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Effects of BaO on crystallization, structure and dielectric properties of $MgO–Al_2O_3–SiO_2$ glass–ceramics for LTCC applications

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ABSTRACT

Cordierite-based glass–ceramics for LTCC applications were prepared by traditional sintering method. And the effects of BaO addition on the crystallization, structure and dielectric properties were investigated by differential scanning calorimetry (DSC), scanning electron microscopy (SEM), X-ray diffractometer (XRD), dilatometer and impedance instrument. The DSC curves displayed that the glass transition temperature (T_g) slowly decreased with the BaO content increasing from 0 to 4 mol%. However, the onset of crystallization temperature (T_x) and crystallization peak temperature (T_c) showed the opposite trend. XRD analysis revealed that μ-cordierite was the major crystal phase for all the glass–ceramic samples, while α-cordierite precipitated as the minor crystal phase with BaO addition. As more BaO was added, the bulk density gradually increased, while the porosity decreased, indicating that BaO improved the sinterability of the glass samples. The dielectric constant showed minimum value with the addition of 2 mol% BaO, and the dielectric loss reached the minimum value when the content of BaO was 3 mol%. Wherein, after heated at 950 °C, glass–ceramics doped with 2 mol% BaO showed a dense structure, a relatively low dielectric constant (4.53), a low dielectric loss (2×10^{-3}) at 1 MHz, and a proper CTE value (3.74×10^{-6}/°C), which can be used to prepare LTCC materials.

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1 Introduction

In recent years, the mushroom growth of microwave devices and communication industry has promoted the development of electronic components towards the direction of smaller size and lighter weight. The emergence of low temperature co-fired ceramics (LTCC) provides a promising direction. LTCC substrate can be used as mechanical support, packaging, signal transmission, and heat dissipation, etc., which could meet the design requirements of most electronic components [1–3].

Glass–ceramics is an important LTCC material that attracts lots of people's attention [4, 5]. For glass–ceramics, the kind and content of crystals, microstructure and defects jointly determine their physical and chemical properties [6]. Through research, changing the composition and heat treatment conditions of glass–ceramics could control the crystal composition and microstructure, in order to achieve expected properties. $MgO–Al_2O_3–SiO_2$ glass–ceramics which take α-cordierite as the main crystalline phase are considered as promising LTCC substrate materials because they have excellent dielectric properties, a low coefficient of thermal expansion matched that of single crystal silicon and excellent mechanical characters [7–10]. However, the α-cordierite has a very high precipitation temperature (> 1350 °C) [11]. In addition, sintering temperature range of cordierite-based glass is relatively narrow, which makes it very difficult to obtain a dense structure below 1000 °C [12].

In order to reduce the sintering temperature of cordierite-based glass–ceramics, many researchers have carried out studies. Chen et al. [13] reduced the melting temperature and crystallization temperature of $MgO–Al_2O_3–SiO_2$ glass–ceramics using ZnO as flux agent. When 11 wt% ZnO was added, the main crystals, α-cordierite and albite were precipitated after sintered at 900–925 °C, and had superb dielectric properties of the resulting glass–ceramics. Yu et al. [14] obtained α-cordierite based glass–ceramics after heated at 900 °C for 6 h using perlite as main raw materials. Song et al. [15] prepare α-cordierite glass–ceramics of single crystal phase with $K_2O–MgO–Al_2O_3–SiO_2$ glass system. Wu et al. [16] used potassium feldspar as the main raw material to prepare glass–ceramics, α-cordierite was precipitated between 900 and 925 °C. Excessive SiO_2 can improve the sinterability and dielectric properties of glass–ceramics. Kang et al. [17] found that appropriate amount of TiO_2 can promote the precipitation and sintering process of cordierite based glass–ceramics, thereby improving the dielectric properties.

Some researches show that the Ba^{2+} as a typical network modifier ion, which can destroy the glass structure and decrease the viscosity of glass. And the sinter temperature of glass–ceramics can be reduced by adding BaO [18–21]. There is no research on the influence of Ba^{2+} on crystallization of $MgO–Al_2O_3–SiO_2$ glass–ceramics. Therefore, this paper aims to research how variable contents of BaO and the different sintering temperatures affect the glass–ceramics in crystallization, structural and dielectric properties. Besides, comparison between the best sample with other similar compositions are also made.

2 Experiments

Table 1 shows the compositions of the glass samples. The content of BaO increased from 0 to 4 mol% with corresponding sample number B1-4. The raw materials used in this work were all analytically pure materials. The raw materials were accurately weighed and thoroughly mixed to obtain glass batches. At 1500–1580 °C, melted batches in a platinum crucible and kept for 3 h. Then bubble free glassy melt was quickly poured into cold distilled water. The initial glasses were ball milled for 3 h. And the obtained glass powders added with polyvinyl alcohol (PVA) solutions with a concentration of 5 wt% were pressed into disc (φ30 mm × 4 mm) and rod (30 mm × 4 mm × 4 mm), under a pressure of 20 Mpa. The pressed samples were dried at 120 °C for 24 h and then transferred to a high-temperature furnace at 450 °C for 3 h to remove PVA. Then the temperatures were increased (at a rate of 5 °C/min) to 900 °C, 925 °C and 950 °C with holding time 1 h,

Table 1 The compositions of the basic glasses with different BaO content (in mol%)

	MgO	Al_2O_3	SiO_2	P_2O_5	B_2O_3	BaO
B0	20.0	20.0	55.0	2.5	2.5	0.0
B1	20.0	20.0	54.0	2.5	2.5	1.0
B2	20.0	20.0	53.0	2.5	2.5	2.0
B3	20.0	20.0	52.0	2.5	2.5	3.0
B4	20.0	20.0	51.0	2.5	2.5	4.0

respectively. The glass–ceramics were cooled down in the furnace to room temperature.

Archimedes method was applied to measure the bulk density and apparent porosity of samples. Bulk density $\rho = M1 \times \rho_w/(M1–M2)$, and apparent porosity = $(M3–M1)/(M3–M2) \times 100\%$, where ρ_w represents the density of water in room temperature, $M1$ represents dry weight of the sample, $M2$ represents the weight of the sample in water, and $M3$ represents the weight after saturated with water. The crystal phases of the samples were analyzed by X-ray diffraction analysis (XRD, D8-ADVANCE, Bruker, Germany) using CuK_α radiation (2θ = 10° to 70°). The characteristic temperatures of glass samples were obtained by differential scanning calorimetry (DSC, Netzsch STA 409, Germany), with Al_2O_3 as the reference material, and the heating rate was 10 °C/min from 25 to 1200 °C. The cross-section of samples was observed by scanning electron microscope (SEM, FEI QUANTA FEG250, USA). The dielectric properties of samples were evaluated by LCR measuring instrument (Agilent 4292A, USA) at 1 MHz. The coefficient of thermal expansion (CTE) for the tested samples was tested by heating from ambient temperature to 600 °C at a heating rate of 5 °C/min through a horizontal double rod dilatometer (Model 1412 STD, Orton, USA).

3 Results and discussion

Figure 1 illustrates the thermal analysis of glass samples doped with different contents of BaO. Results suggested that the glass transition temperature T_g dropped from 790 to 778 °C gradually, whereas the initial crystallization temperature T_x and crystallization peak temperature T_c increased from 936 °C and 978 to 976 °C and 1038 °C, respectively. Meanwhile, compared with sample B0 without BaO, the width of the crystallization peak of the sample increased, the strength decreased, and the shape became flat. As a glass modifier, BaO will raise the amount of non-bridging oxygen in the glass network, resulting in a decrease in viscosity. Therefore the T_g values decreased with BaO content increasing [22]. However, the radius of Ba^{2+} ions is relatively large, which will prevent the migration of small radius ions such as Mg^{2+} [23]. So, the crystallization peak temperature shifted to the high temperature direction, and the intensity of the devitrification peak was significantly weakened.

Figure 2 is the XRD pattern of the glass–ceramics with different amounts of BaO sintered at 950 °C. With BaO increasing from 0 to 4 mol%, the main crystal was μ-cordierite (JCPDS no.14-0249), the minor was α-cordierite (JCPDS no.13-0294), and a small amount of crystal was β-quartz (JCPDS no. 71-0911) only with the BaO addition. As the content of BaO increased, the diffraction peak intensity of α-

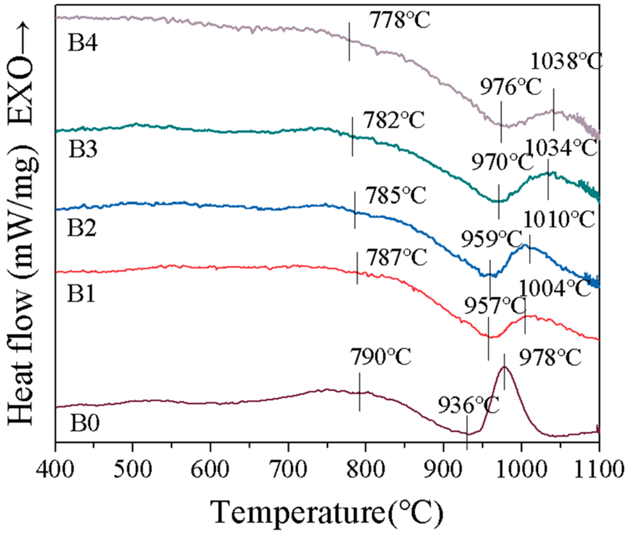

Fig. 1 DSC results for samples (at a heating rate 10 °C/min) with different BaO content

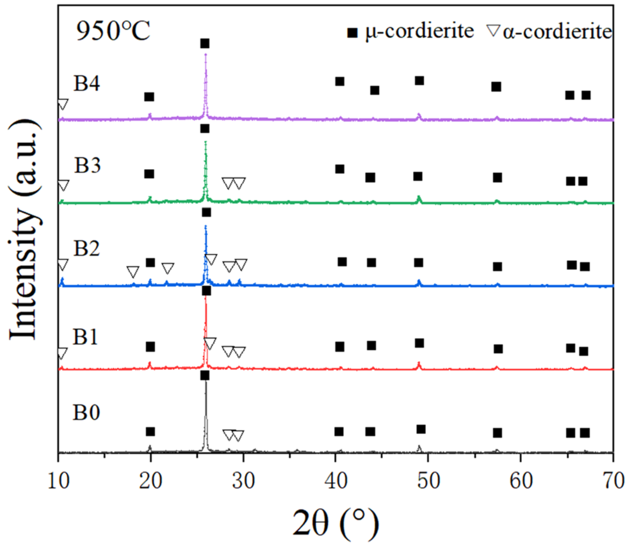

Fig. 2 XRD curves for glass–ceramics with different BaO content after heated at 950°C

cordierite reached a maximum value when BaO was 2%. Normally, the precipitation temperature of μ-cordierite was low, while the crystallization temperature of α-cordierite was high [10, 24]. As the heat treatment temperature or the holding time increased, the main crystal μ-cordierite will convert into α-cordierite. Without BaO adding, the crystallization temperature of the sample was 978 °C, and only μ-cordierite can be observed. When the BaO was introduced, α-cordierite began to precipitate as the minor crystal, which indicated that BaO facilitated the crystallization of α-cordierite. And with more BaO addition, the diffusion and mobility of Mg^{2+} and Al^{3+} was hindered by Ba^{2+}, limiting the formation of α-cordierite.

Figure 3 is the XRD pattern of the glass–ceramics with the content of BaO was 2 mol% sintered at 900 °C, 925 °C and 950 °C. When the glass–ceramics was sintered at 900 °C, only μ-cordierite precipitated. With the sintering temperature increasing, the diffraction peaks of α-cordierite increased and the amount of α-cordierite precipitation increased.

The SEM micrographs of cross-section of samples doped with different contents of BaO sintered at 950 °C are shown in Fig. 4. It can be seen that many pores existed in sample B0. Because the start temperature of crystallization T_x for sample B0 was 936 °C which was lower than the sintering temperature, crystals will precipitate quickly after sintered at 950 °C for 1 h. Then the precipitated crystals in the glassy phase would increase the viscosity, thereby preventing the densification process [17, 25]. The number of pores obviously decreased with the BaO content of samples increasing, which indicated that the sintering properties of glass–ceramics can be improved by adding the BaO. As a network modifier oxide, BaO can reduce the viscosity of the glasses [18]. The higher the content of BaO, the lower the viscosity of the glasses. Meanwhile, with the BaO content increasing, the start temperature of crystallization T_x gradually increased. This meant that during the heat treatment at 950 °C, the rate of crystal precipitation would slow down and the sintering process would proceed more fully. With the BaO $\geq$ 3 mol%, the initial crystallization temperature was greater than or equal to 970 °C, which indicated that the rate of crystal precipitation will be greatly reduced, and the densification process of the sample would play a leading role. Therefore, the B3 and B4 samples had few pores and the highly densified glass–ceramics were prepared.

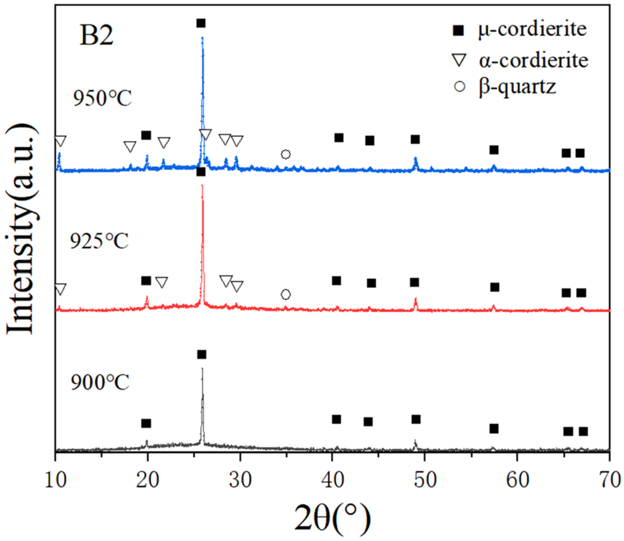

Fig. 3 XRD curves for B2 sintered at 900 °C, 925 °C and 950 °C

The bulk density of samples with different BaO content after sintered at 900–950 °C is shown in Fig. 5. It can be found that the value of the bulk density was positively related to the amount of BaO. For the same sample, the bulk density also increased when the sintering temperature increased. The addition of BaO will decrease the viscosity of glasses, which can speed up the mass transfer process, thereby promoting the densification of the sample. Generally, the viscosity of glass gradually decreased with increasing temperature. Therefore, as the sintering temperature increased, the densification of the samples was significantly promoted, which led to the bulk density increased. The bulk density of glass–ceramics obviously increased with the sintering temperature rose from 900 to 950 °C.

The porosity for samples with varying BaO contents after sintered at 900 °C, 925 °C and 950 °C is shown in Fig. 6. It can be observed that with the sintering temperature or BaO content increasing, the porosity both decreased. This corresponds to the change in bulk density. Because the higher the degree of densification, and the smaller the porosity.

The dielectric constant for samples with varying BaO content heated at different temperatures is shown in Fig. 7. The dielectric constant of glass–ceramics has a great relationship with the kind and content of crystals, porosity, the residual glassy phase composition, etc. [13]. Compared with μ-cordierite, α-cordierite has a lower dielectric constant. The content of α-cordierite gradually reached its maximum value

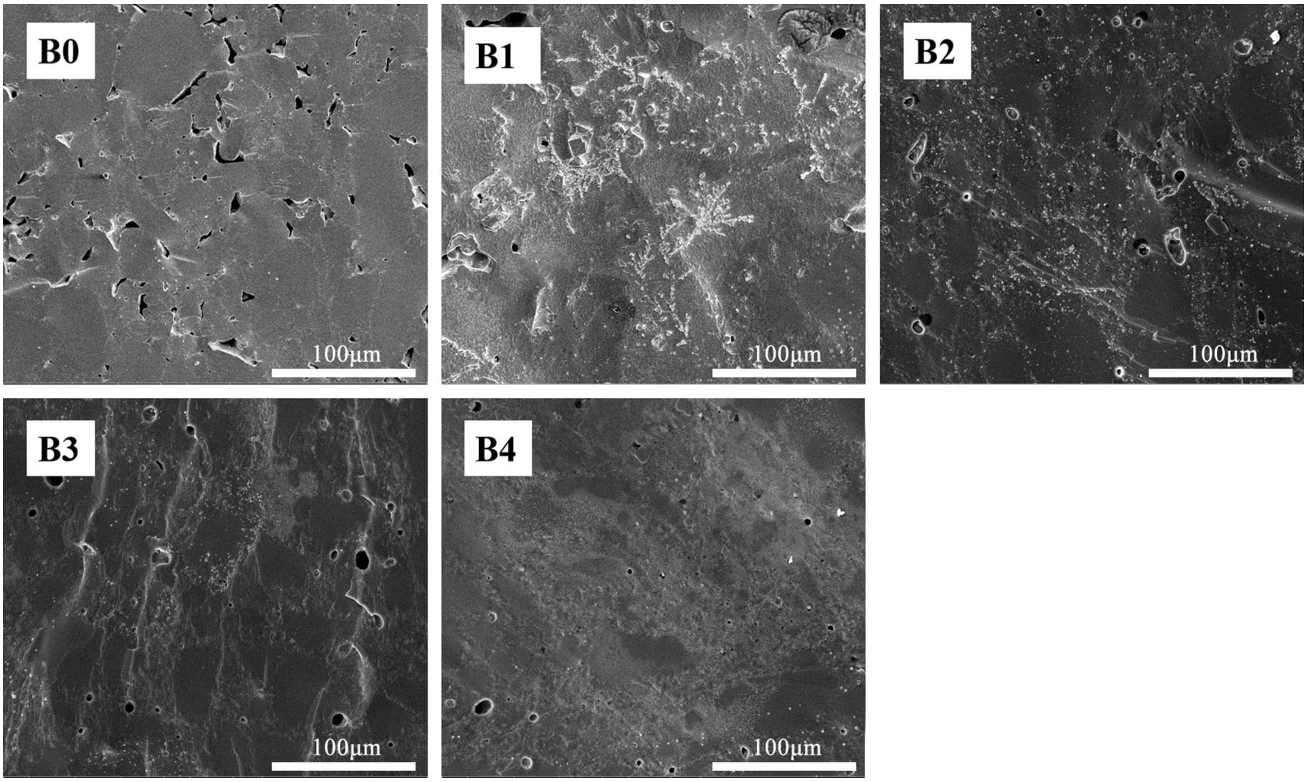

Fig. 4 SEM micrographs of cross-section of samples with different BaO content after sintered at 950 °C

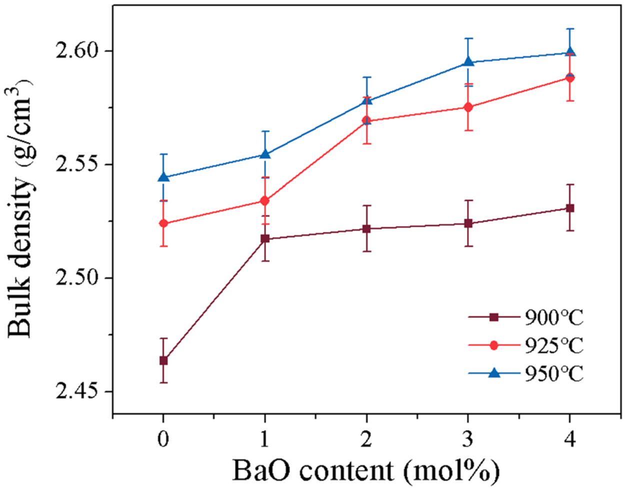

Fig. 5 Bulk density for samples with different BaO content heated at 900 °C, 925 °C and 950 °C

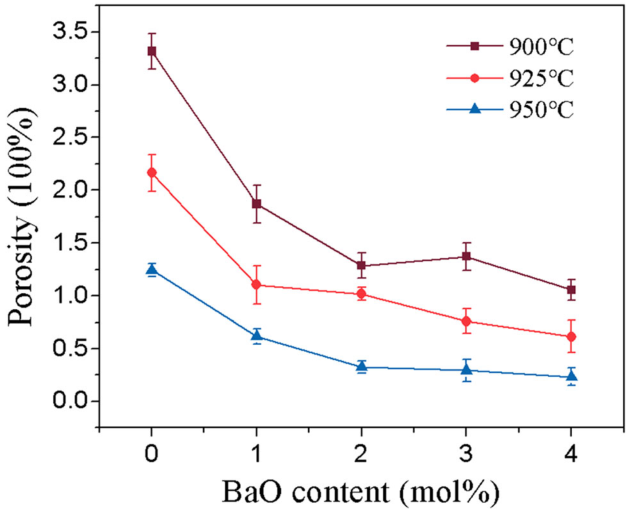

Fig. 6 Porosity for samples doped with varying BaO content after heated at three temperatures (900 °C, 925 °C and 950 °C)

and then dropped when the content of BaO continuous increased. Therefore, as the content of BaO increased from 0 to 4 mol%, the dielectric constant firstly dropped and then rose. When the content of BaO was 2 mol%, the dielectric constant of glass–ceramic sample reached its minimum value. With the sintering temperature increasing from 900 to 950 °C, the microstructure became dense and the porosity decreased, resulting in a lower dielectric constant.

Figure 8 shows dielectric loss for glass–ceramics with varying BaO content heated at 900 °C, 925 °C and 950 °C, respectively. It can be found that the dielectric loss and dielectric constant had the similar trend. The difference was that the dielectric loss reached the minimum value when the BaO content was 3 mol%. The dielectric loss of a material includes inherent loss and extrinsic loss. The intrinsic loss largely depends on the structure of crystals. The external loss is mainly determined by microcracks, structural defects, porosity, and so on [26]. The inherent loss of α-cordierite is relatively low, and the precipitation of α-cordierite will decrease the dielectric loss for glass–ceramic samples. At the same time, the decrease in porosity resulted in a smaller dielectric loss. Therefore, the dielectric loss of the samples gradually decreased with the content of BaO and heat treatment temperature increasing. Besides, the degree of glassy network polymerization also has a great influence on the dielectric loss [27]. The increase of BaO will provide non-bridging oxygen and the glass structure is looser. When the BaO content was increased to 4 mol%, α-cordierite significantly reduced, and the glass network structure was severely destroyed by BaO, which caused an increase in dielectric loss.

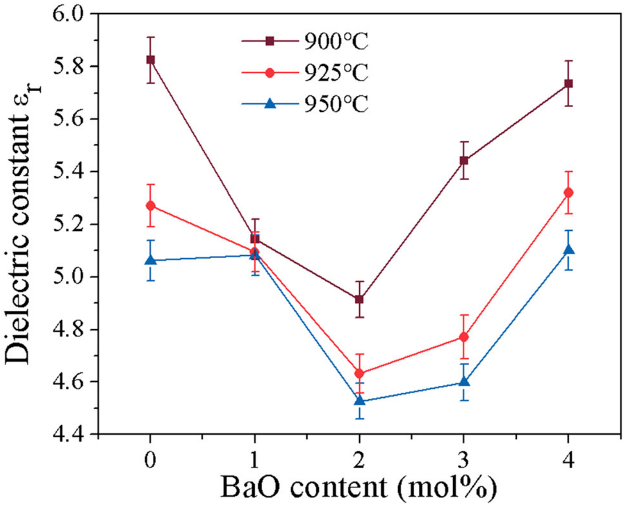

Fig. 7 Dielectric constant for glass–ceramics with varying BaO content heated at different temperatures

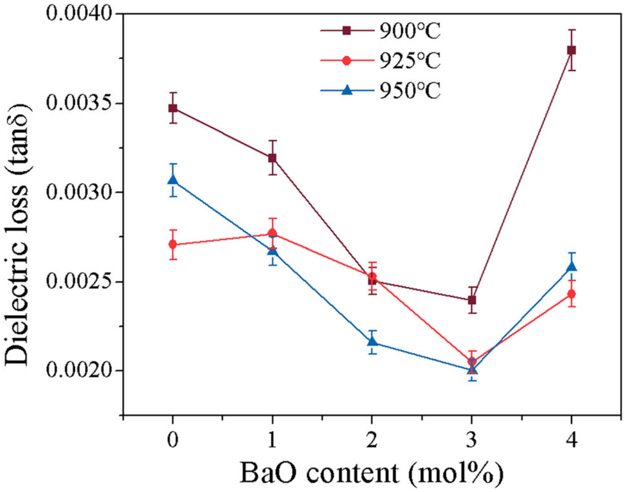

Fig. 8 Dielectric loss for glass–ceramics with varying BaO content heated at different temperatures

Table 2 shows main properties of samples obtained in this paper compared with the data from references [8, 17, 28]. It can be seen that after sintering at 950 °C, the sample B2 had relatively excellent dielectric properties, with an expansion coefficient of 3.74 × 10^{-6} °C^{-1}, which can be used to prepare LTCC material.

4 Conclusion

The results showed the influence of BaO content on crystallization, structure and dielectric properties of $MgO–Al_2O_3–SiO_2$ glass–ceramics. From the experimental results, it can be inferred that the T_g slowly decreased from 790 to 778 °C. While the start temperature of crystallization T_x and crystallization peak temperature T_c increased from 936 °C and 978 to 976 °C and 1038 °C, respectively. With the content of BaO increasing from 0 to 4 mol%, the main crystal of the glass–ceramic was μ-cordierite along with α-cordierite as the minor only with the addition of BaO. As the content of BaO increased, α-cordierite reached a top peak when the content of BaO was 2 mol%. When the content of BaO was 2 mol%, the dielectric constant of

Table 2 Main properties of samples obtained in this paper compared with the data from references [8, 17, 28]

	B2	Ref. [8]	Ref. [17]	Ref. [28]
Sintering temperature (°C)	950	900–925	925	900
CTE (× 10^{-6} °C^{-1})	3.74	4.32–5.87	3.34	≤ 2.5
Dielectric constant at 1 MHz	4.58	6–8	5.44	5.5–6.0
Dielectric loss (× 10^{-3}) at 1 MHz	2	5	2.17	10

the glass–ceramics reached its minimum value. After sintered at a temperature of 950 °C, the dielectric constant of sample B2 can reach 4.53, and the dielectric loss was as low as 2×10^{-3}. The coefficient of thermal expansion was 3.74×10^{-6} °C^{-1}, which was very close to that of silicon components (3.5×10^{-6} °C^{-1}).

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