and 1310 °C respectively. The testing frequency is 100 kHz and testing temperature changed from −45 to 45 °C.

Figure 5 showed that the dielectric constant of BST77 ceramics sintered at 1280 °C reached its maximum-value of 1920 at testing temperature of 5.7 °C. While for the BST77 ceramics sintered at 1310 °C, the maximum dielectric constant achieved to 6,000 at the same testing temperature of 5.7 °C. From Fig. 6, it could be found that the dielectric loss tgδ decreased with the temperature increased from −45 to 45 °C. The dielectric constant peak was caused by the structure phase change from tetragonal to cubic perovskite structure. Compared with the BST ceramics sintered at 1310 °C, the dielectric constant peak of sample sintered at 1280 °C was wider and smoother, and dielectric constant peak dispersion was observed. It was believed to be resulted from a lower particle size of the samples sintered at 1280 °C.

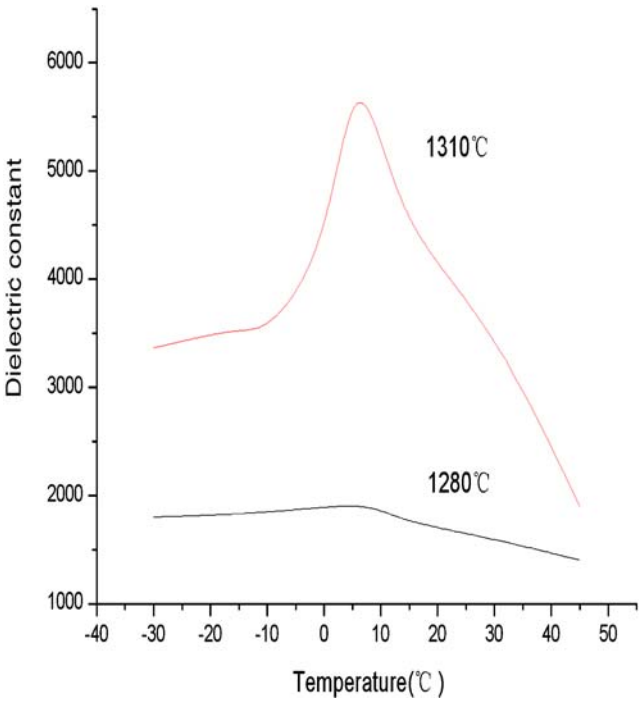

Fig. 5 Dielectric constant vs. temperature of the BST77 Ceramics sintered at 1280 and 1310 °C

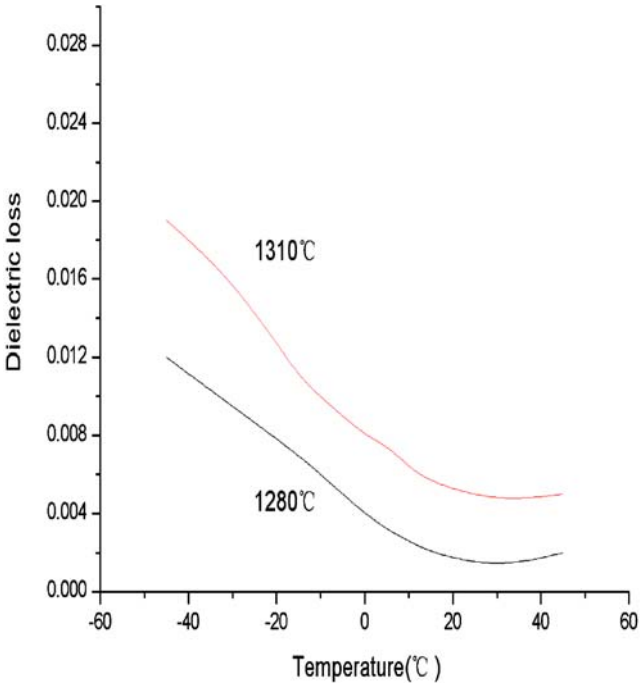

Fig. 6 Dielectric loss vs temperature of the BST77 Ceramics sintered at 1280 and 1310 °C

4 Conclusions

Nanosized $Ba_xSr_{1-x}TiO_3$ powders of different compositions were synthesized by hydrothermal method. The perovskite structure of the BST powders developed through the mutual diffusion between the intermediate phase and TiO_2 phase. The BST powders were well developed and tetragonal crystals were observed. The grain size of the BST powders ranged from 20 to 40 nm. The BST ceramics made from the BST powders prepared by hydrothermal method showed a lower sintering temperature of 1280 °C due to tiny grain size and higher sintering activity of the BST powders prepared by hydrothermal method. Maximum dielectric constant was achieved at the testing temperature of 5.7 °C and the BST ceramics with large grain size showed large dielectric constant.

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