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The effect of Zn–B–Si–O addition on $Ba_{0.7}Sr_{0.3}TiO_3$ by sol–gel process

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Abstract

Barium strontium titanate ($Ba_{0.7}Sr_{0.3}TiO_3$, BST) ceramic and BST glass–ceramics were prepared by sol–gel process and the samples were sintered at different temperatures. Microstructure, bulk density and dielectric property were measured, respectively. The results revealed that the relative density of BST glass–ceramic with 25% (mol%) glass forming content was about 96% after being sintered at 1075 °C and that of BST glass–ceramic (40% glass forming content) sintered at 975 °C was about 97%. The dielectric constant of BST glass–ceramic is lower than that of the BST ceramic and the permittivity of BST glass–ceramic was decreased with the glass content increasing.

Keywords: D. Glass–ceramic; BST; Low-temperature sintering; Sol–gel

1. Introduction

Barium strontium titanate ($Ba_{0.7}Sr_{0.3}TiO_3$, BST) is the solid solution of $BaTiO_3$ and $SrTiO_3$ with excellent dielectric properties, which have been studied extensively. In fabrication miniaturized multiplayer ceramic devices, low sintering temperatures ceramics are needed to co-fire with cheaper and better electric performance conductors, such as sliver and copper [1]. There are several ways to decrease the sintering temperature of ceramics. Among them introducing glasses with low softening temperatures is cheap and effective. There are two approaches to introduce glasses into ceramic compositions [2]. The first is adding low softening temperature glass powder into crystalline ceramics. The second is the "glass–ceramic" approach in which all the starting components are in glass form, then crystalline component crystallized from glass matrix during firing [2]. In this study, the "glass–ceramic" approach was adopted to lower the sintering temperature of BST ceramic.

The gel glasses of Ba–Sr–Ti–Zn–Si–B–O were prepared by sol–gel process. The effect of Zn–Si–B–O addition on BST sintering behaviors and dielectric properties were studied in this paper.

2. Experimental procedure

The compositions of BST ceramic and BST glass–ceramic are given in Table 1. The starting materials were: barium acetate ($Ba(AC)_2$), strontium acetate hemihydrate ($Sr(AC)_2 \cdot 1/2H_2O$), titanium isopropoxide ($Ti(OCH(CH_3)_2)_4$), tributyl borate ($B(OCH_2CH_2CH_2CH_3)_3$), tetraethyl orthosilicate ($(C_2H_5O)_4Si$), acetic acid (HAC), zinc acetate dihydrate ($Zn(AC)_2 \cdot 2H_2O$).

Barium acetate and strontium acetate were dissolved in acetic acid according to the mole ratio of Ba:Sr and stirred at 100 °C for half an hour. After cooling down to room temperature, titanium isopropoxide were added into the Ba–Sr solution. At the same time, zinc acetate was dissolved in deionised water at room temperature and tributyl borate and tetraethyl orthosilicate were mixed with acetic acid and ethanol for half an hour, then, the solution of zinc acetate was added into (B–Si) complex alkoxide solution and stirred. After that, the solution of B–Si–Zn–O was mixed with Ba–Sr–Ti–O solution. Transparent and clear sol of Ba–Sr–Ti–B–Si–Zn–O was formed after stirring, and turned into gel by hydrolysis. The gel was heat treated at 200 °C and annealed at 800 °C. The pure BST powder was prepared by the same procedure without any addition of B–Si–Zn–O solution. The powders were pressed at 1.000 kg/cm^2 to form pellets with 12 mm diameter.

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Table 1
The compositions of powders

Sequence number	Addition	Composition
BST-P	Pure, without addition	$Ba_{0.7}Sr_{0.3}TiO_3$
BST-1	0.5 ZnO–0.4 B_2O_3–0.1 SiO_2 (G)	0.75 ($Ba_{0.7}Sr_{0.3}TiO_3$)·0.25 (G)
BST-2	0.5 ZnO–0.4 B_2O_3–0.1 SiO_2 (G)	0.6($Ba_{0.7}Sr_{0.3}TiO_3$)·0.4 (G)

The dry gel was analyzed by thermo-gravimetric analysis (TG) and differential scanning calorimeter (DSC) (Thermal analyzer: NETZSCH STA449C, Germany). The crystal phase composition was studied by X-ray diffractometer (XRD) (D8 ADVANCE, Bruker, Germany). The microstructure was analyzed by scanning electron microscope (SEM) (Jeol JSM-5510, Japan) and dielectric property was measured by HP 4284A precision LCR meter. The bulk density was measured by Archimedes method (water immersion method).

3. Result and discussion

3.1. Thermal analysis and XRD measurement

Fig. 1 is the DSC and TG curves of BST-P, BST-2 dry gels which were dried at 200 °C.

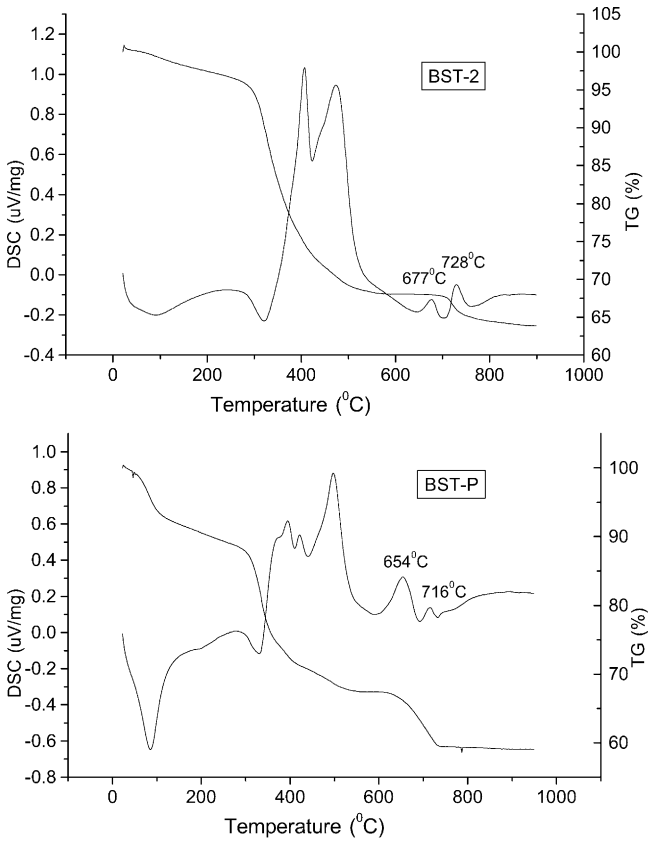

Fig. 1. DSC and TG curves of BST-P, BST-2.

The DSC and TG curves of BST-P, BST-1 and BST-2 are similar. With regard to BST-2, below 350 °C, notable weight loss and two endothermic peaks corresponding to the evaporation of H_2O and other organic solvent occur. Two exothermic peaks are detected at ~405 and ~475 °C. As it can be seen from Fig. 2 there were no crystallization taking place under 500 °C. So, the two exothermic peaks were perhaps caused by the decomposition and burning of organic radicals which resulted in the notable weight loss between 300 and 500 °C. The exothermic peaks at 654 °C in BST-P and exothermic peak at 677 °C in BST-2 were probably due to the crystallization of perovskite BST. XRD patterns (Fig. 2) show that perovskite BST crystallization took place between 600 and 700 °C and the curve of TG shows no weight loss during this temperature area. Above 700 °C, another weight loss appears corresponding to an exothermic peak at 729 °C. Similar peak and weight loss can be detected in BST-P at 718 °C. Except for the growth of perovskite BST crystal there were no other crystallization (Fig. 2), so the weight loss perhaps originated from the release of various side products during alcoxolation and oxolation [3]. Fig. 1 shows the crystallization temperature of BST-P is 654 °C and that of BST-2 is 677 °C. Because of Zn–Si–B–O addition, the crystallization temperature of perovskite BST increased. The same conclusion can also be drawn from the XRD patterns. XRD measurement shows the powder of BST-P heat treated at 600 °C for 10 min, diffraction peaks from (1 1 0) and (2 1 1) planes of BST perovskite phase can be marginally detected, but after being annealed at the same temperature for the same time, nothing can be detected in BST-2.

3.2. SEM studies and density measurement

Fig. 3 (A) is the scanning electron microstructure photograph of BST-1 sintered at 1075 °C for 4 h and (B) is sample BST-2 sintered at 1000 °C for 4 h. Most of the BST-1 and BST-2 grains are very small ($\ll$1 μm).

Fig. 4 gives the relationships between the bulk density, relative density and the sintering temperature. The bulk density decreased with increasing of Zn–B–Si–O content. As shown in Fig. 4, after being sintered at 1075 °C for 4 h, the bulk density of BST-1 was more than 96% of the theoretical density and that of BST-2 sintered at 975 °C for 4 h was 97% of the theoretical density which were the maximum of these two samples' bulk densities. So the sintering temperatures of BST-1 (1075 °C) and BST-2 (975 °C) with addition of Zn–B–Si–O were all lower than the sintering temperature

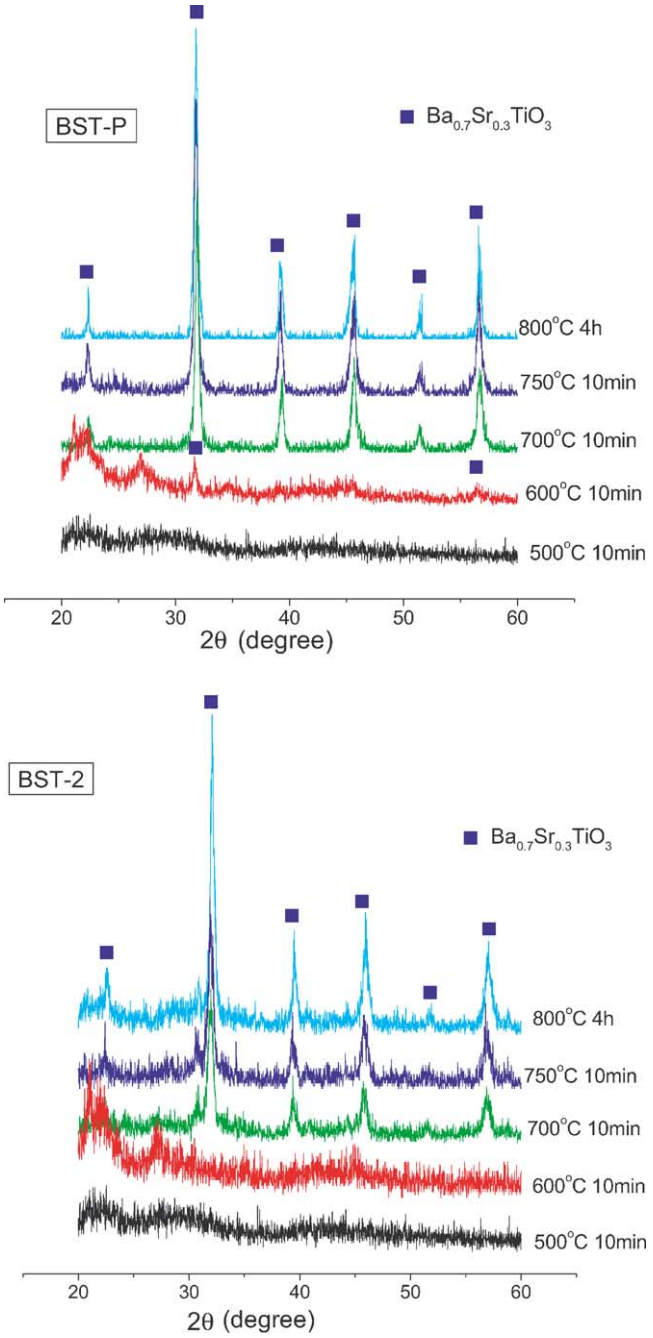

Fig. 2. XRD patterns of BST-P and BST-2.

of BST-P (>1350 °C) [3]. The reason is perhaps Zn–B–Si–O additives transformed into glass phase and the glass forming content softened at sintering temperature, which promoted the densification of BST-1 and BST-2.

3.3. Dielectric properties

Fig. 5 shows the dielectric properties of BST-P sintered at 1290 °C, BST-1 sintered at 1075 °C and BST-2 sintered at 975 °C. The permittivity (ε) of BST-2 is almost the half of that of the BST-1, both of them are far less than that

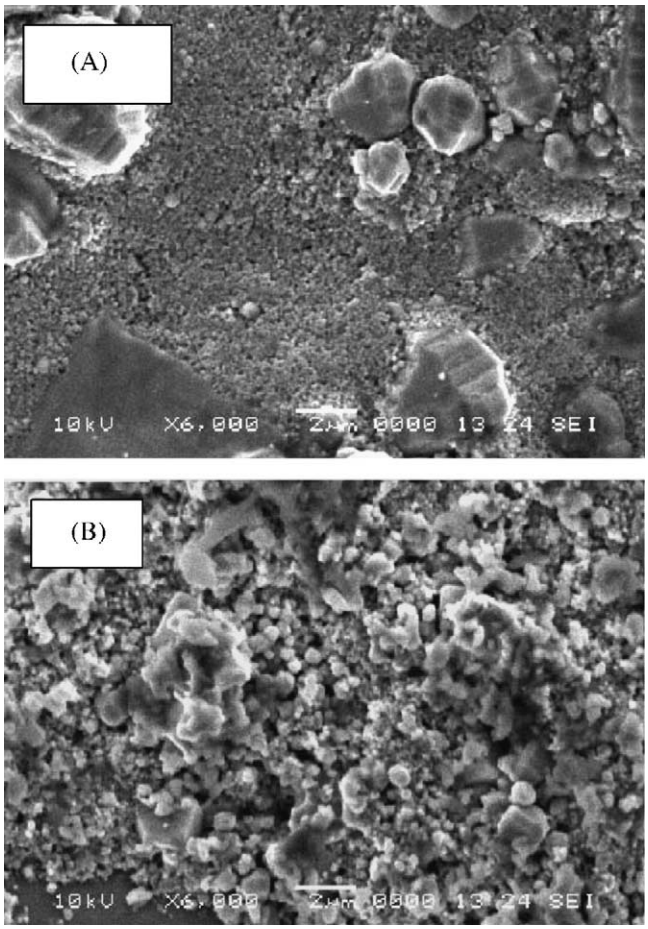

Fig. 3. SEM photographs of sample BST-1, BST-2.

of BST-P. The reason is that the additives of Zn–B–Si–O formed glass phase by sintering, the permittity of glass is small which caused the decreasing of the permittivity of BST-1 and BST-2. In the case of BST-P, the maximum of permittivity (ε_{max}) is observed at 42.2 °C and the ε_{max} of BST-1 and BST-2 can be detected at 25.2 °C, −29 °C, namely the temperature of phase transition (T_c) decreased one by one in BST-P, BST-1 and BST-2 order. Because there was secondary phase ($BaTi_2Si_2O_8$) in existence to bring

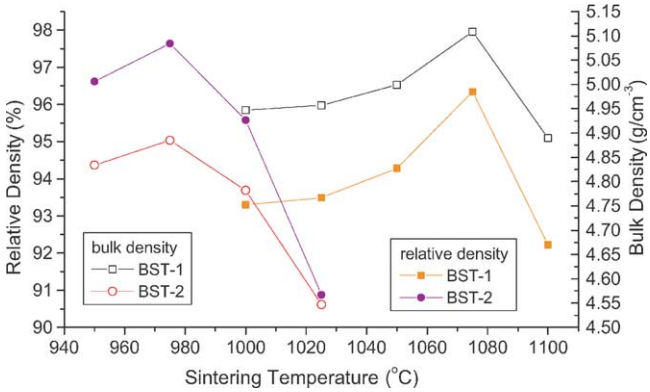

Fig. 4. Bulk density and relative density of samples.

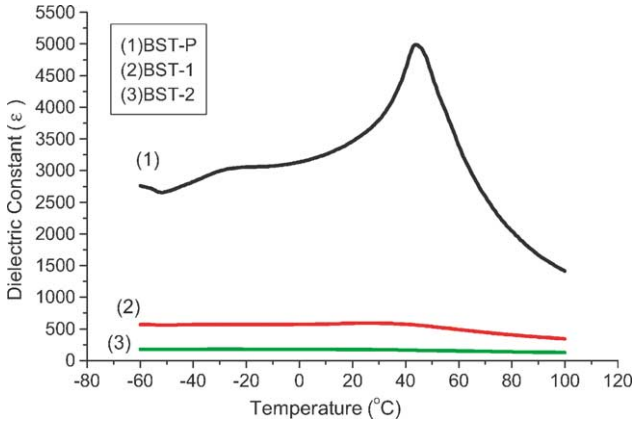

Fig. 5. The curves of ε–T.

about the content of Ba^{2+} decreasing in BST composition, namely the ratio of Ba:Sr decreased. The Curie temperature (T_c) of $BaTiO_3$ is 120 °C, while $SrTiO_3$ is paraelectric material without ferroelectric phase transition [4], so, the Curie temperature of BST is decreased with decreasing of the mole ratio of Ba:Sr. The phase transition peaks of BST-1 and BST-2 are much broadened that may be ascribed to the fine grains of the two samples.

4. Conclusion

In this paper, the gel–glasses of pure Ba–Sr–Ti–O and Ba–Sr–Ti–Zn–Si–B–O were prepared by sol–gel process. The grains of BST grew out from an amorphous gel–glass matrix at proper heat treatment temperatures. The sintering temperature of BST ceramic can be decreased by "glass–ceramic" approach, the sintering temperature of BST-1 is 1075 °C and BST-2 is 975 °C. Because of the glass forming content in existence, the dielectric constant decreased. The Curie temperature was lowered with increasing of the secondary phase content.

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References

[1] T. Takada, S.F. Wang, S. Yoshikawa, Effects of glass additions on (Zr, Sn)TiO_4 for microwave applications, J. Am. Ceram. Soc. 77 (9) (1994) 2485–2488.
[2] H. Jantunex, R. Rautioaho, Compositions of $MgTiO_3$–$CaTiO_3$ ceramic with two borosilicate glasses for LTCC technology, J. European Ceram. Soc. 20 (2000) 2331–2336.
[3] T. Hu, H. Jantunen, A. Uusimaki, S. Leppavuori, $Ba_{0.7}Sr_{0.3}TiO_3$ powders with B_2O_3 additive prepared by the sol–gel method for use as microwave material, Mater. Sci. Semicond. Proc. 5 (2003) 215–221.
[4] D. Bao, Z. Wang, W. Ren, Crystalline kinetics of $Ba_{0.8}Sr_{0.2}TiO_3$ sols and sol–gel synthesis of $Ba_{0.8}Sr_{0.2}TiO_3$ thin film, Ceram. Int. 25 (1999) 261–265.