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Effect of sintering condition on the dielectric properties of $(Ba,Sr)TiO_3$ glass-ceramic

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Abstract

The investigation of the structure and dielectric properties of $(Ba,Sr)TiO_3$-based ferroelectric glass-ceramic was carried out. Attention has been focused on the relationships between sintering conditions, microstructure and dielectric properties. The sintering temperature and time have been found to have pronounced effects on the density, grain growth and dielectric properties of the sintered BST glass-ceramics. When increasing sintering temperature, the dielectric constant increases largely, the dielectric loss, however, does not change obviously at paraelectric state. The tunability of dielectric constant increases largely with the increasing of sintering time form 0.5 to 4 h. A maximum tunability of 39.8% and a low dielectric loss of 0.00612 are obtained under sintering conditions of 1150 °C for 4 h.

Keywords: D. Glass-ceramic; BST; Sintering condition; Dielectric constant; Tunability

1. Introduction

Barium strontium titanate (BST) has recently received much attention for its high electric-field tunability and low dielectric loss. These materials are very promising for practical applications, such as phase shifter, delay lines, tunable filters, steerable antennas, etc. [1–3] When used in these devices, a BST system must possess the following characteristics: low dielectric constant; large tunability; low dissipation factor and low temperature dependence [4]. Presently, further improvement of the performance of BST is still desirable. And the correlation between the material structure and material performance, in particular the most important parameters of tunability and loss, is important in guiding the exploration of new materials.

As we know, the dielectric property, based on the phase transition phenomena in ferroelectric material, is closely related to the crystal structure. On the other hand, the crystal structure of a ferroelectric system is closely dependent on the thermal history and the fabrication method [5,6]. Therefore, the properties of a certain ferroelectric material will finally depend on the sintering condition, including sintering temperature and time.

Based on the above facts, a study of the properties of $(Ba,Sr)TiO_3$-based ferroelectric glass-ceramic is presented in this paper. The effect of sintering conditions on the properties of the material was discussed.

2. Experimental

$(Ba_{0.65}Sr_{0.35})TiO_3$ glass-ceramic powders doped with 2 mol.% $BaO–SiO_2–B_2O_3$ glass were synthesised via a sol–gel method using barium acetate ($Ba(CH_3COO)_2$), strontium acetate ($Sr(CH_3COO)_2{\cdot}(1/2)H_2O$), tetrabutly titanate ($Ti(C_4H_9O)_4$), tetraethyl orthosilicate (TEOS) and tributyl borate ($B(C_4H_9O)_3$) as starting chemicals. All these reagents were, respectively, dissolved into ethanol and acetic acid glacial, and then mixed to get final solution. After ageing and drying the xerogels were calcined at 800 °C, and then crushed and ground by ball milling for 24 h to obtain fine powers. The powders were mixed with 8 wt.% of 10% PVA solution and then pressed into disc-shaped pellets. The green pellets were sintered at a temperature range of 1000–1200 °C for up to 4 h.

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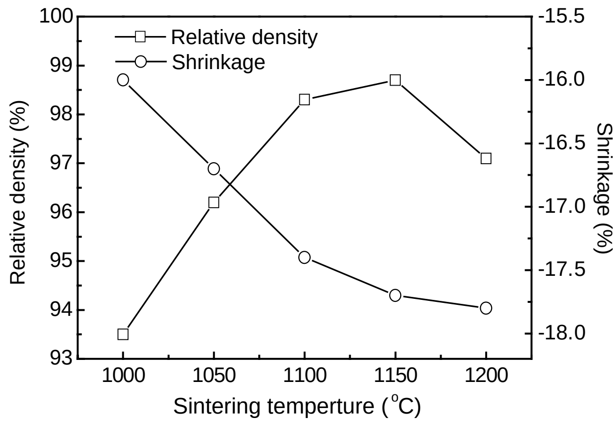

Fig. 1. Relative density and shrinkage as a function of sintering temperature for BST glass-ceramic.

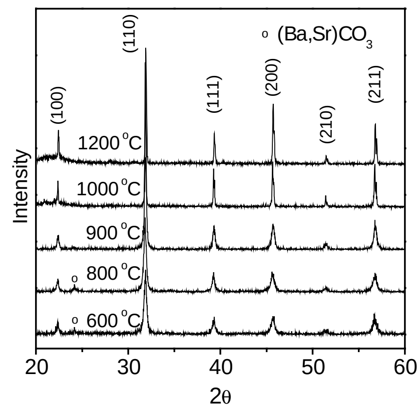

Fig. 2. XRD patterns of BST glass-ceramic xerogels calcined at different temperature.

Bulk density measurements were made using the Archimedes technique. The theoretical densities of samples were determined using the atomic weight and lattice constant. The X-ray diffraction (XRD) analysis was carried out by using Cu Kα radiation with 2θ from 20 to 60°. The microstructures were investigated on the as-fired surfaces of the sintered specimens using scanning electronic microscopy (SEM, JSM EMP-800).

The dielectric constant and loss were measured at a frequency of 100 kHz and at the temperature range of −50 to 100 °C, using a HP4284 LCR meter. The dielectric constant was also measured under various dc fields. The dc field was applied on the polished parallel disks with a thickness of 0.3 mm by a Keithley Model 6517 Electrometer.

3. Results and discussion

The effect of sintering conditions on the sintered (Ba,Sr)TiO_3 glass-ceramics is correlated with their densification, grain growth behavior and dielectric properties. Relative bulk density and shrinkage as functions of sintering temperature have been presented in Fig. 1. A sintering temperature of 1000 °C produced a relative density of approximately 93.5%, this increased to 96.2, 98.3 and 98.7% when sintered at 1050, 1100, and 1150 °C, respectively. However, increasing the sintering temperature further resulted in a reduction of relative density (97.1% at 1200 °C). The shrinkage increases with the increasing of sintering temperature.

The XRD patterns for xerogels of BST glass-ceramic calcined at different temperatures are shown in Fig. 2.

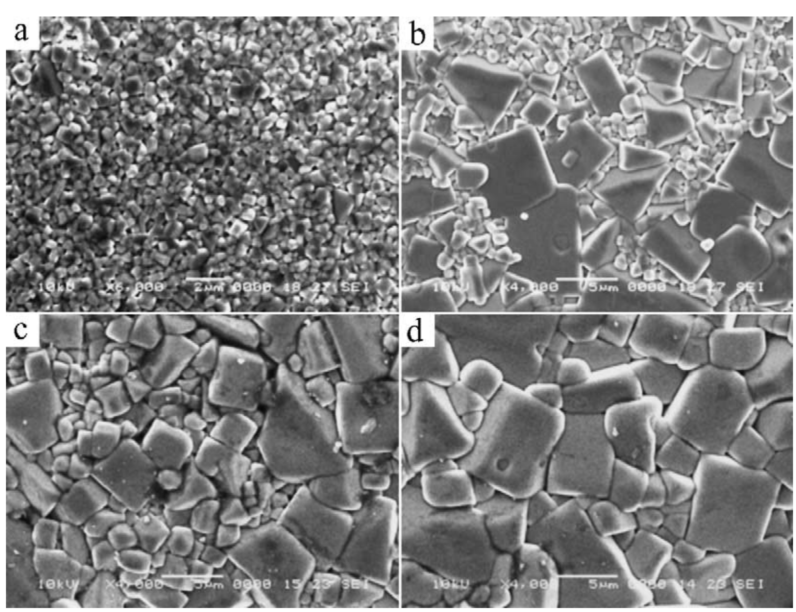

Fig. 3. SEM micrographs of BST samples sintered at (a) 1000 °C, (b) 1050 °C, (c) 1100 °C and (d) 1200 °C for 2 h.

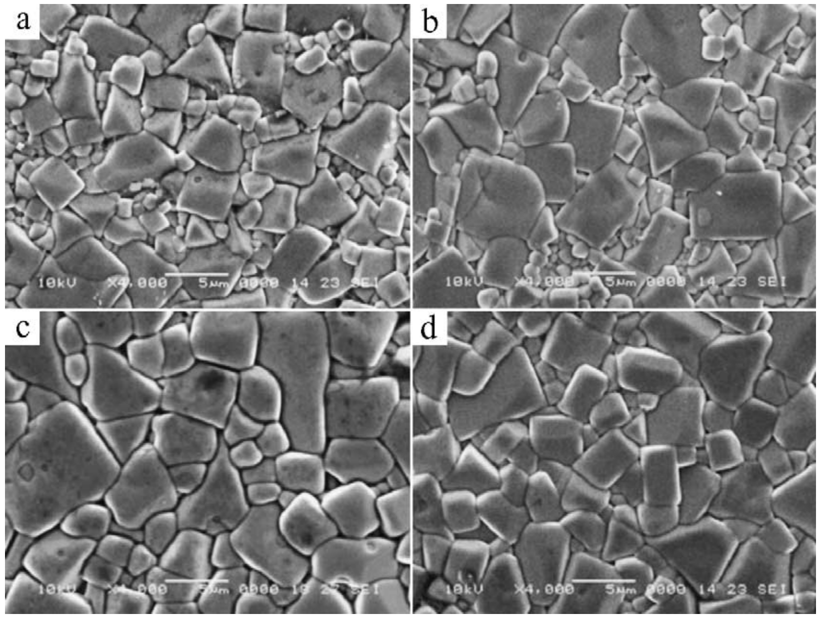

Fig. 4. SEM micrographs of BST samples sintered at 1150 °C for (a) 0.5 h, (b) 1 h, (c) 2 h and (d) 4 h.

Minor trace of $(Ba,Sr)CO_3$ phase is detected at 600 and 800 °C and is decomposed below 900 °C. At higher temperatures, the phase structure is tetragonal perovskite phase of $(Ba,Sr)TiO_3$. No secondary phase is detected by XRD. And the broadening of diffraction peak is obvious at a lower temperature, due to the small grain size.

Micrographs of as-fired surface of BST glass-ceramics sintered at various temperatures from 1000 to 1200 °C are shown in Fig. 3a–d. A mixture of various grain sizes is evident for the sample sintered at 1050 °C, which shows very large grains coexist with very small ones. With the increasing of sintering temperature, the grain size increases largely. The microstructure becomes denser, and the microstructure homogeneity improves.

Fig. 4a–d show the images of the grains of the BST glass-ceramic sintered at 1150 °C for 0.5, 1, 2 and 4 h, respectively. It can be seen that prolonging sintering time is also effective to increase the grain size and improve the microstructure homogeneity.

The variation of dielectric constant and loss with sintering temperature for the BST glass-ceramic is shown in Fig. 5. An obvious feature is that the dielectric constant decreases and its temperature spectrum broadens with the decreasing of sintering temperature. The sample sintered at 1000 °C does not shows a clearly Curie peak. The dielectric loss is much lower in the paraelectric state (~0.006) than in the ferroelectric state (~0.04), owing to the disappearance of domain. With the increasing of sintering temperature, the dielectric loss increases at ferroelectric state, but does not change obviously at paraelectric state. Sintering time has similar effect on the dielectric properties of the samples as that of the sintering temperature.

At 60 °C, the *C–V* curves for samples sintered at 1150 °C for up to 4 h are shown in Fig. 6. It can be seen that the dc field is effective for suppressing the dielectric constant. The dielectric constant is linearly decreased with the increasing of applied dc field in the range of 5–30 kV/cm. The *C–V* curves indicate that it is possible to obtain a high tunability in the paraelectric state.

The tunability (k) was calculated by using the expression:

$$k\,(\%) = \frac{\varepsilon(0) - \varepsilon(E)}{\varepsilon(0)} \times 100 \qquad (1)$$

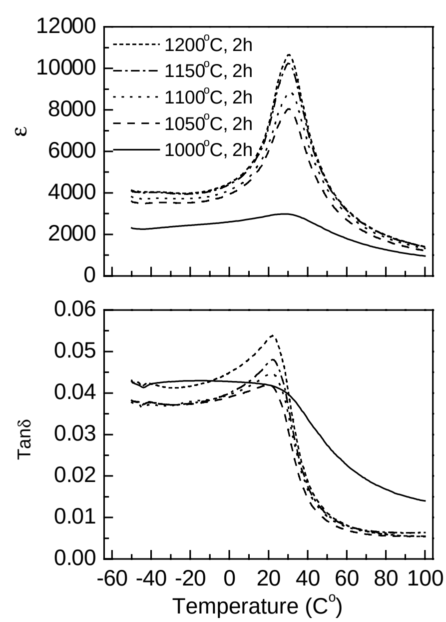

Fig. 5. Temperature dependence of the dielectric constant and dielectric loss for samples sintered at different temperature.

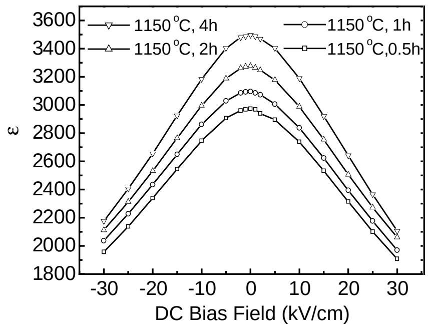

Fig. 6. Dielectric constant versus dc field for BST glass-ceramic sintered at 1150 °C for different time.

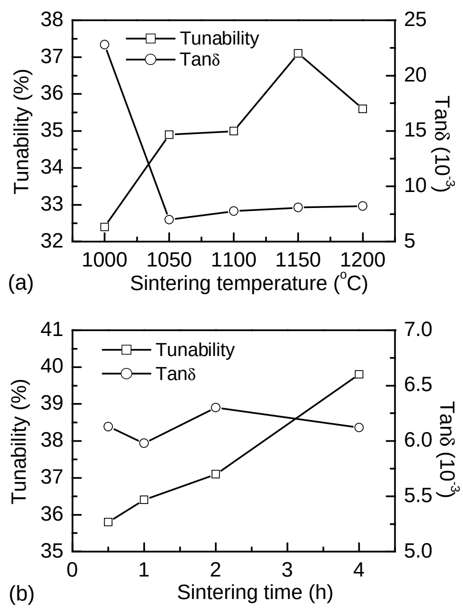

Fig. 7. Dielectric tunability and dielectric loss for BST glass-ceramic sintered at different temperature (a), or for different time (b).

where $\varepsilon(0)$ and $\varepsilon(E)$ represent the dielectric constant at zero and a certain E field, respectively. Effects of sintering temperature and time on the dielectric tunability and loss of samples are shown in Fig. 7. The dielectric tunability increase from 32.4 to 37.1% with the increasing of sintering temperature from 1000 to 1150 °C, increasing the sintering temperature further, however, results in a reduction in tunability (see Fig. 7a). It's obvious that prolonging sintering time is effective to increase tunability (see Fig. 7b). When increasing the sintering time form 0.5 to 4 h, the tunability increases from 35.9 to 39.8%. It could be explained that the grain size and the internal stress among grains affects the dielectric properties. In general, the higher is the sintering temperature, the larger is the grain size and the smaller is the internal stress. The samples with larger grains have greater tunability [7,8]. The sintering conditions do not affect the dielectric loss obviously.

4. Conclusion

The $BaO–SiO_2–B_2O_3$ glass doped BST glass-ceramics of high density and optimised dielectric properties may be fabricated between 1050 and 1200 °C. The sintering temperature and time have been found to have a pronounced effect on the density, grain growth and dielectric properties of the sintered BST glass-ceramic. In general, the dielectric constant and tunability increases with increasing of the sintering temperature or the prolonging of sintering time. Prolonging sintering time is more effective to raise the tunability. A maximum tunability of 39.8% is obtained under sintering conditions of 1150 °C for 4 h.

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