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Effect of TiO₂ doping on crystallization, microstructure and dielectric

properties of CBS glass-ceramics

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Abstract: In this study, calcium borosilicate (CaO-B₂O₃-SiO₂, CBS) glass-ceramics were fabricated using chemically pure CaO, SiO₂, and B₂O₃ as raw materials. Differential scanning calorimetry, X-ray diffraction, scanning electron microscopy, and electrical measurements were conducted to explore the effect of titanium dioxide (TiO₂) doping on crystallization, microstructure, and dielectric properties of CBS glass-ceramics. Furthermore, the influence of sintering temperature and sintering schemes on crystalline phases of CBS glass-ceramics was systematically investigated. Results showed that the increase of TiO₂ content led to the reduction in sintering temperature of CBS glass-ceramics and promoted the precipitation of wollastonite crystal phase. For instance, with the increase of content of TiO₂ from 0 to 3 wt.%, transition temperature and crystallization temperature were reduced by 12.9 and 27.6 °C, respectively. However, excessive TiO₂ affected the precipitation of wollastonite crystal phase, destroyed crystal structure, and damaged close arrangement of crystal grains. Moreover, higher TiO₂ content was found to weaken dielectric properties of CBS glass-ceramics. In this study, the best molar ratio of ingredients, meeting that of ideal target material, is n(Ca): n(Si): n(B) = 1:1:0.6, with doping mass fraction of 2 wt.% of TiO₂. After optimal sintering procedure, dielectric constant of the best sample was found to be 1.4 (1 MHz), 1.3 (10 MHz), and dielectric loss was 3.9×10^{-3} (1 MHz) and 3.8×10^{-3} (10 MHz).

Keywords: Calcium borosilicate, Glass-ceramics, Dielectric properties, Low sintering temperature, Titanium dioxide

1. Introduction

With the rapid development of modern information technology, large-scale and ultra-large-scale integrated circuits have become an important direction of research and development. Electronic packaging technology has evolved from traditional high-density single-layer packaging to stacked three-dimensional packaging, thus multi-layer wiring packaging technology is widely used nowadays [1–3]. Low temperature co-fired ceramic (LTCC) materials, multi-chip modules, chip size package, etc., have emerged in recent years as well-known multidisciplinary components for integration technology [4–6]. Among them, LTCC has become the mainstream of electronic component integration design with its excellent integration density and high frequency characteristics, such as electrical, mechanical, thermal, and process characteristics [7–12].

Calcium borosilicate (CaO-B₂O₃-SiO₂, CBS) glass-ceramics have low dielectric constant, low dielectric loss, and thermal expansion coefficient similar to that of silicon chips. Moreover, these glass-ceramic materials have an excellent match with metallic pastes and ability to reduce high-frequency signal relaxation. Therefore, CBS glass-ceramic materials are considered as one of the most promising LTCC substrate materials to create robust electronics [13–15]. Significant research efforts have been devoted to the study of the component ratios of CBS glass-ceramics, the heat treatment system, and the influence of nucleating agents on their microstructure and properties. As a result, some excellent CBS glass-ceramic materials have also been obtained [16–18].

Zhou et al. [19] studied the effects of different Ca/Si ratios on the microstructure and properties of CBS glass-ceramics. Zhu et al. [20] used CBS glass-ceramic as raw material and added $0.5\%P_2O_5$ and 0.5%ZnO to fabricate LTCC. Chiang et al. [21] systematically studied the densification behavior and properties of CBS glass-ceramics with different compositions, and analyzed the effects of temperature, heating rate, and holding time on the properties of glass-ceramics. Shao et al. [22] prepared CBS glass-ceramic by low temperature water quenching method, and studied the effect of composition on the melting temperature and the influence of added titanium dioxide (TiO₂) on the dielectric properties of CBS glass-ceramics. Chang et al. [23] studied the crystallization kinetics and mechanism of low dielectric,

low temperature and co-fired CBS glass-ceramics.

He and Gao [24] investigated the effect of added boron on the crystallization, microstructure, and dielectric properties of CBS glass-ceramics. Zhu et al. [25] used P_2O_5 and ZnO as additives to optimize the synthesis conditions of CBS glass-ceramics for LTCC. Hsiang et al. [26] studied the effects of ZrO₂ addition on the crystallization behavior, sintering characteristics, and dielectric properties of CaO-MgO-Al₂O₃-SiO₂ glass-ceramics. Zhou et al. [27] investigated the effects of La₂O₃-B₂O₃ as a sintering aid on the flexural strength and microwave dielectric properties of CBS glass-ceramics. Furthermore, Wang et al. [28] studied the effects of the addition of Li₂CO₃, TiO₂, and Al₂O₃ on the densification and microwave dielectric properties of CBS glass-ceramics.

As a nucleating agent, TiO_2 has always been the focus of research. For instance, G. A. Khater [29] explored the effect of TiO₂ nucleating agent on the crystallization behavior and microstructure of glass-ceramics based on blast furnace slag. Yang et al. [30] studied the effect of TiO_2 addition on the crystallization, microstructure, and mechanical properties of stainless steel slag glass-ceramics. Rezvani et al. [31] investigated the effects of Cr₂O₃, Fe₂O₃, and TiO₂ as nucleating agents on the crystallization behavior of SiO₂-Al₂O₃-CaO-MgO(R₂O) glass-ceramics. Mukherjee et al. [32] analyzed the influence of TiO₂ content on the crystallization and microstructure of machinable glass ceramics. Ebadzadeh and Ghasemi [33] studied the effect of adding TiO₂ on the stability of t-ZrO₂ in mullite-ZrO₂. Dugué et al. [34] studied the effects of structural transformation and spectral properties of Ni-doped magnesium aluminosilicate glass-ceramics doped with TiO₂ and ZrO₂ nucleating agents on broadband near-infrared light. The above mentioned studies clearly show that TiO₂ as a nucleating agent can significantly promote the crystallization of glass-ceramics and improve their performance. However, studies focusing on the content of TiO₂ are rare and the influence of TiO₂ as nucleating agent on the crystal phases and microstructure of CBS glass-ceramics has not been explored yet. Therefore, the role of TiO_2 in CBS glass-ceramics should be further investigated.

In this study, CBS glass-ceramics were prepared from chemically pure materials. The effects of different contents of TiO_2 and sintering process on the crystal phase and microstructure of CBS glass-ceramics were studied. Moreover, the effect of TiO_2 on the dielectric properties of glass-ceramics was analyzed from the perspective of crystal structure and microstructure evolution. Finally, the optimum doping content of

 TiO_2 and heat treatment system were determined to obtain CBS glass-ceramics with excellent properties.

2 Experimental

2.1 Raw materials and design

CBS glass-ceramics are wollastonite-based crystalline materials. Wollastonite has low dielectric constant ($\varepsilon_r = 5$) and dielectric loss ($\tan \delta = 1 - 3 \times 10^{-4}$). In the preparation of CBS glass-ceramics, different crystalline phases such as CaB₂O₄, CaB₂SiO₈, CaSiO₃, and CaSiO₄ precipitate due to different sintering systems and compositions. Different types and quantities of crystalline phases can be obtained by selecting suitable sintering system to obtain materials with different properties [35–37].

Chemically pure raw materials were used in this study. Distribution ratio of the raw materials was $Ca_xSi_yB_zOn$. According to the preliminary experimental results [24], we configured the raw materials according to the molar ratio of the elements in the composition X:Y:Z = 1:1:0.6. The molar fraction of the raw materials was converted into mass fraction, and then the compounding scheme was set according to the different doping amount of TiO₂, the detailed composition of formulation I, II, III, and IV is listed in Table 1.

	101110	(8).		
Formulation	CaO	SiO ₂	B_2O_3	TiO ₂
Formulation I	40.88	43.79	15.33	0
Formulation II	40.47	43.36	15.18	1
Formulation III	40.06	42.92	15.02	2
Formulation IV	39.65	42.48	14.87	3

Table 1. The detailed composition of raw materials according to different formulations (g)

2.2 Experiment process

The ingredients were prepared according to the designed ingredient list (Table 1)

and operated according to the experimental procedure, schematically illustrated in Fig. 1 [38–40].



Fig. 1. Flow chart for the glass melting process and characterization

2.3 Characterization

Differential scanning calorimetry (DSC) was performed (STA409C integrated thermal analyzer, NETZSCH Co.) to determine the heat treatment system of glass-ceramics. Briefly, the sample for DSC was crushed into powder using a DF-4 electromagnetic type ore grinder and sieved through a 200 mesh. The powder sample was weighed using an electronic balance and 20 mg of the sample was used for DSC experiments. α -Al₂O₃ was used as the standard reference, argon gas was used as the shielding gas, and the heating rate was 10 °C min⁻¹.

The phase composition was determined by X-ray diffraction (XRD) using an M21X-SRA X-ray diffractometer (MAC Science Co., Ltd, Japan) equipped with graphite crystal diffracted-beam monochromator. The working voltage and the working current of the tube were 40 KV and 300 mA, respectively. CuKα radiations with a

wavelength of 1.5406 Å were used as the X-ray source and XRD patterns were recorded in the 2 θ range of 20–60° at a scanning speed of 0.044°/sec.

Microstructure of the prepared samples was characterized by scanning electron microscopy (SEM, ZEISS, Germany). Before microstructural analysis, the sample was etched for 15 s in 2 wt.% hydrofluoric acid solution, ultrasonically cleaned for 3 min, dried, and then sprayed with gold. The working voltage of 20 kV and working current of 4–20000 pA were used. The maximum resolution of SEM images was 1 nm.

The dielectric properties of the samples were measured using an impedance analyzer (E4990A, Keysight, USA). Sample was first sprayed with gold on both sides to maintain electrical conductivity. The frequency range of the E4990A impedance analyzer was from 20 Hz to 120 MHz, providing a basic accuracy of 0.045% over a wide impedance range.

The density of the glass-ceramics was measured using the Archimedes method. The dry weight m_1 and hanging weight m_2 of the sample were determined by using an electronic balance. Sample density ρ was calculated as follows:

$$\rho = \frac{m_1}{m_1 - m_2} \times \rho_H \tag{2-1}$$

 ρ_{H} is the density of the plasma water, 1 g/cm³.

3 Results and discussion

Uniformly mixed powder was poured into a platinum crucible and heated in a muffle furnace to 1360 °C. The melted glass liquid was obtained by maintaining the temperature for 2 h at 1360 °C. The molten glass was then quickly poured into deionized water at room temperature to obtain water quenched sample. The water-quenched samples of CBS glass-ceramics based on the formulations I, II, III, and IV were crushed and sieved through a 200-mesh sieve before DSC measurements. The results of the test are shown in Fig. 2.

The endothermic peak of DSC curve corresponds to the transition temperature (T_g) and softening temperature (T_f) of glass, and the exothermic peak corresponds to the crystallization temperature of glass. The results of the DSC detection show that

the transition temperatures of formulation I, II, III, and IV are 683.5, 676.2, 672.3, and 670.6 \Box , respectively, and the crystallization temperatures are 885.3, 872.6, 861.9, and 857.7 \Box , respectively. This indicates that the T_g and crystallization temperatures gradually decrease with the increase of TiO₂ content. When the mass percentage of TiO₂ increases from 0 to 3%, the transition temperatures decrease by 12.9 \Box , and the crystallization temperature decreases by 27.6 °C. This can be attributed to the existence of Ti⁴⁺ in tetracoordinated state in the molten glass and the base glass formed by extreme cold. Radius of Ti⁴⁺ is larger than that of Si⁴⁺, and the bond energy of the Ti–O bond is lower than that of Si–O; therefore, Ti⁴⁺ partially replaces Si⁴⁺ in the silicon–oxygen tetrahedron structure, thus destroying the complex silicon tetrahedral system, reducing the viscosity of glass, increasing its fluidity, facilitating the diffusion of ions, and finally reducing the crystallization temperature of glass [29]. The peak value of exothermic peak represents the crystallization strength, and the crystallization of glass-ceramics is enhanced with the increase of TiO₂ content.



Fig. 2. The DSC curves of CBS glass-ceramics with different compositions

Samples with formulation I were molded and placed in a muffle furnace for heating and sintering. According to the DSC image of formulation I, different sintering systems were designed to prepare samples 1–5, and the specific scheme is

summarized in Table 2. In general, glass powder was heated to the vicinity of the glass softening temperature, maintained for one hour, heated to near crystallization temperature, and then followed by two hours insulation. This heat treatment system is referred to as two-step sintering.

Sample no.	Sintering regimes
1#	Heating up to 800 °C at a heating rate of 3 °C min ⁻¹ . After 2
1#	h of holding time, cooling with a muffle furnace
2#	Heating up to 900 °C at a heating rate of 3 °C min ⁻¹ . After 2
2#	h of holding time, cooling with a muffle furnace
2#	Heating up to 900 °C at a heating rate of 5 °C min ⁻¹ . After 2
5#	h of holding time, cooling with a muffle furnace
	Heating up to 700 °C at a heating rate of 3 °C min ^{-1} . After 1
4#	h of holding time, the temperature was increased to $850 \ ^{\circ}C$
	(3 °C min ⁻¹). After 2 h of holding time, the samples were
	cooled down with muffle furnace.
	Heating up to 700 °C at a heating rate of 3 °C min ⁻¹ . After 1
<i></i>	h of holding time, the temperature was increased to 900 $^{\circ}$ C
5#	(3 °C min ^{-1}). After 2 h of holding time, the samples were
	cooled down with muffle furnace.

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XRD measurements were used to explore the effects of different composition and sintering system on the precipitation, phase composition, and crystal phase transformation of CBS glass-ceramics. SEM was utilized to study the effects of different composition and sintering system on the microstructure and densification sintering of CBS glass-ceramics. The impedance analyzer was used to study the dielectric properties of CBS glass-ceramics and determine the optimal sintering system.

Fig. 3 shows the XRD patterns of samples 1–5.



Fig. 3. The XRD patterns of samples 1–5.

XRD patterns of samples 1-5 reveal that the main crystalline phase of each sample is wollastonite, with a small amount of quartz and dicalcium silicate. The ratio of CaO to SiO₂ in the batch is 1:1, which conforms to the composition design of wollastonite. However, some Ca and wollastonite combine to form Ca₂SiO₄; therefore, the remaining (SiO_4) is self-associated to form cristobalite phase. Sample 1 was sintered at 800 °C, which is lower than its crystallization temperature of 885.3 °C, thus resulting in a relatively low content of wollastonite crystal phase. The crystal phases of samples 2–5 are roughly similar. Compared to the crystal phase of sample 1, the amount of wollastonite crystal phases in the samples 2-5 gradually increases, and the quartz crystal phase content relatively decreases. This shows that increasing sintering temperature and adopting two-step sintering method can make the samples precipitate more wollastonite crystalline phase. Two-step sintering can lead to the growth and nucleation of nucleus at low nucleation rate. When numerous nuclei are uniformly formed in the glass, the temperature increases to the temperature near the maximum value of crystal growth rate for heat preservation treatment. Thus, a large number of uniform microcrystals can be grown in the glass, so that the samples can acquire excellent properties.

Fig. 4 shows the SEM images of samples 1–5. In general, the microstructures of samples 2 and 3 and 4 and 5 are, respectively, similar; therefore, the SEM images of samples 1, 3, and 5 are presented herein. Sample 1 shows a large amount of glass

liquid phases, few crystal grains, and a large number of voids, which can be attributed to the incomplete sintering. Compared to sample 1, sample 3 shows a relative decrease in the liquid phase and increase in crystalline grains, and most grains are closely connected with each other, which indicates significant improvement in crystallization. However, as-formed sample 5 is dense with a large number of acicular wollastonite grains, and the crystal grains are full and closely arranged, with average particle size of about $5 \,\mu\text{m}$.



Fig. 4. SEM images of samples 1, 3, and 5 (See Table 2 for sintering regimes).

The dielectric properties of samples 1-5 were analyzed using an impedance analyzer and the density of the samples was measured using the Archimedes method. The results are presented in Table 3 (Fig. 5). The dielectric constants of samples 1–5 are generally lower than 7, which meet the expected target. Furthermore, the density of samples 1-5 increases gradually, which indicates that the densification of structure was enhanced. It should be noted that the density of sample 3 is slightly larger than sample 2 and sample 5 is slightly larger than sample 4, which is why the dielectric constant of sample 3 is lower than sample 2, and the dielectric constant of sample 5 is lower than sample 4. In addition, the dielectric constant of sample 3 is comparatively lower, which is 5 at 1 MHz and 10 MHz, however, its dielectric loss is higher, reaching 1.27×10^{-2} . The dielectric constant of sample 5 is 6, and the dielectric loss is 2.3 $\times 10^{-3}$ at 1 MHz and 3.37 $\times 10^{-3}$ at 10 MHz, which can be attributed to good crystallization and dense structure. Moreover, the dielectric properties of sample 5 meet the expected requirements of dielectric constant and dielectric loss of less than 7 and 5×10^{-3} , respectively. Considering dielectric constant and dielectric loss, sample 5 is the optimal sample and meets the market requirements.

a 1	Density	Frequency	Dielectric	Dielectric
Sample no.	(g/cm^3)	(MHz)	constant (ϵ_r)	$loss(10^{-3})$
1	1.07	1	8	3.9
1	1.97	10	7	9.8
2		1	6	13.2
	2.26	10	6	18.7
3	2.20	1	5	6.0
	2.28	10	5	12.7
4	2.24	1	7	5.9
	2.34	10	8	18.7
5	2.37	1	6	2.3

Table 3. The dielectric constant, dielectric loss and density of samples 1–5.

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Fig. 5. The dielectric constant and dielectric loss of samples 1–5.

The results of XRD, SEM, and the dielectric properties of samples 1–5 were comprehensively analyzed. The results indicated that the increase of the sintering temperature or the use of two-step sintering could precipitate more wollastonite crystal phase and enhance sample performance. Therefore, among formulations I, II,

III, and IV, the optimal sintering system was selected to prepare the samples. The details are presented in Table 4.

	Sample	Sintering regimes
	no.	
		Heating up to 700 °C at a heating rate of 3 °C min ^{-1} .
Formulation I	5	After holding for 1 h, the temperature was increased
		to 900 °C (3 °C min ⁻¹). After holding for 2 h,
		samples were cooled down in a muffle furnace
		Heating up to 700 °C at a heating rate of 3 °C min ⁻¹ .
Formulation II	6	After holding for 1 h, the temperature was increased
		to 892 °C (3 °C min ⁻¹). After holding for 2 h,
		samples were cooled down in a muffle furnace
		Heating up to 700 °C at a heating rate of 3 °C min ⁻¹ .
Formulation III	7	After holding for 1 h, the temperature was increased
		to 882 °C (3 °C min ⁻¹). After holding for 2 h,
		samples were cooled down in a muffle furnace
		Heating up to 700 °C at a heating rate of 3 °C min ⁻¹ .
Formulation IV	8	After holding for 1 h, the temperature was increased
		to 872 °C (3 °C min ⁻¹). After holding for 2 h,
		samples were cooled down in a muffle furnace

Table 4. Sintering regimes for formulations I, II, III, and IV

XRD measurements were carried out to analyze the crystal structure of samples 5–8 and results are shown in Fig. 6.

The main crystalline phase of each sample is wollastonite. With the increase of the content of TiO_2 , the diffraction peak of the main crystalline phase becomes sharper and the peak value is higher, which indicates the presence of more wollastonite phase in samples and also the samples undergo better crystallization. However, in sample 5 without TiO_2 doping, only a small amount of crystal grains is formed due to the difficulty of nucleation and crystal growth. Few wollastonite phase and more danburite and quartz phases are observed in SEM image of sample 5. These results indicate that TiO_2 doping contributes to the precipitation of wollastonite crystalline phase. Moreover, noteworthy, a small amount of anatase (TiO_2) and

titanium silicide (TiSi₂) were also detected for sample 7, and these impurities crystalline phases increased significantly in sample 8, which led to the weakening of the properties of the sample. This result indicates that an optimum amount of TiO_2 doping is required, and if the amount exceeds the optimum value, new crystalline phases are introduced.

Therefore, the effect of TiO_2 doping on CBS glass-ceramics was further investigated. According to the analysis, in the glass network structure, Ti ions act as network intermediates, and elemental Ti exists in the tetracoordinated and hexacoordinated states in the glass. In the molten glass and the extremely cold formed base glass, Ti ions exist in a tetracoordinate state. However, Ti ions exist in a hexacoordinated form at the nucleation temperature, and this structure is greatly different from the network structure formed by glass. When the content exceeds the solubility, it precipitates out from the glass matrix to form a Ti-rich phase, which causes the glass to be phase-separated, thereby promoting glass crystallization.



Fig. 6. XRD patterns of samples 5–8.

The factsage software was used to simulate the change of the crystal phase of the CBS-based glass-ceramic system in the temperature range of 500–1000 °C and results are shown in Fig. 7.

According to the software calculation results, the wollastonite phase content of the samples with 1 and 2 wt.% (mass fraction) of TiO_2 increased gradually, while the

content of quartz and cyanite phases decreased slightly, compared to the samples without added TiO₂. Moreover, the content of wollastonite crystal phase containing 3 wt.% (mass fraction) TiO₂ was slightly less than that of 2% TiO₂ sample. This is consistent with the experimental results. It is thus confirmed that TiO₂ doping can promote the precipitation of wollastonite crystal phase; however, excessive TiO₂ doping introduces a new crystal phase and reduces the content of wollastonite crystal phase in sample.



Fig. 7. Thermodynamic calculation of CBS glass-ceramic system

Fig. 8 presents SEM images of samples 5–8. Sample 5 corresponding to formulation I is densely formed by a large number of acicular wollastonite crystal grains, and the crystal grains are full and closely arranged, and the average particle diameter is about 5 μ m. Sample 6 of formulation II is made up of a large number of crystal grains, and the crystal grains are evenly and completely filled, and the average particle diameter is in the range of 3–5 μ m. Sample 7 of formulation III consists of closely arranged crystals, the grains are well developed, the structure is dense, and the

average particle size is in the range of $3-5 \mu m$, showing a good microscopic arrangement. SEM image of sample 8 of formulation IV exhibits that the crystal grains are loosely arranged, the particle sizes are different, and the degree of densification is inferior to that of samples 5–7. This is attributed to the fact that the higher TiO₂ content produces more crystal nuclei, which interfere with the crystal growth, affect the dense arrangement of the wollastonite crystal phase, and produce a small amount of Ti-containing crystal phase. This further affects the compactness of the microstructure. This is consistent with the XRD detection results, which indicates that certain amount of TiO₂ doping promotes the crystallization and enhances the densification. However, excessive TiO₂ leads to the precipitation of the Ti-containing crystal phase and affects the microstructure of sample.



Fig. 8. SEM images of samples 5–8 (See Table 4 for sintering regimes).

The results of the dielectric properties of samples 5-8 and the density of the samples are presented in Table 5 and Fig. 9. The dielectric constant of samples 5-7 gradually decreases with the increase of TiO₂ content, and maintains within a

reasonable range, which indicates that the increase of TiO_2 content can enhance the dielectric properties of samples. However, the performance of sample 8 was slightly lower than that of sample 7, indicating that excessive TiO_2 would impair the dielectric properties of sample. Excellent dielectric property of sample 7 is attributed to the large content of wollastonite crystal phase, and uniform grain development, dense structure, thereby reducing the number of polarizable atoms per unit volume, and greatly reducing the structural loss of the samples. Moreover, this makes the samples obtain lower dielectric constant and dielectric loss, which is consistent with the results of XRD and SEM.

Comparative analysis indicates that sample 7 of formulation III is the optimal sample and meets the market requirements. Its dielectric constant is 1.4 (1 MHz), 1.3 (10 MHz), and the dielectric loss is 3.9×10^{-3} (1 MHz), 3.8×10^{-3} (10 MHz).

Density	Frequency	Dielectric constant	Dielectric loss
(g/cm^3)	(MHz)	(ε_r)	(10^{-3})
2 27	1	6	2.3
2.37	10	6	3.4
2 50	1	2.1	6.8
2.30	10	2.2	7.9
2 70	1	1.4	3.9
2.70	10	1.3	3.8
2.16	1	2.3	4.8
2.40	10	2.4	5.4
	Density (g/cm ³) 2.37 2.58 2.70 2.46	$\begin{array}{c c} Density & Frequency \\ \hline (g/cm^3) & (MHz) \\ \hline 2.37 & 1 \\ 10 \\ \hline 2.58 & 1 \\ 10 \\ \hline 2.58 & 10 \\ \hline 10 \\ \hline 2.46 & 1 \\ 10 \\ \hline \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

Table 5. Dielectric o	constant,	dielectric	loss and	density	of samples	s 5–8.
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Fig. 9. Dielectric constant and dielectric loss of samples 5-8.

4. Conclusions

In this study, CBS glass-ceramics with four formulations were obtained to investigate the effect of TiO_2 on crystal phase, microstructure, and dielectric properties. In summary, following conclusions can be drawn:

- (1) TiO₂ doping reduced the transition temperature and crystallization temperature of CBS glass-ceramics and promoted the precipitation of wollastonite crystal phase. With the increase in the mass fraction of TiO₂ from 0 to 3 wt.%, the transition temperature and crystallization temperature of CBS glass-ceramics decreased by 12.9 and 27.6 °C, respectively. However, excessive TiO₂ caused the CBS glass-ceramics to precipitate a hetero-crystalline phase, which led to the destruction of close arrangement of the crystal grains in the microstructure. Furthermore, two-step sintering promoted crystallization, enhanced densification, and reduced dielectric constant and dielectric loss. The two-step sintering was carried out at a temperature higher than the crystallization temperature of 20 °C, and the performance of the sample was found to be superior.
- (2) Herein, sample 7, with the composition of CaO: SiO₂: $B_2O_3 = 1:1:0.6$ and doping mass fraction of 2 wt.% of TiO₂., exhibited the best performance, which meets the requirements for the target materials. The sintering system was heated to 700 °C at a rate of 3 °C min⁻¹, held for 1 h, and heated to 882 °C at the same rate. After 2 h of heat preservation, samples were cooled down in a muffle furnace. After two-step sintering process, the sample 7 acquired dielectric constant of 1.4 (1 MHz), 1.3 (10 MHz), and a dielectric loss of 3.9×10^{-3} (1 MHz), 3.8×10^{-3} (10 MHz).

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References

- O. Dernovsek, M. Eberstein, W.A. Schiller, et al. LTCC glass-ceramic composites for microwave application[J]. Journal of the European Ceramic Society, 2001, 21(10):1693-1697.
- [2] H. Wang, Z. He, D. Li, et al. Low temperature sintering and microwave dielectric properties of CaSiO₃-Al₂O₃ ceramics for LTCC applications[J]. Ceramics International, 2014, 40(3):3895-3902.
- X. Chen, W. Zhang, S. Bai, et al. Densification and characterization of SiO₂-B₂O₃ -CaO-MgO glass/Al₂O₃ composites for LTCC application[J]. Ceramics International, 2013, 39(6): 6355-6361.
- [4] J. Rodel, A. B. N. Kounga, M. Weissenberger-Eibl, et al. Development of a roadmap for advanced ceramics: 2010-2025 [J]. Journal of the European Ceramic Society, 2009, 29(9):1549-1560.
- [5] S. Arcaro, F.R. Cesconeto, F. Raupp-Pereira, et al. Synthesis and characterization of LZS/α-Al₂O₃ glass ceramic composites for applications in the LTCC technology[J]. Ceramics International, 2014, 40(4):5269-5274.
- [6] L. J. Golonka. Technology and application of Low Temperature Cofired Ceramic (LTCC) based sensors and Microsystems[J]. Bulletin of the Polish Academy of Sciences-Technical Sciences, 2006, 54(2):221-231.
- [7] L. Yuan, B. Liu, N. Shen, et al. Synthesis and properties of borosilicate/AlN composite for low temperature co-fired ceramics application[J]. Journal of Alloys and Compounds, 2014, 593:34-40.
- [8] N. Mori, Y. Sugimoto, J. Harada, et al. Dielectric properties of new glass-ceramics for LTCC applied to microwave or millimeter-wave frequencies[J]. Journal of the European Ceramic Society, 2006, 26(10-11):1925-1928.
- [9] H. Dannheim, A. Roosen. Effect of metallization on the lifetime prediction of mechanically stressed low-temperature co-fired ceramic multilayers[J]. Journal of the American Ceramic Society, 2005, 88(8):2188-2194.
- [10] A. Karamanov, M. Pelino. Induced crystallization porosity and properties of sintereds diopside and wollastonite glass-ceramics[J]. Journal of the European Ceramic Society, 2008, 28(3):555-562.

- [11] K. Singh, I. Bala, V. Kumar. Structural, optical and bioactive properties of calcium borosilicate glasses[J]. Ceramics International, 2009, 35(8):3401-3406.
- M. He, M.Q. Wu, Z.R. Zhang, et al. Quantitative analysis of crystalline and remaining glass phases in CaO–B₂O₃–SiO₂ ternary system glass ceramics[J]. Journal of Alloys and Compounds, 2010, 506(2):757-760.
- [13] G.H. Chen, L.J. Tang, et, al. Synthesis and characterization of CBS glass/ceramic composites for LTCC application[J]. Journal of Alloys and Compounds, 2008, 478(1-2):858-862.
- [14] C.S. Cheng, C.C. Chou, C.S. Chen, et al. Microwave dielectric properties of glass-MCT low temperature co-firable ceramics[J]. Journal of the European Ceramic Society, 2004, 24(6):1795-1798.
- [15] H.K. Zhu, M. Liu. H. G. Zhou, et al. Preparation and properties of low-temperature co-fired ceramic of CaO–SiO₂ –B₂O₃ system[J]. Journal of Materials Science: Materials in Electronics, 2006 17(8):637-641.
- [16] J.H. Jean, C.R. Chang, C.D. Lei, Sintering of a Crystallizable CaO-B₂O₃-SiO₂
 Glass with Silver[J]. Journal of the American Ceramic Society, 2004, 87(7):1244-1249.
- [17] S. Kemethmüller, M. Hagymasi, A. Stiegelschmitt, et al. Viscous Flow as the Driving Force for the Densification of Low-Temperature Co-Fired Ceramics[J]. Journal of the American Ceramic Society, 2007, 90(1):64-70.
- [18] D.U. Tulyaganov, M.J. Ribeiro, J.A. Labrincha. Development of glass-ceramics by sintering and crystallization of fine powders of calcium-magnesium-aluminosilicate glass[J]. Ceramics International, 2002, 28(5):515-520.
- [19] X.H. Zhou, B. Li, S.R. Zhang, et al. Effect of Ca/Si ratio on the microstructures and properties of CaO-B₂O₃ -SiO₂ glass-ceramics[J]. Journal of Materials Science: Materials in Electronics, 2009 20(3):262-266.
- [20] H. Zhu, M. Liu, H. Zhou, et al. Preparation and properties of low-temperature co-fired ceramic of CaO–SiO₂–B₂O₃ system[J]. Journal of Materials Science Materials in Electronics, 2006, 17(8):637-641.
- [21] C.C. Chiang, S.F. Wang, Y.R. Wang, et al. Densification and microwave dielectric properties of CaO-B₂O₃-SiO₂ system glass-ceramics[J]. Ceramics International, 2008, 34(3):599-604.
- [22] H. Shao, T. Wang, Q. Zhang. Preparation and properties of CaO-SiO₂-B₂O₃

glass-ceramic at low temperature[J]. Journal of Alloys Compounds, 2009, 484(1):2-5.

- [23] C.R. Chang, J.H. Jean. Crystallization kinetics and mechanism of low-dielectric, low-temperature, cofirable CaO-B₂O₃-SiO₂ glass-ceramics[J]. Journal of the American Ceramic Society, 1999, 82(7):1725-1732.
- [24] D.F. He. C Gao. Effect of boron on crystallization, microstructure and dielectric properties of CBS glass-ceramics[J]. Ceramics International, 2018, 44(14): 16246-16255.
- [25] H.K. Zhu, H. Zhou, M. Liu, et al. Low temperature sintering and properties of CaO-B₂O₃-SiO₂ system glass ceramic for LTCC applications[J]. Journal of Alloys and Compounds, 2009, 482(1-2): 272-275.
- [26] H.I. Hsiang, S.W. Yung, C.C. Wang. Effects of the addition of alumina on the crystallization, densification and dielectric properties of CaO-MgO-Al₂O₃-SiO₂, glass in the presence of ZrO₂[J]. Ceramics International, 2014, 40(10):15807-15813.
- [27] X.H. Zhou, E.Z. Li, S.L. Yang, et al. Effects of La₂O₃-B₂O₃ on the flexural strength and microwave dielectric properties of low temperature co-fired CaO-B₂O₃-SiO₂ glass-ceramic[J]. Ceramics International, 2012, 38(7):5551-5555.
- [28] S.F. Wang, C.C. Chiang, Y.R. Wang, et al. Effects of additives on the densification and microwave dielectric properties of binary CaO-B₂O₃-SiO₂ glass[J]. Japanese Journal of Applied Physics, 2010, 49(49):1-5.
- [29] G.A. Khater. Influence of Cr₂O₃, LiF, CaF₂ and TiO₂ nucleants on the crystallization behavior and microstructure of glass-ceramics based on blast-furnace slag[J]. ceramics International, 2011, 37(7):2193-2199.
- [30] J. Yang, S.G. Zhang, B. Liu, et al. Effect of TiO₂ on Crystallization, Microstructure and Mechanical Properties of Glass-ceramics[J]. Journal of Iron and Steel Research, International, 2015, 22(12):1113-1117.
- [31] M. Rezvani, B. Eftekhari-Yekt, M. Solati-Hashjin, et al. Effect of Cr₂O₃, Fe₂O₃ and TiO₂ nucleants on the crystallization behavior of SiO₂-Al₂O₃-CaO-MgO (R₂O) glass-ceramics[J]. Ceramics International, 2005, 31(1):75-80.
- [32] D.P. Mukherjee, S.K. Das, Influence of TiO₂ content on the crystallization and microstructure of machinable glass-ceramics[J]. Journal of Asian Ceramic Societies, 2015, 4(1):55-60.
- [33] T. Ebadzadeh, E. Ghasemi. Effect of TiO_2 addition on the stability of t-ZrO₂ in

mullite-ZrO₂ composites prepared from various starting materials[J]. Ceramics International, 2002, 28(4):447-450.

- [34] A. Dugué, O. Dymshits, et al. Structural transformations and spectroscopic properties of Ni-doped magnesium aluminosilicate glass-ceramics nucleated by a mixture of TiO₂ and ZrO₂ for broadband near-IR light emission[J]. Journal of Alloys and Compounds, 2019, 780:137-146.
- [35] H.K. Zhu, H.Q. Zhou, M. Liu, et al. Microstructure and microwave dielectric characteristics of CaO–B₂O₃–SiO₂ glass ceramics[J]. Journal of Materials Science Materials in Electronics, 2009, 20(11):1135-1139.
- [36] C.C. Chiang, S.F. Wang, Y.R. Wang, et al. Characterizations of CaO–B₂O₃–SiO₂ glass–ceramics: Thermal and electrical properties[J]. Journal of Alloys and Compounds, 2008, 461(1-2):612-616.
- [37] S.F. Wang, Y.R. Wang, Y.F. Hsu, et al. Densification and microwave dielectric behaviors of CaO–B₂O₃–SiO₂ glass-ceramics prepared from a binary glass composite[J]. Journal of Alloys and Compounds, 2010, 498(2):211-216.
- [38] P.Y. Li, S.B. Wang, J.G. Liu, et al. Effects of B₂O₃ content and sintering temperature on crystallization and microstructure of CBS glass–ceramic coatings[J]. Applied Surface Science, 2015, 356:1180-1188.
- [39] L.C. Ren, X.F. Luo, L.S. Hu, et al. Synthesis and characterization of LTCC compositions with middle permittivity based on CaO-B₂O₃-SiO₂ glass/CaTiO₃ system[J]. Journal of the European Ceramic Society, 2016, 37(2):619-623.
- [40] H.Y. Yang, E.Z. Li, C.L. Sun, et al. The Influence of Sintering Temperature on the Microwave Dielectric Properties of Mg₂SiO₄ Ceramics with CaO-B₂O₃-SiO₂ Addition[J]. Journal of Electronic Materials, 2017, 46(2):1048-1054.

 TiO_2 reduced the sintering temperature of CBS glass-ceramics.

TiO₂ promoted the precipitation of wollastonite crystal phase.

Excessive TiO₂ destroyed crystal structure, and damaged close arrangement of crystal

grains.