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Study on the structure and dielectric properties of $BaO–SiO_2–B_2O_3$ glass-doped $(Ba,Sr)TiO_3$ ceramics

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Abstract

$(Ba,Sr)TiO_3$ (BST)-based ferroelectric glass-ceramic powders with different $BaO–SiO_2–B_2O_3$ glass content, ranging from 0 to 30 mol%, were prepared by a sol–gel process. The crystalline structure and morphology were studied by XRD and SEM, respectively. The temperature dependence of dielectric constant and loss ($\varepsilon - T$), dielectric constant versus applied dc field ($C–V$) was measured for the BST glass-ceramics. Effects of doping glass on the structures and the dielectric characteristics of the BST glass-ceramics were discussed. Experimental results show that the BST glass-ceramics with pure perovskite phase can be well sintered at a lower temperature compared to the conventional BST ceramics. The dielectric constant and tunability decrease with the increasing of glass content. The sample with a glass content of 2 mol% shows a dielectric constant tunability of 37.1% and a dielectric loss of 0.008 at the paraelectric state.

Keywords: D. Glass-ceramic; BST; Sol–gel; Dielectric constant; Tunability

1. Introduction

Barium strontium titanate (BST) has been recognized as an ideal material for multiplayer ceramic, thick film capacitor and phase shifter because of its outstanding dielectric properties. The trends of electronic packaging are toward miniaturization and cost saving [1–3]. $(Ba,Sr)TiO_3$ has a sintering temperature of ~1400 °C [4]. Such a high temperature is almost impossible for BST to co-fire with electrode materials, and increases manufacturing cost. Therefore, studies of $(Ba,Sr)TiO_3$ ceramics have focused on decreasing the sintering temperature and improving the dielectric properties. The addition of a fluxing agent with BST, such as glass, is an effective method, which promotes densification by liquid phase sintering at low temperatures.

Adding glass sintering aids, however, may not always result in good dielectric properties. This is especially true if the dielectric constant is diluted by the presence of a continuous glass boundary phase. Thus, the key steps are to tailor the glass composition and to reduce the glass content and porosity [5,6]. $BaO–SiO_2–B_2O_3$ glass has a higher dielectric constant in comparison with many glass materials, and BaO is effective in raising the dielectric constant [7].

In this study, we used $BaO–SiO_2–B_2O_3$ glass as sintering aids to fabricate BST glass-ceramics with a pure perovskite phase, and reported how the glass dopant affects the dielectric properties of BST ceramics.

2. Experimental

The precursors used to prepare $(1-x)$ mol% $(Ba_{0.65}Sr_{0.35})TiO_3 + x$ mol% $(BaO–SiO_2–B_2O_3)$ (x = 0, 2, 5, 10, 20, 30) powders were barium acetate ($Ba(CH_3COO)_2$, purity > 9.0%), strontium acetate ($Sr(CH_3COO)_2{\cdot}1/2H_2O$, purity > 99.0%), tetrabutyl titanate ($Ti(C_4H_9O)_4$, purity > 98.0%), tetraethyl orthosilicate (TEOS, purity > 98.0%) and tributyl borate ($B(C_4H_9O)_3$, CP). All these reagents were, respectively, dissolved into ethanol and acetic acid glacial, and then mixed to get final solution. The flow chart is shown in Fig. 1. After aging and drying, the xerogels were calcined at 800 °C for 4 h, then crushed and ground by ball milling with ethanol 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 with a diameter of 12 mm. The green pellets were sintered at 1340 or 1150 °C for 2 h.

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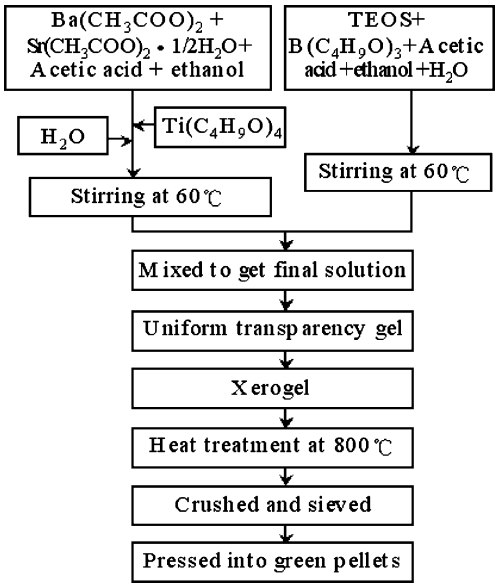

Fig. 1. Flow chart for the preparation of BST glass-ceramics.

Bulk density measurements were made using the Archimedes technique, using distilled water as liquid medium. The theoretical density ρth of the samples was determined using the atomic weight and lattice constant. The X-ray diffraction analysis was carried out 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).

Ag paste was painted onto the surface of the polished parallel disks as the electrode and fired at 520 °C for 20 min. The dielectric constant and loss were measured using a HP4284 at a frequency of 100 kHz and at the temperature range of −50 to 100 °C. The dielectric constant was also measured under various dc field. At each equilibrium temperature, the dc field was applied on the specimens in the following consecutive cycles including (1) increasing from 0 to 30 kV/cm, (2) decreasing from 30 kV/cm to 0, (3) from 0 to −30 kV/cm by switching the polarity of field, (4) from −30 kV/cm to 0, and (5) increasing from 0 to 30 kV/cm. The data were collected after two cycles. To get a comprehensive understanding about the effect of dc field on the dielectric properties of (Ba,Sr)TiO_3 glass-ceramics, *C–V* properties were measured at three different temperatures: −10 °C, the Curie temperature (T_c) and 60 °C (around T_c).

3. Results and discussion

The effect of glass content on the sintered (Ba,Sr)TiO_3 glass-ceramics is correlated with their densification, grain growth behavior and dielectric properties. Table 1 shows the composition, sintered temperature, relative density and porosity of all samples. The density of the samples is above 95% of the theoretical value. The relative density increases initially with the increasing of glass content, and then decreases for the glass content beyond 10 mol%.

Table 1
The composition, sintering temperature, relative density and porosity of all samples

Sample	Glass content (mol%)	Sintering temperature (°C)	ρ_{rel} (%)	Porosity (%)
BST0	0	1340	96.5	3.5
BST1	2	1150	98.7	1.3
BST2	5	1150	97.8	2.2
BST3	10	1150	97.9	2.1
BST4	20	1150	97.1	2.9
BST5	30	1150	95.3	4.7

The XRD patterns for xerogels of BST4 calcined at different temperatures are shown in Fig. 2a. At 600 °C the (Ba,Sr)TiO_3 perovskite phase starts to crystallize, and the amount increases with the increasing of temperature. Minor trace of (Ba,Sr)CO_3 phase is detected at 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 observed from the XRD patterns. The other samples have similar patterns with BST4.

Moreover, with the increasing of glass content, a clear shift of the (2 1 0) diffraction peaks to higher initially and then to lower 2θ values can be seen in Fig. 2b. It could be explained that the Ba^{2+} ions enter the BaO–SiO_2–B_2O_3 glass when the glass content is small, or enter the BST perovskite lattice when the glass content is above 10 mol%. Thus, the Ba:Sr ratio in the BST phase changes with different glass content. As can also be seen in the T_c shift discussed in the following.

Fig. 3 shows the effect of glass dopant on the microstructure of the (Ba,Sr)TiO_3 glass-ceramics. No abnormal grain growth is observed. The grain size of the samples increases

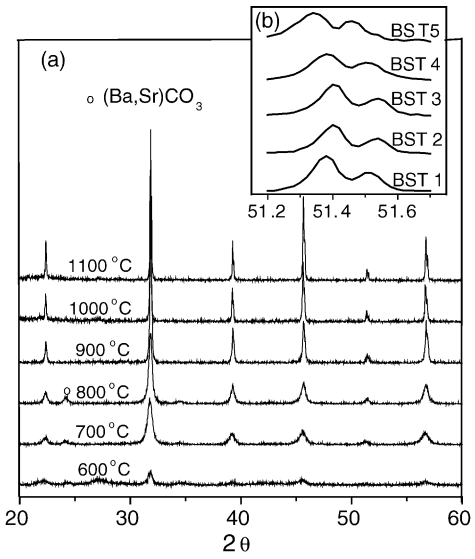

Fig. 2. XRD patterns of BST4 xerogels calcined at different temperatures.

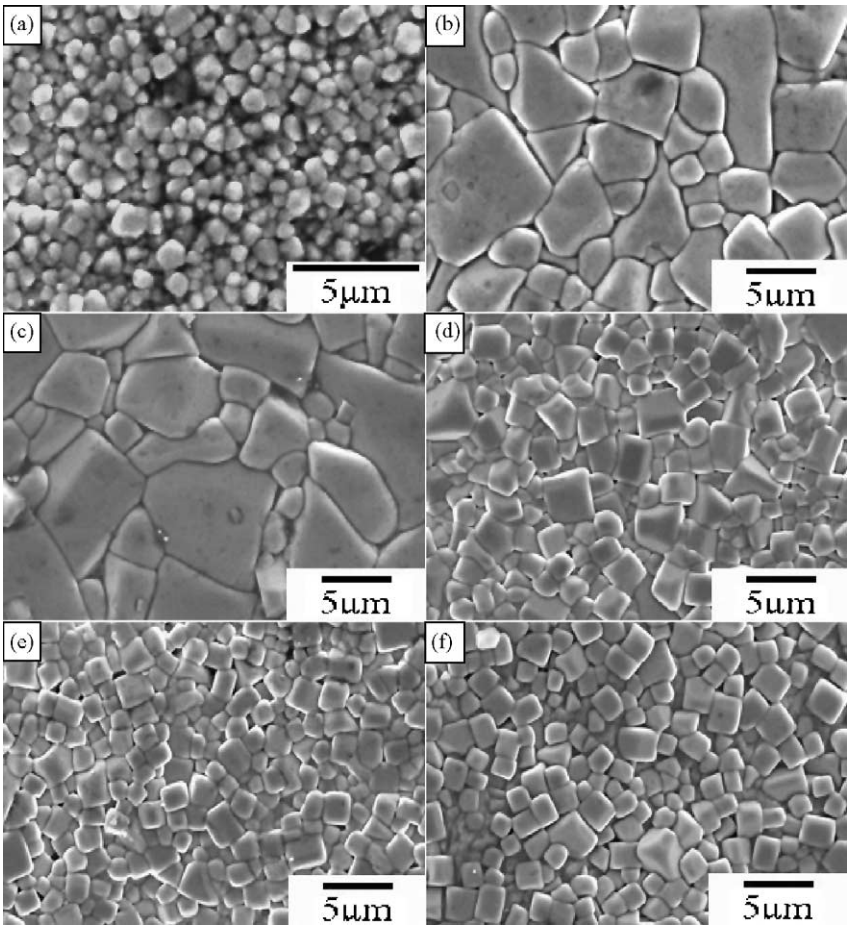

Fig. 3. SEM micrograph of BST samples: (a) BST0, 1340 °C (b) BST1, 1150 °C (c) BST2, 1150 °C (d) BST3, 1150 °C (e) BST4, 1150 °C and (f) BST5, 1150 °C.

initially and then decreases slightly for the glass content beyond 10 mol%. This indicates that adding 2–5 mol% glass can greatly improve sintering property of BST ceramic. A glass content more than 10 mol% on the contrary restrains the growing of the grains, this being interpreted that the glass phase present at the grain boundaries hinders the ion diffusion and inhibits the grain growth. The SEM images show more pores in BST4 and BST5, which is consistent with the measurement data of relative density and porosity.

Temperature dependence of dielectric properties of the specimens is denoted in Fig. 4. The dielectric constant (ε) decreases and its temperature spectrum broadens with increasing glass content, due to the doping of low-ε glass. However, the values for the maximum dielectric constant (ε_{max}) of BST1 and BST2 are larger than that of BST0. The density measurements and SEM show that BST1 and BST2 have larger grain size and lower density of pores than BST0. Thus, the samples with a glass content of 2 or 5 mol% have larger ε_{max} than BST0.

A slight shift of T_c for different samples can also be observed from these curves. It could be interpreted in term of the change of the Ba:Sr ratio, as discussed above. Decreasing the Sr^{2+} concentration in the BST structure sys-

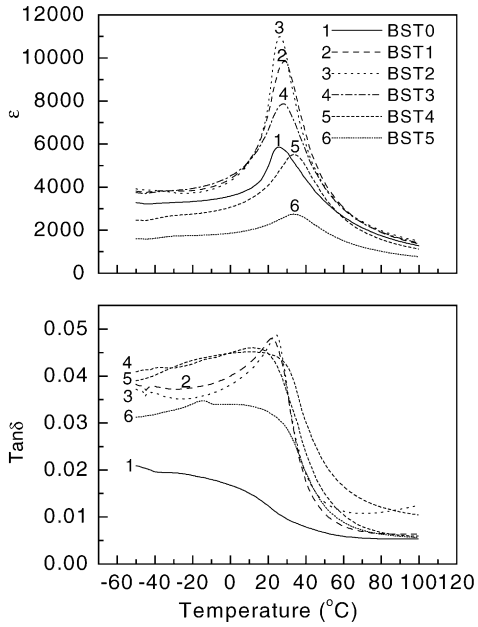

Fig. 4. Temperature dependence of the dielectric constant and dielectric loss for samples.

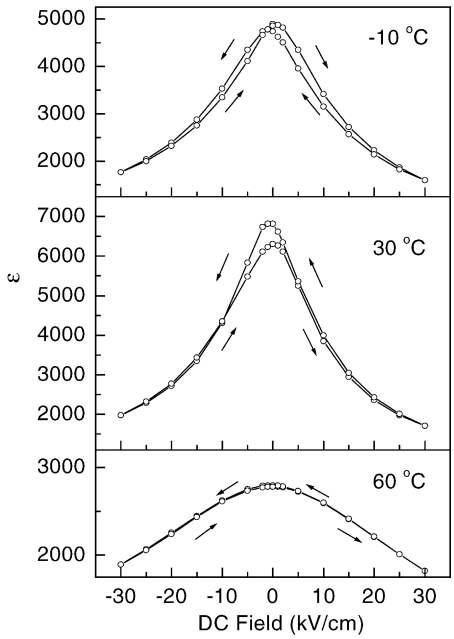

Fig. 5. Direct field dependence of the dielectric constant for sample BST3 at different temperatures.

tematically raises the T_c at a rate of 2.3 K/mol% [8,9]. The T_c for sample BST1 and BST5 are 25 and 33 °C, respectively. That means a maximum change of 3.5 mol% for Ba:Sr ratio.

The dc field dependence of ε at different temperatures for sample BST3 is shown in Fig. 5. Applying dc field, especially in the neighborhood of T_c, reduces the dielectric constant. At −10 °C, the dc field dependence of ε shows a typical "butterfly" loops behavior corresponding to its ferroelectric structure. While at 60 °C (above T_c), the hysteretic behavior of ε with the variation of dc electric field is not obvious, corresponding to its paraelectric structure. The tunability (k) was calculated by using the expression:

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

where $\varepsilon(0)$ and $\varepsilon(E)$ represent the dielectric constant at zero and a certain E field, respectively. For BST3, k exhibits a value of ∼66% at −10 °C, ∼75% at 30 °C (T_c), ∼35% at 60 °C. The dielectric loss exhibits a value of ∼0.04 at −10 °C, ∼0.05 at 30 °C and ∼0.006 at 60 °C. The dielectric loss is usually lower in the paraelectric state than in the ferroelectric state, owing to the disappearance of domain. The influence of dc field on the dielectric loss is much less than that on the dielectric constant. The tunability for (Ba,Sr)TiO_3 glass-ceramics with different glass content is shown in Fig. 6. The dielectric tunability decreases with increasing of glass content. The samples doped a glass content from 2 to 10 mol% behave the largest tunability than BST0. It could be explained that the grain size and the internal stress among grains affects the dielectric properties. The larger grains have the smaller stress [10,11]. Therefore, sample BST2 and BST3 has the best tunable characteristics. Conclusion The BaO–SiO_2–B_2O_3 glass-doped (Ba,Sr)TiO_3 ceramic have been characterized. The results demonstrated that adding BaO–SiO_2–B_2O_3 glass to BST promoted sintering at low temperature by the formation of liquid phase with a low melting point. And there is a slight change of the Ba:Sr ratio in the BST structure according to different glass content. The dielectric constant decreases and its temperature spectrum broadens with increasing glass content. When applying a dc field, the dielectric constant reduces strongly, especially in the neighborhood of T_c. The tunability of the samples is affected by the glass content and the grain size.

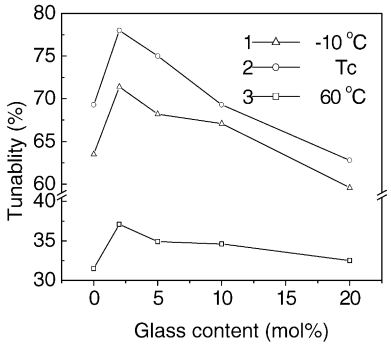

Fig. 6. Tunability for different samples at −10 °C, T_c and 60 °C.

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References

[1] L.C. Sengupta, S. Sengupta, Novel ferroelectric materials for phased array antennas, IEEE Trans. Ultrason. Ferroelectr. Frequency Control 44 (1997) 792–797.
[2] Y. Sakabe, Recent process on multiplayer ceramic capacitors, MRS Int. Meet. Adv. Mater. 10 (1989) 119–129.
[3] B.S. Chiou, K.C. Liu, J.G. Duh, M.C. Chung, Development of temperature-stable thick-film dielectrics: III. Role of glass on the microstructure evolution of a thick-film dielectrics, IEEE Trans. Comp. Hybrid. Manufact. Technol. 14 (1991) 645–649.
[4] J.W. Liou, B.S. Chiou, Dielectric characteristics of doped $Ba_{1-x}Sr_xTiO_3$ at paraelectric state, Mater. Chem. Phys. 51 (1997) 59–63.
[5] I. Burn, Flux-sintered $BaTiO_3$ dielectrics, J. Mater. Sci. 17 (1982) 1398–1408.
[6] Y. Kuromitsu, S.F. Wang, S. Yoshikawa, R.E. Newnham, Interaction between barium and binary glasses, J. Am. Ceram. Soc. 77 (1994) 493–498.

[7] J.M. Wu, H.L. Huang, Microwave properties of zinc, barium and lead borosilicate glasses, J. Non-Cryst. Solids 260 (1999) 116–124.
[8] G.A. Smolenskii, K.I. Rozgachev, Dielectric properties of solid solutions in the system of barium titanate–strontium titanate, Zh. Tekh. Fiz. 24 (1954) 1751–1760.
[9] B. Jaffe, W.R. Cook, H. Jaffe, Piezoelectric Ceramics, Academic Press, London, 1971.
[10] J.W. Zhai, X. Yao, L.Y. Zhang, H. Chen, Direct-current field dependence of dielectric properties in B_2O_3–SiO_2 glass doped $Ba_{0.6}Sr_{0.4}TiO_3$ ceramics, J. Mater. Sci. 37 (2002) 3739–3745.
[11] X.F. Liang, W.B. Wu, Z.Y. Meng, Dielectric and tunable characteristics of barium strontium titanate modified with Al_2O_3 addition, Mater. Sci. Eng. B99 (2003) 366–369.