Effect of sintering temperature on dielectric properties of barium titanate glass-ceramic composites

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Barium titanate based glass-ceramics with high relative density and high dielectric constant were prepared via melt quenching followed by controlled crystallization. The effects of sintering process on phase composition, microstructure and dielectric properties were studied. The results reveal that cubic $BaTiO_3$ phase is formed in the samples after crystallized at 1200 °C to 1230 °C for 1 hour. The relative density rises up to a relatively high value of 98.6% and almost no pores are found after crystallized at 1230 °C. The dielectric constant of the sample increases with the increasing crystallization temperature and reaches 1030 after crystallized at 1230°C.

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1. Introduction

With extraordinary dielectric properties, barium titanate glass-ceramics are promising for use in power electronics, multilayer ceramic capacitors, ferroelectric material components, and so on [1]. Barium titanate glass-ceramics are composed of barium titanate ceramic phase and glass matrix. This kind of glass-ceramics exhibits the high dielectric constant, the high breakdown strength and thus high energy storage density because of the ceramic phase of high dilectric constant and the pore-free glass matrix [2-4]. Glass-ceramics can achieve excellent dielectric properties by designing the material composition and controlling the sintering process [5].

In the current, the preparation process of glass-ceramics mainly includes integral crystallization, sol-gel and sintering methods [6-7]. Jichun Chen [8] used an internal nucleation approach to study the effect of the Ba/Ti ratio on the microstructure and dielectric properties of barium titanate glass-ceramics. When the ratio of Ba/Ti is 1.48, both the dielectric constant (~440) and the dielectric loss (0.073) reach relatively high values after being heat treated at 1000 °C. However, experimental data are not available when the ratio of Ba/Ti is between 1.23 and 1.39, because the samples cannot be crystallized anymore. Yong Zhang [9] prepared (Ba,Sr)TiO_3(BST) glass-ceramics by sintering method. The results show that the dielectric constant at room temperature reachs about 400 after crystallizated at 1050 °C. Wu et al. [10] used sol-gel approach to investigate the relationships among sintering process, phase microstructure and dielectric properties of BST-based ferroelectric glass-ceramics. The results show that the samples with higher relative density exhibit higher dielectric constant accordingly, when the glass content maintained the same levels.

Currently, the overall performance of glass-ceramics has been improved greatly, however, the dielectric constant is still insufficient for practical application and need to be developed further. In addition, it has high requirements for glass formability when we preparing glass-ceramics through the traditional method, which limits the practical application of many glass ceramics having a high dielectric constant. In this paper, the glass-ceramic samples with higher dielectric constant of barium titanate system were prepared via sintering methods, and the effect of crystallized temperature on properties of barium titanate glass-ceramics was studied. Therefore, we could have a better understanding of the selection of raw materials. However, this preparing process may decrease the compactness of the sample because it destroys the pore-free properties of the glass-ceramics, so the effect of crystallized temperature on porosity was studied. So in this case, better control of the pores and improved dielectric constant are keys for improving the performance of glass-ceramics.

2. Experimental procedures

Barium titanate glass-ceramic were synthesized via melting quenching process. The well-mixed powders of 62wt% $BaCO_3$(A.R.), 22wt% TiO_2(A.R.), 7wt% Al_2O_3(A.R.), 7.5wt% SiO_2(A.R.) and 0.5wt% Ni_2O_3(A.R.) were melted in a platinum crucible at 1480 °C for 2-3h. Then the homogeneous melt was rapidly cast into water to form the glass slags. After washed and dried, the water quenching glass slags were pulverized in a PTFE tank

using ethanol as grinding media for 12h and dried. After sieved through a 200-mesh screen, the obtained glass powders were uniaxially pressed at 4 MPa, which are 2 mm-thick and 20 mm-diameter, and then following cold isostatic pressing. Finally, the samples were sintered. Through the preliminary forecast experiments, the final crystallization temperatures of the glass-ceramics samples were determined at the range of 1200-1230 °C (1200 °C, 1210 °C, 1220 °C, 1230 °C).

X-ray diffraction (XRD; model MSAL-XD2, Micro-Structure Analysis Laboratory, Beijing) was used to analyze phase composition. The field emission scanning electron microscopy (FE-SEM: Hitachi S4800) was used to investigate microstructure. Precision LCR meter (HP-4284A, Agilent Technologies, Inc, USA) was used for measuring the temperature characteristics of the dielectric constant. The ferroelectric tester (RT6000HVA, Radiant Technology, Albuquerque, NM, USA) was used to test the leakage current curves of samples which infiltrated in silicon oil to avoid flashover at room temperature.

3. Results and discussion

The relative density of barium titanate glass-ceramic sa-mples are investigated by Archimedes drainage, and the results are shown in Fig. 1. As the crystallization temperature increases, the relative density increases significantly. This is mainly because the liquid phase in the matrix increases as the crystallization temperature increases, which promotes the grain growth, so the relative density of the samples increases [11,12]. The sample realizes the maximum relative density of 98.6% after sintered at 1230 °C. When the crystallization temperature exceeds 1230 °C, the samples become deformed due to the formation of liquid phase in the samples.

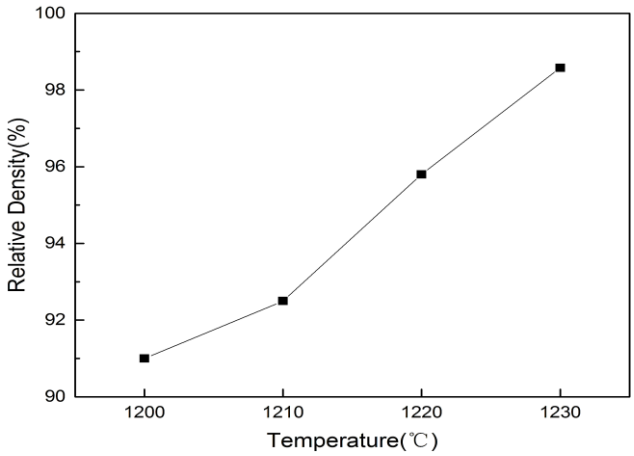

Fig. 1. The variation curve of relative density of samples with crystallization temperature

Fig. 2 shows SEM images of the crystallized samples at different temperatures, it indicates that the variation of crystallization temperature has no significant influence on the XRD patterns of the samples, barium titanate phase with perovskite structure has been formed under different treatment processes. In addition, from the perspective of diffraction intensity, the diffraction peak intensity of barium titanate phase increases with the increase of crystallization temperature, which indicates that the content of precipitated crystal phase increases with the increase of crystallization temperature, and the crystallization of material is the most thorough at 1230 °C. Fig. 3 shows the microstructure of the samples after sintered at 1200 °C, 1210 °C, 1220 °C and 1230 °C. Pores can be observed in the samples sintered at relatively lower temperature in Fig. 3(a), and decrease with the increase of crystallization temperature in Fig. 3(b) and (c). In particular, after sintered at 1230 °C, the samples have almost no pores, as shown in Fig. 3(d).

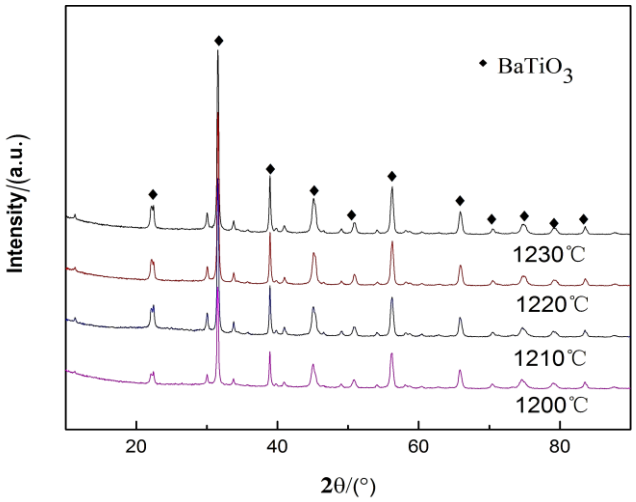

Fig. 2. XRD patterns of samples crystallized at different Temperatures

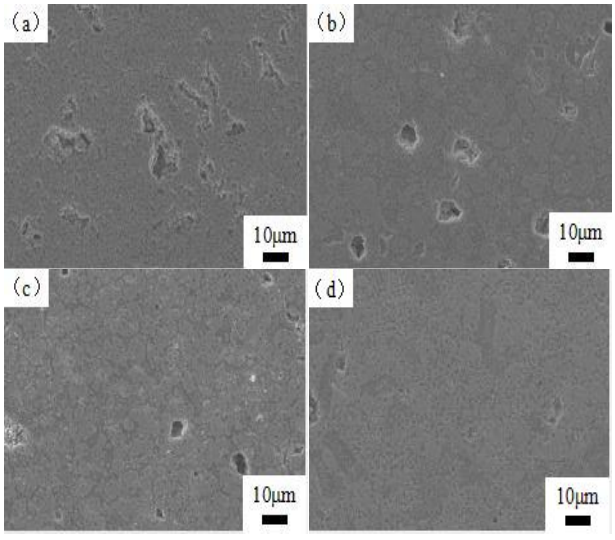

Fig. 3. SEM images of samples crystallized at (a) 1200 °C, (b)1210 °C, (c)1220 °C, (d)1230°C

Fig. 4 indicates the dielectric constant and dielectric loss measured as a function of the crystallization tempera-

ture at 1 kHz at room temperature. The dielectric constant of the samples increases with the increasing crystallization temperature. As shown in Fig. 4, the crystallized samples at different crystallization temperatures all have higher dielectric constant. This is mainly due to the formation of a barium titanate ceramic phase having a high dielectric constant, which is consistent with the XRD results shown in Fig. 2. In particular, the barium titanate glass-ceramics samples at 1230 °C show the highest dielectric constant (~1030). The reason why the dielectric constant increases significantly at 1230 °C maybe result from larger grain sizes. Meanwhile, the dielectric loss of the samples decreases with increasing temperature, which is mainly due to the reduction of pore in the sample.

Fig. 5 shows the curve of dielectric constant versus temperature. As can be seen from the figure, the dielectric constants of samples treated at different crystallization temperatures all exhibit positive temperature characteristics. And at the same test temperature, the dielectric constant of the glass-ceramics samples increases as the sintering temperature increases, which promotes the crystallization.

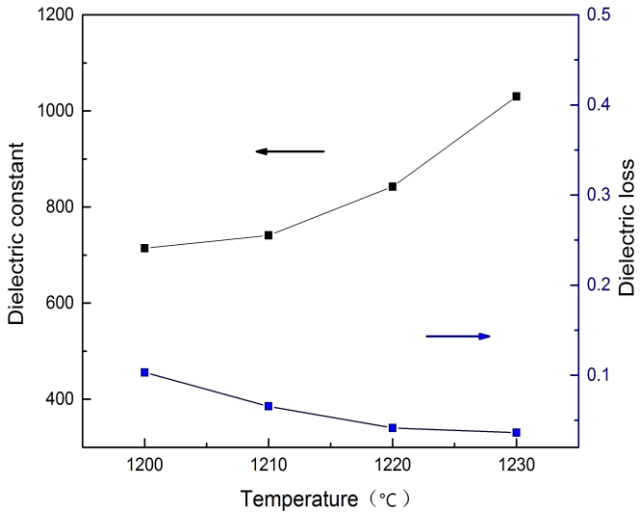

Fig. 4. Dielectric constant and dielectric loss as functions of different crystallization temperatures (measured at 1 kHz)

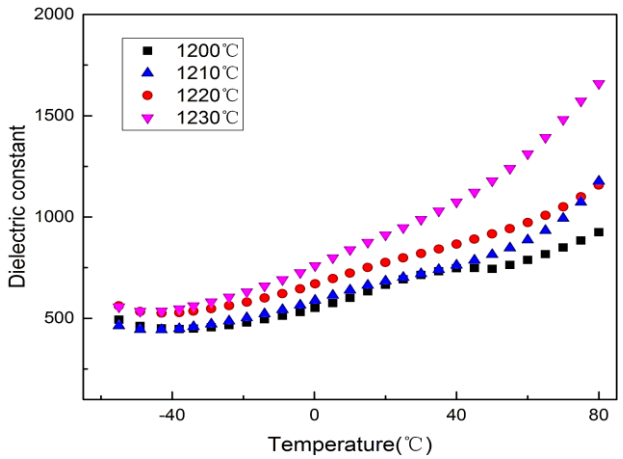

Fig. 5. Dielectric constant as a function of testing temperature for the samples crystallized at different temperatures (measured at 1 kHz)

Fig. 6 indicates the leakage current of barium titanate glass-ceramics with the different crystallization temperatures. As can be seen from the figure, the samples all show that their leakage current increases with the increase of the applied electric field strength. This is due to increase in the applied electric field strength causes an increase in the carrier concentration in the glass ceramic, which leads to an increase in the conductivity of the material. It can be seen from the figure that as the crystallization temperature increases, the leakage current density gradually decreases, which may be due to the pore decreases as the crystallization temperature increases [13].

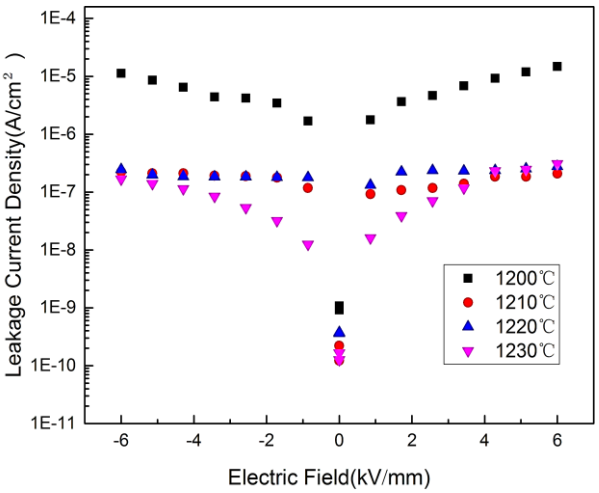

Fig. 6. Leakage current curves of the glass-ceramics samples crystallized at different temperatures

4. Conclusion

Barium titanate glass-ceramics were fabricated successfully. The main crystal phase of $BaTiO_3$ was formed under different crystallization temperatures. Microstructural observation shows that the samples have almost no pore after crystallized at 1230 °C. In other words, Good dielectric properties are realized in the samples crystallized at 1230 °C, of which the dielectric constant is up to 1030 and the relative density reaches 98.6 %.

Acknowledgments

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