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# Preparation and dielectric properties of barium strontium titanate glass-ceramics sintered from sol–gel-derived powders

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**Abstract**

Homogeneous barium strontium titanate (BST) glass-ceramic has been successfully prepared by sol–gel process. Experimental results showed that perovskite barium strontium titanate phase formed at 700 °C. Much smaller sized BST grains are obtained and the grain boundaries are not distinct in the sintered glass-ceramic systems. The grain grown with the sintering temperature increased. The glass-ceramic samples were sintered at lower temperatures compared to the conventional barium strontium titanate ceramic. The dielectric permittivity of BST glass-ceramic samples generally decreased as the amounts of Zn–B–Si–O glass added. The dielectric permittivity of BST glass-ceramic samples generally increased and dielectric dissipation of BST glass-ceramic samples decreased as the sintering temperature increased. With the decreasing of grain size, the dielectric peaks of BST glass-ceramic samples become lower and broader.


*Keywords:* A. Sol–gel process; C. Dielectric properties; D. Glass-ceramics; Barium strontium titanate

## 1. Introduction

Ferroelectric barium strontium titanate (BST) ceramics have shown tunable dielectric properties and lower dielectric losses at room temperature and microwave frequencies, which makes them attractive for applications in frequency agile microwave devices [1,2]. Pure BST ceramic has to be sintered at 1350 °C [3,4], and therefore only platinum or refractory metals can be used as inner conductors. These materials are expensive, their electrical performance is poor, and the cost-effective fabrication of high-quality components is difficult. One method of decreasing the sintering temperature is to add sintering aids that have low melting temperatures and create liquid phases below the sintering temperature [5,6]. The liquid phases promote densification and at low temperatures, but these phases generally degrade electrical properties. The Zn–B–Si–O glass is a good liquid phase sintering aid and exhibits low dielectric loss in microwave region [7].

Recently, we reported works on fine-grained ferroelectric glass-ceramics prepared by annealing the gel bulks derived from the sol–gel method without going through the melting and quenching procedure [8]. This technique provides a new approach to mixing ferroelectric phase and glass phase homogeneously. In this paper, we report our experimental results and studies on the structural features and dielectric properties of barium strontium titanate-based glass-ceramic prepared by sintered from sol–gel-derived powders.

## 2. Experimental procedure

### 2.1. Preparation of barium strontium titanate glass-ceramics powders

The precursors used for preparing Ba–Sr–Ti–Zn–B–Si–O gels were barium nitrate ($Ba(NO_3)_2$), strontium nitrate ($Sr(NO_3)_2$), tetra-*n*-butyl titanate ($C_{16}H_{36}O_4Ti$), zinc nitrate ($Zn(NO_3)_2$), ethyl silicate ($Si(OCH_2CH_3)_4$), tripropyl borate ($B(OCH_2CH_2CH_3)_3$) and citric acid. The atomic ratio of Ba:Sr:Ti/0.60:0.40:1.0 is used. For composition with Zn–B–Si–O glass additive (abbreviated as BSTZ1-sg and BSTZ2-sg), their atomic ratios were BST:Zn–B–Si–O = 90:10 (BSTZ1-sg) and 80:20 (BSTZ2-sg). The barium nitrate and strontium nitrate powders were at first dissolved in appropriate amounts of $H_2O$, citrate acid stirred at 90 °C until the solution become transparent and cooled it down to

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room temperature. The tetra-*n*-butyl titanate solution was added in an appropriate amount of citric acid solution by stirring at 70 °C. After the above solution turned clear, the (BST) solution was prepared by mixing titanium solution and barium and strontium solution stoichiometrically. The Zn–B–Si–O glass solution was obtained by mixing zinc acetate ($Zn(CH_3COO)_2$), ethyl silicate ($Si(OCH_2CH_3)_4$), and tripropyl borate ($B(OCH_2CH_2CH_3)_3$) in butyl alcohol by stirring at 50 °C. The Ba–Sr–Ti–Zn–B–Si–O solution was fabricated by mixing the BST solution and the Zn–B–Si–O glass solution stoichiometrically. The resulting Ba–Sr–Ti–Zn–B–Si–O solution formed transparent sols at 60 °C. The gels were formed at 90 °C. Thermal decomposition of the gels was conducted at a heating rate of 1 °C min$^{-1}$ in static air, at 750 °C, in an $Al_2O_3$ boat, and cooled it to room temperature. Small BST crystallites were formed in these firing processes. The fired gels were then crushed and ground by ball mill with ethanol for 24 h to obtain fine glass-ceramic powders. The fine glass-ceramic powders were pressed into disc-shaped pellets with a diameter of 10 mm. The pellets were subsequently sintered in air for 2 h at various temperatures. The surfaces of these glass-ceramic and ceramic samples were polished before the Ag paste electrodes were formed at 600 °C.

### 2.2. Characterization

A differential thermal analysis (DTA/TG) (Model NETZSCH STA449C Germany) was performed for the BST glass-ceramic gels to investigate their thermal decomposition behavior. Powder X-ray diffraction (XRD) measurements were carried out to examine the crystallization and structural development of BST glass-ceramic powders. An X-ray powder diffractometer (Model BRUKER Advanced Bruker Axs Co., Germany) was used with Cu Kα radiation at 40 kV and 40 mA and scan rates of 4° min$^{-1}$ from 20 to 60° ($2\theta$). Scanning electron micrograph (Model JEOL-5510LV, Japan) was used to examine crystallite size and morphology of BST glass-ceramic samples. Dielectric properties of the glass-ceramic samples were characterized using a programmed HP4284 LCR meter. All the electrical measurements were performed at a relative humidity of about 60%.

## 3. Results and discussion

### 3.1. Thermal analysis and XRD measurement of BST glass-ceramic powders

The thermal analysis results of the BST glass-ceramic gel with a heating rate of 10 °C min$^{-1}$ are shown in Fig. 1. In the DTA/TGA curve, weight loss at a temperature below 600 °C is attributed to the evaporation of the solvent and the decomposition of organic complex. Another weight loss takes place at temperature range 600–900 °C. The X-ray diffraction patterns for BST glass-ceramic samples annealed

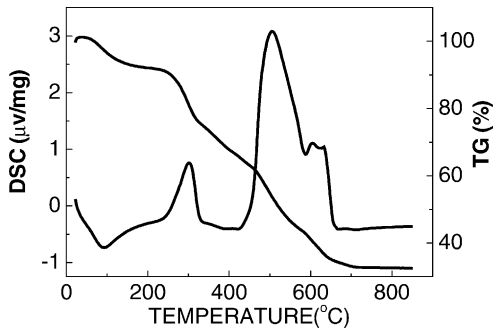


Fig. 1. DSC and TG curves of BST glass-ceramic gel with a heating rate of 10 °C min$^{-1}$.

in air for 2 h at different temperatures are shown in Fig. 2. The X-ray results show that amorphous solid is formed at 600 °C, and the $Ba_{1-x}Sr_xTiO_3$ phase is formed at 700 °C. The $Ba_{1-x}Sr_xTiO_3$ phase at 700 °C is in cubic structure, and there is no existence of a secondary phase. The X-ray diffraction peak of BST glass-ceramic powders become sharp with annealing temperature increasing. The synthetic temperature of $Ba_{1-x}Sr_xTiO_3$ phase was 300 °C lower than that of the conventional solid reaction method [1]. The thermal analysis and the X-ray diffraction results show that thermal decomposition proceeded in three stages: solvents removing, organic complex decomposing, and $Ba_{1-x}Sr_xTiO_3$ phase forming. A further increase in the sintering temperature promotes the formation of BST, but no new chemical reactions take place.

### 3.2. Microstructure of BST glass-ceramic samples

Fig. 3 gives the SEM pictures of BST glass-ceramic samples sintered in air for 2 h at different temperatures. Much smaller sized BST grains are obtained in the sintered glass-ceramic systems. The BSTZ1-sg sample can be sintered well at 1050 and 1150 °C. The average grain size after sintering at 1050 °C is about 0.8–1 μm. The average grain size after sintering at 1150 °C is about 2–3 μm. The grain boundaries are not distinct in Fig. 3a and b. The BSTZ2-sg

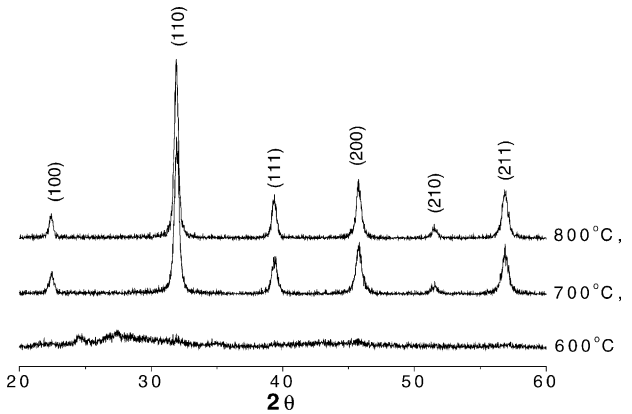


Fig. 2. XRD pattern for BST glass-ceramic powder calcining at different temperature.

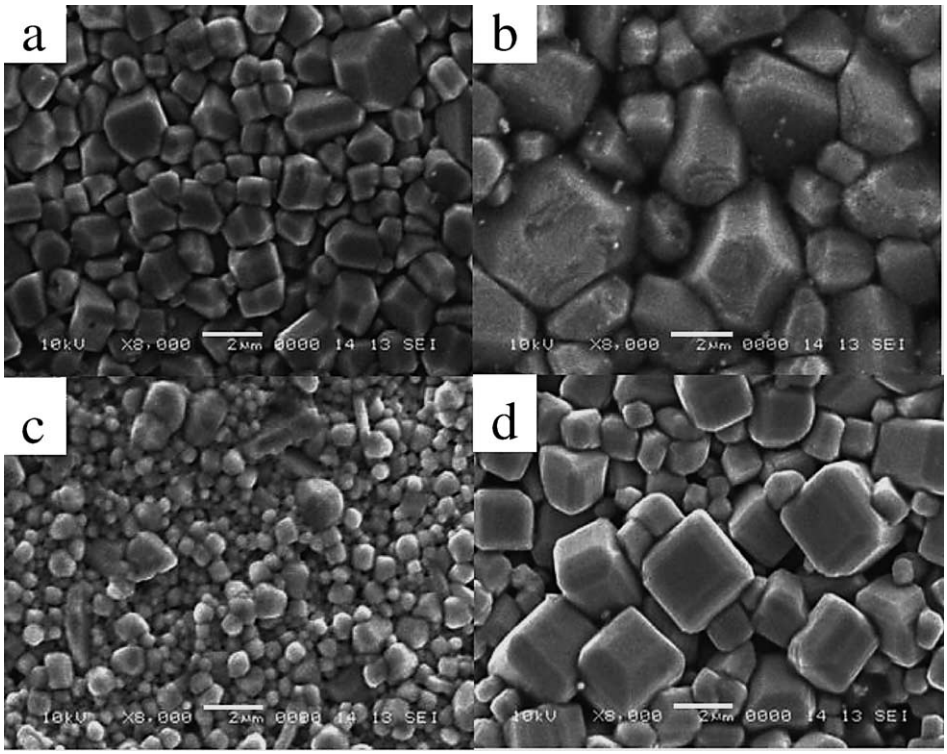


Fig. 3. SEM image of the BST glass-ceramic samples sintered at various temperatures in air for 2 h: (a) BSTZ1-sg 1050 °C; (b) BSTZ1-sg 1150 °C; (c) BSTZ2-sg 1000 °C; (d) BSTZ2-sg 1100 °C.

sample can be sintered well at 1000 and 1100 °C. The average grain size after sintering at 1000 °C is about 0.6 μm. The average grain size after sintering at 1100 °C is about 1–2 μm. The grain boundaries are not distinct in Fig. 3. The grain grown with the sintering temperature increased. No ferroelectric domains can be seen from the small BST grains in the glass-ceramic samples. Because the glass phases and the BST phase are homogeneously mixed, the glass-ceramic samples can be sintered well at much lower temperature than the pure BST ceramic.

### 3.3. Dielectric properties of BST glass-ceramic samples

The temperature dependence of the dielectric properties for the glass-ceramic samples is presented in Figs. 4 and 5.

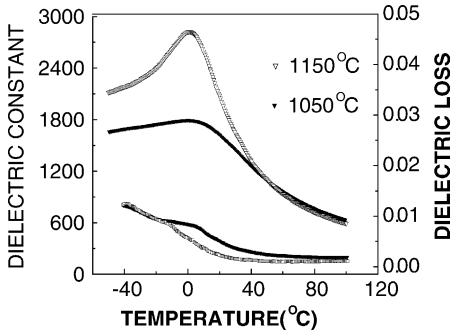


Fig. 4. Temperature–dielectric curve of BST glass-ceramic BSTZ1-sg sample sintered at different temperatures.

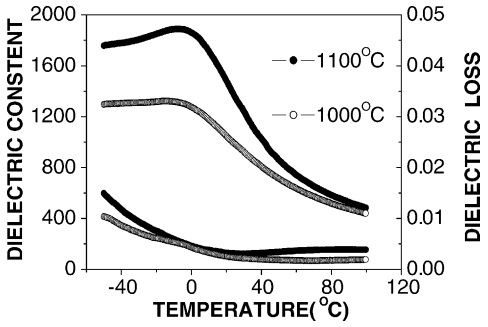


Fig. 5. Temperature–dielectric curve of BST glass-ceramic BSTZ2-sg sample sintered at different temperatures.

The dielectric permittivity of BST glass-ceramic samples generally decreased as the amounts of Zn–B–Si–O glass additive. The dielectric permittivity of BST glass-ceramic samples generally increased and dielectric loss of BST glass-ceramic samples decreased as the sintering temperature increased. The grain-size effect in the glass-ceramic samples can be observed apparently. With the decrease of grain size, the dielectric peaks of BST glass-ceramic samples become lower and broader.

## 4. Conclusions

Homogeneous barium strontium titanate glass-ceramic has been successfully prepared by sol–gel process. The

barium strontium titanate phase formed at 700 °C. Much smaller sized BST grains are obtained in the sintered glass-ceramic systems. The glass-ceramic samples were sintered at lower temperatures compared to the conventional barium strontium titanate ceramic. The dielectric permittivity of BST glass-ceramic samples generally decreased as the amounts of Zn–B–Si–O glass increased. The dielectric permittivity of BST glass-ceramic samples generally increased and dielectric loss of BST glass-ceramic samples decreased as the sintering temperature increased. With the decreasing of grain size, the dielectric peaks of BST glass-ceramic samples become lower and broader.

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