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SiO_2/Al_2O_3 ratio dependence of microstructures and dielectric properties in barium strontium titanate glass ceramics

Xiaozhen Song, Yong Zhang *, Yongzhou Chen, Dongliang Yang, Ziqin Shen

Beijing Key Laboratory of Fine Ceramics, State Key Laboratory of New Ceramics and Fine Processing, Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, PR China

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ABSTRACT

(Ba, Sr)TiO_3-Al_2O_3-SiO_2 glass ceramic system with various SiO_2/Al_2O_3 ratios was investigated by X-ray diffractometry (XRD), scanning electron microscopy (SEM), dielectric spectroscopy and impedance spectroscopy. The XRD results demonstrated that the proper SiO_2/Al_2O_3 ratio could promote the crystallization of the major crystalline phase from the glass matrix. The dielectric property investigations showed that the dielectric constant passes through a maximum value while the dielectric breakdown strength has a minimum value with increasing SiO_2/Al_2O_3 ratio. Meanwhile, the complex impedance analyses suggest the resistance of the glass-crystal interface rapidly decreases and the capacitance of the crystal slightly decreases with the increase of SiO_2/Al_2O_3 ratio. The relaxation mechanisms of the (Ba, Sr)TiO_3 glass ceramics changed from localized relaxation to long range conductivity as the SiO_2/Al_2O_3 ratio was increased from 1.43 to 1.83. The variations in the dielectric response and the activation energy of the glass-crystal interface in the (Ba, Sr)TiO_3 glass ceramics with the ratio of 2.40 could be attributed to the crystallization of fresnoite phase.

1. Introduction

Ferroelectric glass ceramics have attracted much interest in recent years. Especially, barium strontium titanate (BST) based glass ceramics containing ferroelectric crystallites of high permittivity homogenously embedded in glass matrix make these materials to be the strong candidates for the applications in high energy density capacitors [1–4]. In comparison with conventional ceramic dielectrics prepared by solid-state mixing and firing, glass ceramics prepared using melting and subsequent controlled crystallization technology can achieve low porosity levels and hence high breakdown voltages [5]. Furthermore, controlled crystallization can yield submicrometer or nanometer grains which may exhibit lower dielectric losses and lower electric-field dependence of permittivity [6].

Previous research on synthesis of barium titanate based glass-ceramic materials by melting and subsequent controlled crystallization technology has shown some problems [7]. It was very difficult to get transparent original glass with low content of network formers in the investigated compositions due to rapid devitrification especially for large-sized glass articles production [1,8]. However, for the glass composition with higher silica content, the crystallization of the perovskite phase would be impeded through the formation of secondary crystalline phases [8,9]. Furthermore, the ferroelectric and dielectric properties of glass-ceramics usually are diluted by the network former (e.g., SiO_2, B_2O_3, etc.) [10] and glass network intermediate (e.g., Al_2O_3) [11,12].

In BaO-SrO-TiO_2-Al_2O_3-SiO_2 glass-ceramic system, Al_2O_3 and SiO_2 are both important components. Herczog [1] has previously reported that the crystallization of the glass ceramics leads to two or more phases in a diffusion-controlled process where $BaAl_2Si_2O_8$ could act as a grain-growth inhibitor of the major phase (Ba, Sr)TiO_3. Therefore, an exact control of crystalline size is possible. In addition, in tetrahedral coordination, Al_2O_3 replaces SiO_2 in the glass network, but at larger concentrations acts as a network modifier. For this dual role, Al_2O_3 may enhance or inhibit crystallization [11–13]. However, the effect of SiO_2/Al_2O_3 ratio on the microstructure of barium strontium titanate glass-ceramics has not been elaborated in detail.

The study of impedance spectroscopy in multicomponent glass ceramics is very important since the associated physical properties are dependent on electrical responses of glass, crystal and glass-crystal interface in the system. Therefore, it becomes important to measure the impedance spectra of the BST ferroelectric glass-ceramics. Thus, in the present work, BST glass ceramics were prepared by melting and controlled crystallization techniques, and the microstructures, the temperature dependence of dielectric constant and dielectric loss, and the dielectric breakdown strength

* Corresponding author.
E-mail address: yzhang@tsinghua.edu.cn (Y. Zhang).

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(BDS) were examined as a function of SiO_2/Al_2O_3 ratio. Moreover, impedance spectroscopy of the BST glass ceramics with various SiO_2/Al_2O_3 ratios has been investigated.

2. Experimental procedure

Parent glass compositions in this study were represented by a chemical formula, $28.8BaO\text{-}7.2SrO\text{-}28TiO_2-2BaF_2\ \text{-}xSiO_2\text{-}yAl_2O_3$ (x=20, 21, 22 and 24 mol%). The sum of Al_2O_3 and SiO_2 concentration (x+y) was kept at 34 mol%. Glass samples were prepared from well mixed powders of $BaCO_3$, $SrCO_3$, TiO_2, BaF_2, SiO_2, and Al_2O_3 (≥99.0% purity). All raw materials were prepared by ball-milling for 6 h in ethanol media using zirconia balls in polyethylene jars. After drying, the mixtures were melted in a platinum crucible at 1550 °C for 4 h. The melt was poured into a preheated Φ30 mm × 20 mm copper mould. Then the casted glass was immediately annealed at 650 °C for 6 h to relieve residual stresses. The as-annealed glass was cut to obtain a thin slab with the thickness of 1 mm. Finally these samples with various SiO_2/Al_2O_3 ratios were heated in air at 1050 °C for 4 h to convert the glasses into glass ceramics. The crystallized samples were painted with silver paste and then fired at 550 °C for 20 min to prepare electrodes for dielectric measurements.

X-ray diffraction (XRD, Model-D8 Advance, Bruker AXS, Karlsruhe, Germany) and field emission scanning electron microscopy (SEM, Model Quanta 200 FEG, FEI, Eindhoven, the Netherlands) were used to investigate the phase evolution and microstructure of the crystallized samples. Polished specimens were etched with 0.5 wt% HF aqueous solution. The morphology of the (Ba, Sr)TiO_3 and $BaAl_2Si_2O_8$ crystalline phases were exposed because the glassy matrix dissolved in HF solution. The dielectric temperature curve was measured in a temperature range of −50–150 °C using a HP 4284 LCR meter at various frequencies and an ac voltage of 1 V. The disk-shaped specimens with the thickness of 1 mm were used to measure the dc breakdown strength with a high-voltage source HF5013K (Huiyou Electronics Co. Ltd., Changzhou, China) using a voltage ramp rate of about 1 kV/s at room temperature. All samples were immersed in silicon oil to prevent flashover and corona discharge. The measured values of dielectric breakdown strength were ranked and the probability of failure P_i was calculated using the following formula:

$$P_i = i/(n+1) \tag{1}$$

Where i is the ith sample to be ranked and n is the sum of specimens tested. A statistical distribution commonly used to represent the strength of brittle materials is proposed by Weibull [14]. And the breakdown strength of the samples with various SiO_2/Al_2O_3 ratios was evaluated by the two-parameter Weibull analysis [15–17],

$$P_i = 1 - \exp[-(E_i/E_b)^{\beta}] \tag{2}$$

where E_i is the measured breakdown strength for the i th specimen in the experiments, E_b is the characteristic breakdown strength, β is the shape parameter. The impedance data were carried out using the same LCR meter over frequencies from 20 Hz to 1 MHz in a temperature range of 350–520 °C.

3. Results and discussion

3.1. Microstructural evolution

The XRD patterns of the BST glass-ceramics with various SiO_2/Al_2O_3 ratios were shown in Fig. 1. It was found that the major

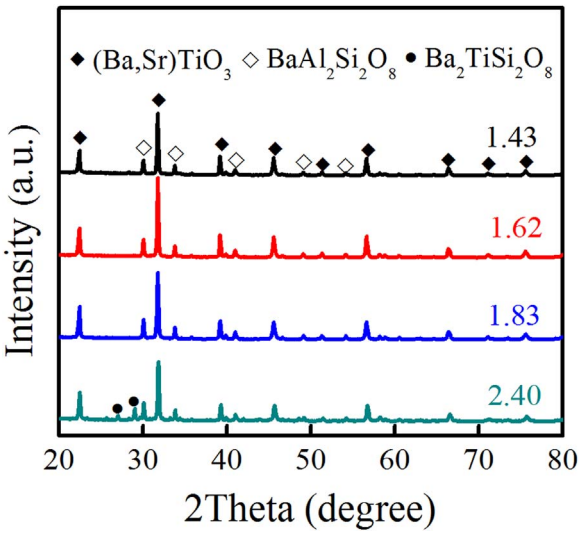

Fig. 1. X-ray diffraction patterns for the BST glass ceramics with various SiO_2/Al_2O_3 ratios.

crystalline phase, (Ba, Sr)TiO_3 (BST) perovskite, and the minor phase, $BaAl_2Si_2O_8$ feldspar, were formed over the entire investigated range of SiO_2/Al_2O_3 ratio. However, the XRD pattern of the sample with the SiO_2/Al_2O_3 ratio of 2.40 reveals that a minor additional phase was found. Moreover, the relative intensity of the major diffraction peaks of BST crystal does not increase gradually with increasing SiO_2/Al_2O_3 ratio. When the SiO_2/Al_2O_3 ratio was increased from 1.43 to 1.62, the relative intensity of BST diffractions increased, while it was weakened when the SiO_2/Al_2O_3 ratio was increased to 2.40, indicating that the proper SiO_2/Al_2O_3 ratio could promote the crystallization of the major crystalline phase from the glass matrix. And a secondary minor phase (fresnoite, $Ba_2TiSi_2O_8$) appears when the SiO_2/Al_2O_3 ratio was increased to 2.40.

Fig. 2 illustrates the microstructures of the BST glass ceramics with various SiO_2/Al_2O_3 ratios. It could be seen from Fig. 2 that the specimens with various SiO_2/Al_2O_3 ratios showed distinct bulk crystallization characteristics. The residual glass phase was removed from the surface, while the crystalline phases in the specimens were preserved. And a typical homogeneous structure was observed and the grains were surrounded by glassy matrix. As shown in Fig. 2, the studied glass ceramics go through sufficient crystallization in air at 1050 °C for 4 h. In addition, these samples exhibited almost unchanged morphology of the crystalline phases. However, the variation of the SiO_2/Al_2O_3 ratio had an obvious effect on the volume fraction of the residual glass in the BST glass ceramics. Moreover, the crystalline phases decrease slightly and the volume fraction of the residual glass phase increases obviously with increasing SiO_2/Al_2O_3 ratio. This change could be attributed to the effect of SiO_2/Al_2O_3 ratio. When the SiO_2/Al_2O_3 ratio is up to 2.40, SiO_2 content is relatively high, at the same time, Al_2O_3 could serve as a network former, which would generate a stable random network in the glass matrix during the crystallization process. With the decrease in the SiO_2/Al_2O_3 ratio, SiO_2 content is relatively low while Al_2O_3 is relatively high. Al_2O_3 switched to act as a network modifier weakening the network and promoting the crystallization. This dual role of Al_2O_3 may be explained in terms of the structural role of Al^{3+} ion. This ion can be four or six coordinated with oxygen giving rising to tetrahedral AlO_4 or octahedral AlO_6 groups. When it is tetrahedrally coordinated, it takes part as a network former. While the coordination number changes to six fold, it works as a network modifier.

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