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Synthesis and dielectric properties of $Ba_2TiSi_2O_8$ glass-ceramics from the sol–gel process

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Abstract The $Ba_2TiSi_2O_8$ glass-ceramics were prepared by sol–gel process using barium acetate, titanium butoxide, tetraethoxyorthosilicate and boric acid as raw materials. Because of the existence of glass and sintering additive, the $Ba_2TiSi_2O_8$ glass-ceramics can be sintered at 880 °C in air. The structure of sintered sample was characterized by means of XRD and SEM. XRD patterns showed that fresnoite $Ba_2TiSi_2O_8$ is the dominant crystalline phase in the sintered samples. SEM images indicated that the shape of $Ba_2TiSi_2O_8$ grains varied with the molar ratio of ([$Ba(Ac)_2$/$Ti(OBu^n)_4$/$Si(OEt)_4$]). With an increase of $Si(OEt)_4$ content, the length/diameter ratio of $Ba_2TiSi_2O_8$ grains decreases. The $Ba_2TiSi_2O_8$ glass-ceramics studied in this work have ε_r in the range of 6–12 (100 MHz) and demonstrate very low dielectric losses ($\tan\delta < 2\times10^{-3}$, 100 MHz). The experimental results suggested that the $Ba_2TiSi_2O_8$ glass-ceramics could be used as dielectric materials for low temperature co-fired ceramics (LTCC) process.

Keywords Dielectric properties · Sol–gel process · $Ba_2TiSi_2O_8$ glass-ceramics

1 Introduction

Since fresnoite $Ba_2TiSi_2O_8$ was found by Alfons et al. in 1965 [1], it received considerable attentions because of its pyroelectric and piezoelectric properties. Scientific researches on $Ba_2TiSi_2O_8$ glass-ceramics were focused on the synthetic methods by which the grain-oriented composites could be prepared [2–6]. Indeed, due to $Ba_2TiSi_2O_8$ has comparably low dielectric constants (about 12) and small thermal expansion coefficient (10^{-6}) [3], $Ba_2TiSi_2O_8$ glass-ceramics are also advantageous for using as dielectrics materials in high frequency. Thus, the main objective of this work was to synthesize the proper $Ba_2TiSi_2O_8$ glass-ceramics that could be used as dielectric materials for LTCC process.

For a long time, glass and glass-ceramics have been prepared by melting a mixture of oxide or carbonates. The main disadvantages of this method are the poor homogeneity of melt and the high processing temperature (>1400 °C) [7, 8]. More recently, the sol–gel technique has been widely used as an alternative method for preparing glass or glass-ceramics [9–12]. Starting from liquid molecular precursor, the sol–gel method offers the advantages of good chemical homogeneity and high purity. Furthermore, due to their large surface area and high intrinsic energy, the sol–gel-derived powders show high sintering ability. These characteristics are beneficial for LTCC dielectrics. Thus, in the present work, $Ba_2TiSi_2O_8$ glass-ceramics was synthesized by sol–gel process using barium acetate, titanium butoxide, tetraethoxyorthosilicate and boric acid as starting precursors. The bulk density, crystal phase, microstructure and dielectric properties of sintered samples were presented and discussed.

2 Experimental procedure

Analytical grade barium acetate, titanium butoxide, tetraethoxyorthosilicate and boric acid were chosen as starting materials. Besides the requirements of the main crystal phase, tetraethoxyorthosilicate was also used as the glass former. Boric acid was served as sintering additive. Anhydrous ethanol and acetic acids were respectively used as solvent

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and chemical additives. The stoichiometric quantities of the main components are in the molar ratio of $Ba(Ac)_2$/Ti$(OBu^n)_4$/$Si(OEt)_4$=5:7:19 (defined as sample A), 5:7:16 (sample B) and 5:8:13 (sample C), respectively. The mol ratio of {H_3BO_3/[$Ba(Ac)_2$+Ti$(OBu^n)_4$+ $Si(OEt)_4$]} is 0.05 in all samples.

2.1 Preparation of samples

The synthesis procedure of the Ba–Ti–Si–B–O gel is demonstrated in Fig. 1. $Si(OEt)_4$ was prehydrolyzed in ethanol and acetic acid for 60 min after addition of water with the molar ration of H_2O/$Si(OEt)_4$=1. Subsequently, the solutions of Ti$(OBu^n)_4$, $Ba(Ac)_2$ and H_3BO_3 were added and mixed with the former solution in turn. Finally, water was added to induce complete precipitation of each alkoxide at 80 °C. Gelation of the solution occurred within 1 days. After dried in air at 105 °C, the gel was crushed into powders with an agate mortar and then was precalcined in air at 800 °C for 2 h to remove the residual organics. To prepare the bulk samples, the precalcined powders were mixed with 3 wt% polyvinyl alcohol and then were pressed uniaxially in stainless steel die under a pressure of 3 MPa for pellet specimens (10 mm in diameter, about 1 mm thick). The green specimens were sintered at 850, 880, 900 and 920 °C for 3 h in air, respectively.

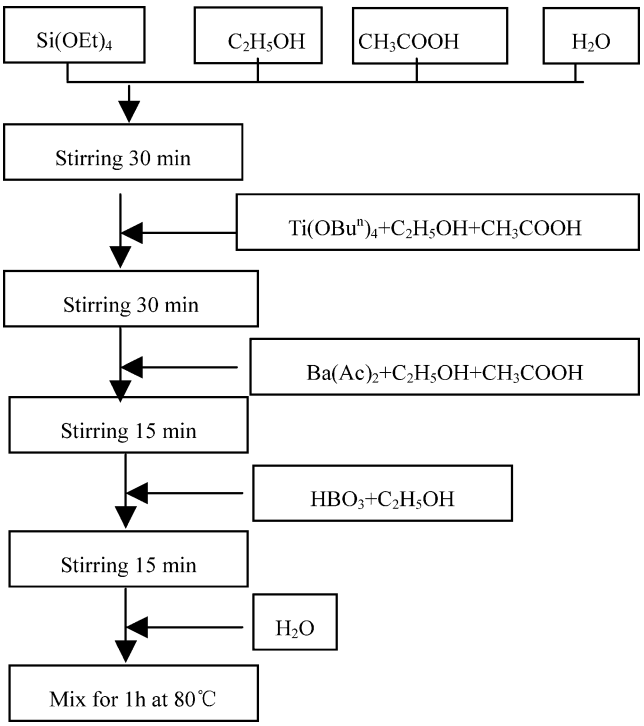

Fig. 1 Flow chart for preparation of Ba–Ti–Si–B–O gel

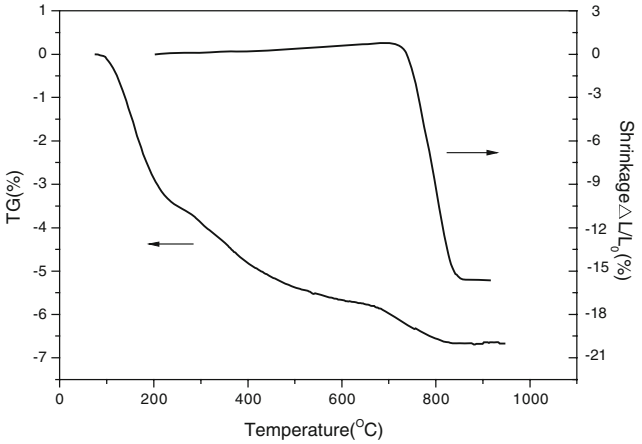

Fig. 2 TG–TMA curves of sample B

2.2 Characterization

Thermogravimetric analysis (TG) was performed using SETARAM TGA92 differential thermal analyzer. The bulk density of sintered specimen was measured by Archimedes' principle. Crystal structure of sintered samples was characterized by XRD method using Cu K_α (λ=1.5418 Å, Rigaku D/MAX-3B Diffractometer, Japan). Microstructure of fractured surface of sintered specimens was observed by Scanning Electron Microscope (JEOL, JSM-6301F, Japan). The variations of dielectric constant and loss tangent with frequency were measured by Agilent E4991A RF impedance material analyzer (Japan).

3 Results and discussion

Figure 2 shows the TGA–TMA curves. A gel powder dried at 105 °C and a sample precalcined at 600 °C were used for TG and TMA measurement, respectively. The result of TG

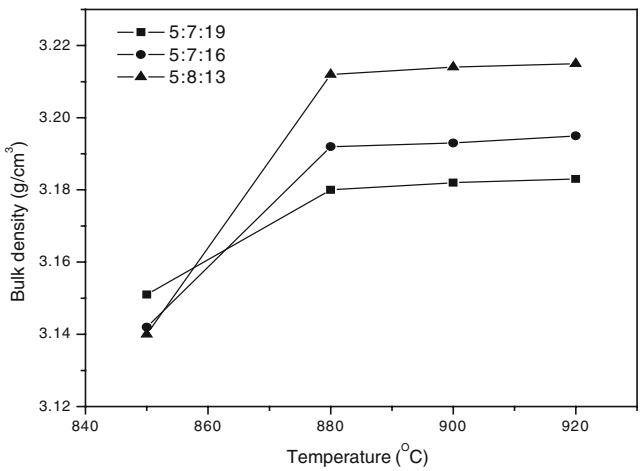

Fig. 3 Bulk density of samples sintered at different temperature

showed that the total weight loss was about 7% and the weight loss had taken place mainly below 820 °C, above which no more significant weight loss occurred. The TMA curve illuminated that the sample had no obvious shrinkage above 860 °C, which means that the green specimens could be sintered at about 860 °C in air.

Figure 3 shows the bulk density of samples sintered at different temperature. It can be seen that there is no obviously change in the bulk density when sintering temperature is above 880 °C. This indicated that the $Ba_2TiSi_2O_8$ glass-ceramics could be sintered at 880 °C. It is also noted that the bulk density increases with the decrease of $Si(OEt)_4$ content. This phenomenon is consistent with the fact that the bulk density of $Ba_2TiSi_2O_8$ is larger than that of remnant glass.

XRD was performed on the heat-treated powder and sintered samples to characterize the crystallization of the sample. Figure 4 shows the typical XRD patterns obtained on the powder precalcined at 600, 800 °C for 2 h and samples sintered at 850, 880 °C for 3 h. It is clearly that the powder precalcined at 600 °C was amorphous crystalline and that precalcined at 800 °C was polycrystalline. The main lines in the latter XRD pattern are attributed to crystalline fresnoite.

The microstructure of sintered samples was carried out using field emission SEM. Here, 1 M HF acid solutions were used to etch the fractured surface of sintered samples. Figure 5(a–b) show the SEM images of etched sample A and C, respectively. It was found that the shape of the $Ba_2TiSi_2O_8$ grains varied with the molar ratio of $Ba(Ac)_2$/$Si(OEt)_4$/$Ti(OBu^n)_4$. With an increase of $Si(OEt)_4$ content, the length/diameter ration of $Ba_2TiSi_2O_8$ grain decreases. This phenomenon may be related to the viscosity of sintered sample. During $Ba_2TiSi_2O_8$ crystallization, the viscosity of sintered sample increases with the increasing of glass content. Among three different samples, the impediment to $Ba_2TiSi_2O_8$ crystal growth is largest in sample A. Thus the

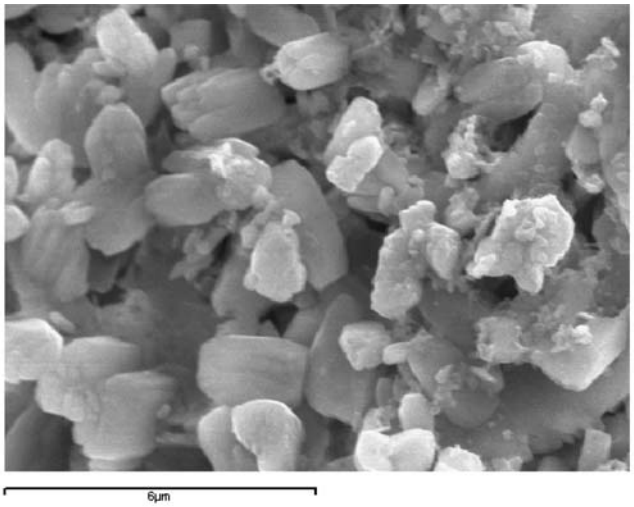

Fig. 5 SEM micrographs of the etched samples for (**a**) sample A; (**b**) sample C

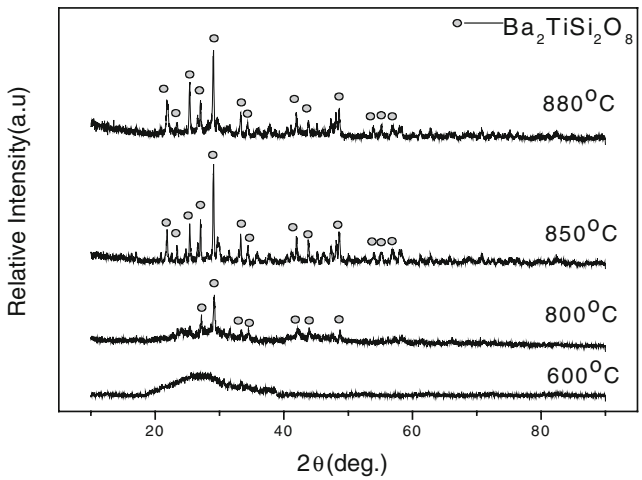

Fig. 4 XRD patters of the presintered gel and sintered sample B

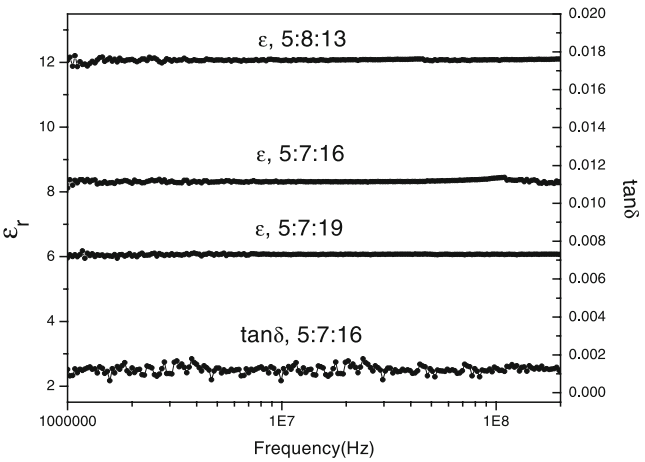

Fig. 6 Frequency dependence of dielectric constants and loss tangent

anisotropy of $Ba_2TiSi_2O_8$ crystal growth may be hindered by the remnant glass in sample A. With the decrease of glass content, the impediment to crystal growth decreased and then the anisotropy of $Ba_2TiSi_2O_8$ crystal growth is shown.

Figure 6 shows the variations of dielectric constant and loss tangent with frequency. In response to the higher dielectric constant of $Ba_2TiSi_2O_8$ (12) relative to that of SiO_2 (4–5), the dielectric constant of the samples decreases with the increase of $Si(OEt)_4$ content in the starting precursors. For example, in sample A, the dielectric constant is 6.1 (100 MHz). However, the dielectric constant of sample B increases to 12 (100 MHz). Moreover, the loss tangents of all samples are below 2×10^{-3} at the range from 1 to 200 MHz. Here, only the loss tangent of sample B is shown.

4 Conclusion

The $Ba_2TiSi_2O_8$ glass-ceramics was synthesized by sol–gel process using barium acetate, titanium butoxide and tetraethoxyorthosilicate as starting precursors. Due to the existence of remnant glass and sintering additive, the $Ba_2TiSi_2O_8$ glass ceramics can be sintered at 880 °C in air. The microstructure of sintered samples showed that the shape of $Ba_2TiSi_2O_8$ grains varied with the molar ratio of $Ba(Ac)_2$/$Ti(OBu^n)_4$/$Si(OEt)_4$. With an increase of $Si(OEt)_4$ content, the length/diameter ratio of $Ba_2TiSi_2O_8$ grains decreases. By varying the molar ratio of $Ba(Ac)_2$/$Ti(OBu^n)_4$/ $Si(OEt)_4$, the dielectric constant of $Ba_2TiSi_2O_8$ glass ceramics could be tunable in the range of 6–12. The low sintering temperature (<900 °C), along with low dielectric constant (6–12) and low loss tangent ($<2\times10^{-3}$), make the $Ba_2TiSi_2O_8$ glass ceramics attractive for using as LTCC dielectrics.

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