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Low temperature preparation of the β-$CaSiO_3$ ceramics based on the system $CaO–SiO_2–BaO–B_2O_3$

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ABSTRACT

The dense β-$CaSiO_3$ ceramics based on the system $CaO–SiO_2–BaO–B_2O_3$ are fabricated by traditional solid-state preparation process at a densification temperature range of 930–970 °C. The introduction of BaO and B_2O_3 to the binary system $CaO–SiO_2$ is achieved by the means of a chemical combination of H_2SiO_3, H_3BO_3, Ca $(OH)_2$ and $Ba(OH)_2·8H_2O$, which finally results in the formation of a hydrated barium borate phase with low melting characteristics. In turn, by a liquid phase sintering aid of the hydrated barium borate, the densification temperature of β-$CaSiO_3$ ceramics can be decreased availably and the dense microstructure can be achieved accordingly. The β-$CaSiO_3$ ceramics with the optimum content of BaO and B_2O_3 can express good mechanical strength (bending strength: 133 MPa) and excellent dielectric properties (ε_r: 6.5; loss: 5×10^{-4}).

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1. Introduction

Nowadays, β-$CaSiO_3$, i.e., β-wollastonite is widely applied to low temperature co-fired ceramic (LTCC) technology due to its excellent dielectric properties (ε_r: 5, tan α: $1.0–3.0 \times 10^{-4}$) and good thermal stability [1]. As one of technological characteristics of LTCC, the sintering temperature of β-$CaSiO_3$ ceramics cannot exceed the melting point of electrode materials such as a silver solder (melt point: 961 °C). According to the technical characteristics, the preparation of the dense β-$CaSiO_3$ ceramics with the densification temperature below 960 °C become difficult by using traditional solid-state process, since the sintering temperature range of pure $CaSiO_3$ is very narrow and high [2]. At present, most of the preparations of dense $CaSiO_3$ ceramics mainly depend on the fabrication of $CaO–B_2O_3–SiO_2$ glass ceramics [3–5] and sol–gel methods [6,7]. The $CaO–B_2O_3–SiO_2$ glass ceramics with a low densification temperature range of 800–900 °C are prepared via the devitrification of the $CaO–SiO_2–B_2O_3$ glasses with a melting temperature beyond 1300 °C. Also, the sol–gel methods can availably decrease the densification temperature of the $CaSiO_3$ ceramics by mixing the chemical constituents at a molecular level in solution. In addition, in order to obtain the dense $CaSiO_3$ ceramics by a more convenient method, Wang et al. [8] used B_2O_3 as a flux to improve the traditional solid-state process and obtain the dense β-$CaSiO_3$ ceramics at 1100 °C. In the above methods, the traditional solid-state preparation process with the addition of fluxes is relatively simple, but a lower densification temperature need to be achieved by a choice of fluxes to match the melting point of a silver electrode materials. Barium borate is characterized by low melting characteristics (melting temperature: 800–900 °C) [9–12], it, thus, is widely used to decrease the sintering temperature of ceramic materials as a flux. In present work, the introduction of BaO and B_2O_3 to the binary system $CaO–SiO_2$ is expected to achieve the low temperature preparation of dense β-$CaSiO_3$ ceramics. Especially, by the means of a chemical combination of H_3BO_3 and $Ba(OH)_2·8H_2O$, a hydrated barium borate phase can be formed easily from the hydrated products of H_2SiO_3, H_3BO_3, Ca $(OH)_2$ and $Ba(OH)_2·8H_2O$ (a quaternary system $CaO–SiO_2–BaO–B_2O_3$). Consequently, the dense β-$CaSiO_3$ ceramics with the low densification temperature can be achieved availably by a liquid phase sintering aid of barium borate. In addition, dielectric, thermal and mechanical properties of the β-$CaSiO_3$ ceramics are investigated in detail in terms of its major crystal phases and microstructures. The objective of the work is to develop a convenient way for the fabrication of the dense β-$CaSiO_3$ ceramics with a low densification temperature, which can match with the melting point of a sliver electrode material.

2. Experimental

H_2SiO_3, H_3BO_3, Ca $(OH)_2$ and $Ba(OH)_2·8H_2O$ with purity higher than 99% were used as the starting materials. According to the designed compositions in Table 1, the above materials were weighed and milled with de-ionized water for 7 h. The weight ratio of the water to solid was regulated to 4/1. Upon treatment, the slurries were dried at 80 °C and then were pre-sintered at 700 °C for 3 h. Subsequently, the pre-sintered powders with the particle size of 0.5–1.0 μm were molded into

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Table 1
The chemical composition of the $CaSiO_3$ ceramic specimens.

Specimen	Composition (wt.%)	B_2O_3/(BaO + B_2O_3) (mol%)	The content of BaO and B_2O_3 in the specimen (wt.%)
CB1	35CaO–30SiO_2–15BaO–20B_2O_3	74	35
CB2	40CaO–30SiO_2–10BaO–20B_2O_3	81	30
CB3	45CaO–30SiO_2–5BaO–20B_2O_3	90	25
CB4	40CaO–40SiO_2–10BaO–10B_2O_3	67	20
CB5	40CaO–40SiO_2–5BaO–15B_2O_3	87	20
CB6	45CaO–40SiO_2–5BaO–10B_2O_3	81	15
CB7	45CaO–45SiO_2–5BaO–5B_2O_3	69	10

green bodies under a compressive stress of 20 MPa. Finally, the specimens were obtained by continuously sintering the green bodies at 400 °C for 3 h, 700 °C for 3 h and selected densification temperature (930–970 °C) for 15 min. The specimens were analyzed by using a scanning electron microscope (JSM-6490LV, Japan), a X-ray powder diffraction patterns and a differential scanning calorimetry (NETZSCH STA449C, Germany, heating at a rate of 10 °C min^{-1}), the X-ray powder diffraction patterns were recorded on a D/Max-IIIA machine (Rigaku Industrial Corporation, Japan) using Cu Kα Radiation (40 kV, 30 mA) with a scanning rate of 2° min^{-1}. The coefficient of thermal expansion (CTE) values of the specimens in a temperature range of 25–400 °C were tested by a dilatometer (NETZSCH DIL402PC, Germany, heating at a rate of 3 °C min^{-1}). Dielectric constant and dielectric loss were tested by a PRECISION LCR METER instrument (Agilent 4284A, U.S.A.).

3. Results and discussion

Due to low melting characteristics, barium borate is widely used to decrease the densification temperature of ceramic materials as a flux agent. As the application for the preparation of $CaSiO_3$ ceramics, the formation of a hydrated barium borate phase in hydrated products of H_2SiO_3, H_3BO_3, $Ca(OH)_2$ and $Ba(OH)_2{\cdot}8H_2O$ is important to achieve the low temperature preparation of $CaSiO_3$ ceramics. Fig. 1 represents the XRD pattern of a ceramic slurry based on the system CaO–SiO_2–BaO–B_2O_3 and dried at 80 °C. As is shown on the XRD pattern, the ceramic slurry is composed of hydrated barium borate, hydrated calcium silicate as well as the other compounds. It indicates that hydrated barium borate and hydrated calcium silicate can be easily synthesized by the means of the chemical combination of H_2SiO_3, H_3BO_3, $Ca(OH)_2$ and $Ba(OH)_2{\cdot}8H_2O$. Fig. 2 shows TG and DSC curves of two ceramic slurries and a hydrated product of the chemical combination of H_3BO_3 and $Ba(OH)_2{\cdot}8H_2O$. As is seen form the TG and DSC curve of the three specimens, it can be estimated that, with an elevated temperature, a dehydration of hydrated products, a chemical combination of barium or calcium compounds and silicon or boron polymer molecules, a vaporization of B_2O_3 and melting are continuously occurring. In addition, a endothermal peak at about 110 °C is observed on the DSC curve of the ceramic slurry 1, which could be correlative to the evaporation of water molecules of residual $Ba(OH)_2{\cdot}8H_2O$ and H_2SiO_3 in the ceramic slurry. According to the phase diagram of the binary system BaO–B_2O_3 [9,13], the onset of a liquid phase in the binary system BaO–B_2O_3 can be observed at least 869 °C. Specially, in the phase diagram of the binary system BaO–B_2O_3, a low eutectic zone is located at a range of 50–70 mol% B_2O_3 content, which consequently supplies a reference for the design of the flux agent of barium borate. Furthermore, considering the volatility of B_2O_3, the B_2O_3 content in the BaO–B_2O_3 composition designed in the work is totally higher than that in the eutectic composition. As a reference, a specimen with 50BaO–50B_2O_3 percent composition by mass and a $CaSiO_3$ ceramic specimen with 30CaO–20SiO_2–30BaO–20B_2O_3 percent composition by mass are made by sintering their green bodies at 900 °C for 60 min and 950 °C for 15 min, respectively. The pictures of the two reference specimens are shown on Fig. 3. It can be seen that the sintered specimen with 50BaO–50B_2O_3 composition is a glassy form whereas the sintered $CaSiO_3$ ceramic specimen is a melting form. Especially,

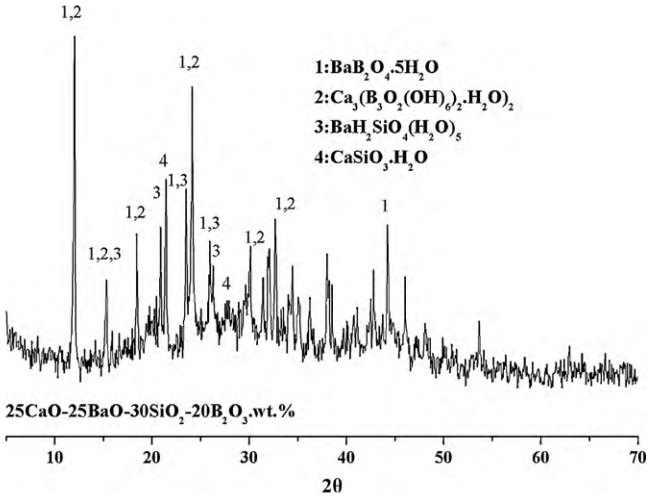

Fig. 1. The XRD pattern of $CaSiO_3$ ceramic slurry.

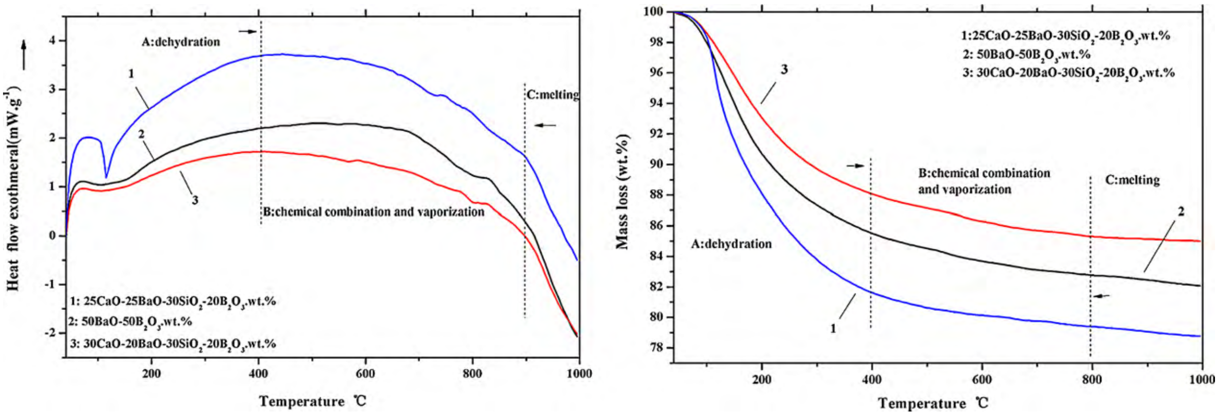

Fig. 2. The DSC curves of two $CaSiO_3$ ceramic slurries and a hydrated product of the chemical combination of H_3BO_3 and $Ba(OH)_2{\cdot}8H_2O$.

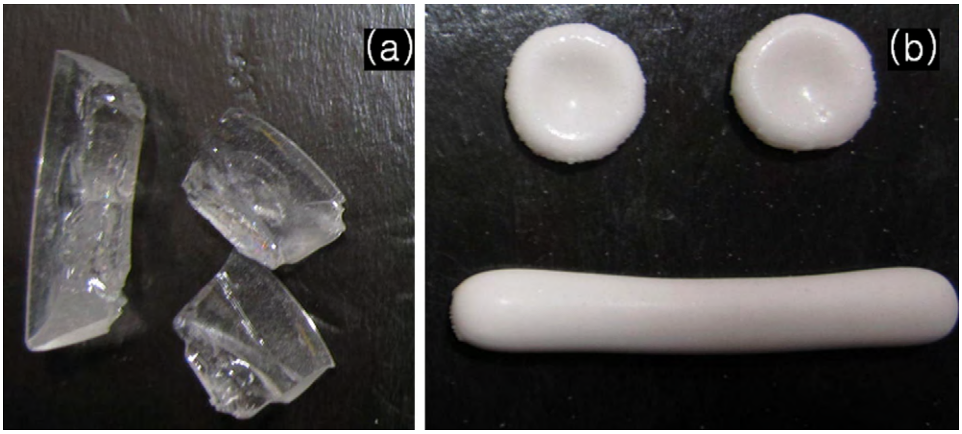

Fig. 3. The pictures of the two reference specimens. (a) A specimen with $50BaO–50B_2O_3$ percent composition by mass and sintered at 900 °C for 60 min; (b) a $CaSiO_3$ ceramic specimen with $30CaO–20SiO_2–30BaO–20B_2O_3$ percent composition by mass and sintered at 950 °C for 15 min.

according to the XRD analysis results shown on Fig. 4, the sintered specimen with $50BaO–50B_2O_3$ composition is a non-crystalline form, indicating that it can be melted completely at least 900 °C. Consequently, it suggests that the introduction of BaO and B_2O_3 to the binary system $CaO–SiO_2$ can greatly lower the densification temperature of $CaSiO_3$ ceramics so as to availably improve its sintering behavior. However, in order to obtain the dense $CaSiO_3$ ceramics with a high content of a $CaSiO_3$ phase, the existence of excessive BaO and B_2O_3 content in the $CaSiO_3$ ceramics is not expected. According to the results, a serial of the $CaSiO_3$ ceramic specimens based on the system $CaO–SiO_2–BaO–B_2O_3$ were made by traditional solid-state preparation process. The XRD patterns of the $CaSiO_3$ ceramic specimens are represented in Fig. 4. As is shown on Fig. 4, a β-$CaSiO_3$ phase can be observed in the XRD patterns of all $CaSiO_3$ ceramic specimens. In connection with the composition of the $CaSiO_3$ ceramics, it is found that the intensity of the diffraction patterns of β-$CaSiO_3$ phase is getting stronger with decreasing the content of BaO and B_2O_3 in the composition. Correspondingly, the relative content of the β-$CaSiO_3$ phase in the specimens, which is obtained by XRD analytical software (MDI Jade.6.5), is increasing. It indicates that the $CaSiO_3$ ceramics with a high content of a β-$CaSiO_3$ phase can be availably fabricated by the regulation of the BaO and B_2O_3 content in the composition at a sintering temperature below 1000 °C. Consequently, on the basis of the classical theory of the liquid phase sintering [14], the fabrication of the $CaSiO_3$ ceramics can be understood as the mechanism that, by a melting phase of barium borate, the β-$CaSiO_3$ phase formation and the occurrence of the densification were achieved along with crystal particle dispersing, rearrangement, solution-precipitation and solid-state sintering. It can be seen that the preparation method of the $CaSiO_3$ ceramics is not only relative convenient but also can availably obtain the single phase β-$CaSiO_3$ ceramics at a relative low densification temperature. As is well known, glass ceramics and glass/ceramic [15] composites are applied widely to LTCC multi-layer structures due to their low sintering temperatures and tailored dielectric properties. However, the manufactures of most of glass materials are usually a complex processes including melting, cooling and crystallization. Especially, as LTCC applications, a single phase ceramic materials is more favorable to achieve the high reliability and a good thermal stability. Therefore, the $CaSiO_3$ ceramics obtained by the present preparation process is available for LTCC applications as a candidate material. On the other hand, one can see that the presence of the other crystal phases in the $CaSiO_3$ ceramics is still correlative with the BaO and B_2O_3 content in the composition. As a high BaO and B_2O_3 content, crystal phases of the $CaSiO_3$ ceramics (CB1, CB2, CB3) also include $Ba_2Ca(B_2O_3)_2$ compounds, but it is gradually disappear with decreasing the content of BaO and B_2O_3 in the composition. The results indicate that excessive BaO and B_2O_3 in the composition are unbeneficial to fabricate the $CaSiO_3$ ceramics with a high content of a β-$CaSiO_3$ phase. It is worth noting that, while the content of BaO and B_2O_3 in the composition is less than

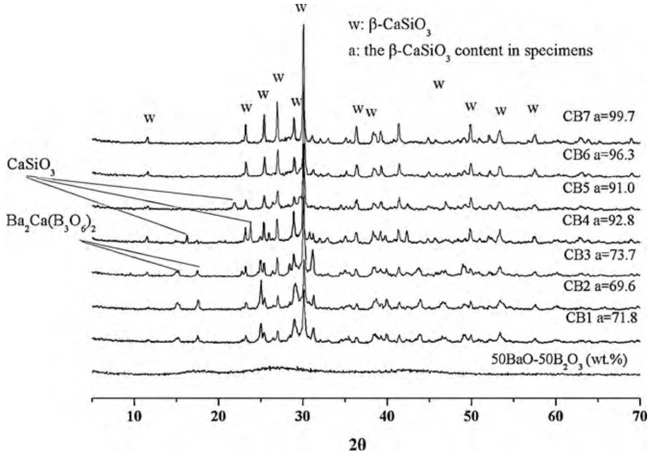

Fig. 4. The XRD patterns of the $CaSiO_3$ ceramic specimens.

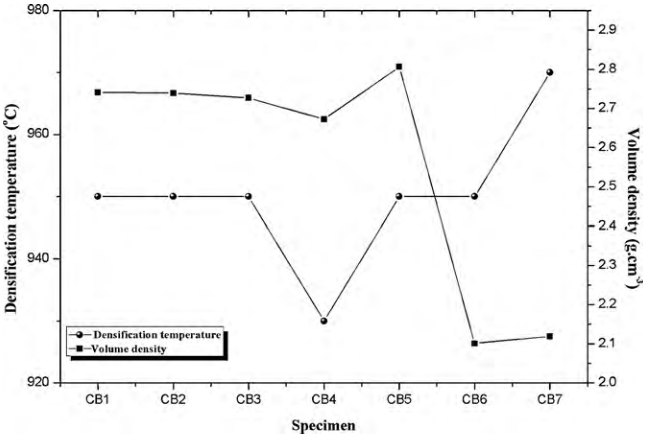

Fig. 5. Densification temperature and volume density of the $CaSiO_3$ ceramic specimens.

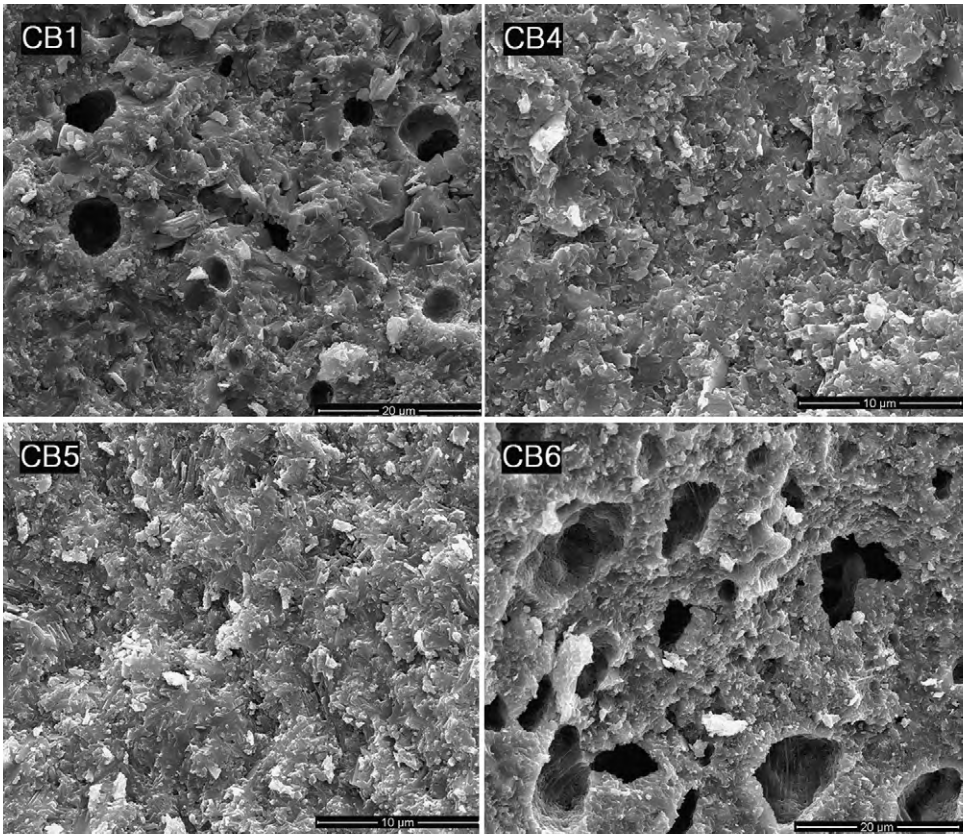

Fig. 6. The cross-section SEM images of the $CaSiO_3$ ceramic specimens.

20 wt.%, there are not any barium and borate compounds in the $CaSiO_3$ ceramics besides a small quantity of the other types of $CaSiO_3$ crystals, indicating that the BaO and B_2O_3 components exist in the $CaSiO_3$ ceramics only as a glassy form.

On the other hand, with the variation of the BaO and B_2O_3 content in the composition, the densification temperature and the volume density of the $CaSiO_3$ ceramics are changed accordingly. Densification temperature and volume density dependence of the composition are shown on Fig. 5. It is found that, in addition to the specimens CB4 and CB7, the densification temperature of all specimens is located at 950 °C. Due to the fact that the amounts of the liquid phase in the $CaSiO_3$ ceramics is increased with increasing the BaO and B_2O_3 content in the composition, the specimen CB7 with BaO and B_2O_3 fraction in the amounts of 10 wt.% has a higher densification temperature(up to 970 °C) than the other specimens. It is believed that the high densification temperature of the specimen CB7 is attributed to the absence of a liquid phase, which consequently also results in the porosity and a low volume density. The low volume density of the specimens CB6 and CB7 is explained in this case by the fact that the amount of a liquid phase in the two specimens is too small to fill all pores. In contrast with the specimens CB6 and CB7, the volume density of the other specimens is centralized mainly on the range of 2.67–2.80 g cm^{-1}. The above results are shown accordingly on the cross-section SEM images of the $CaSiO_3$ ceramics. As is shown on Fig. 6, a porous microstructure can be observed in the micrograph of the specimen CB6, indicating that it is in agreement with its low volume density. It, thus, can be believed that barium borate play an important role in the improvement of the sintering behavior of the $CaSiO_3$ ceramics. However, the specimen CB1 with a high content of BaO and B_2O_3 similarly

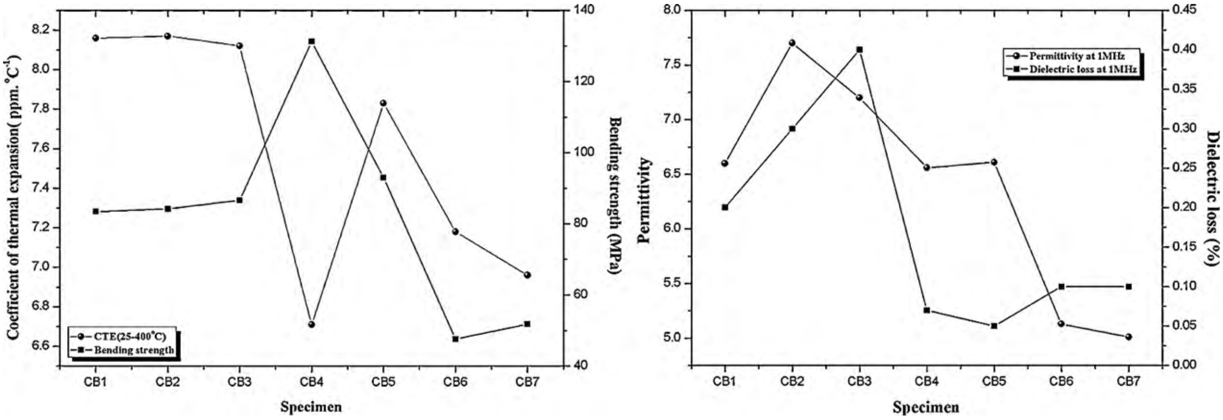

Fig. 7. Thermal, mechanical and dielectric properties of the $CaSiO_3$ ceramic specimens.

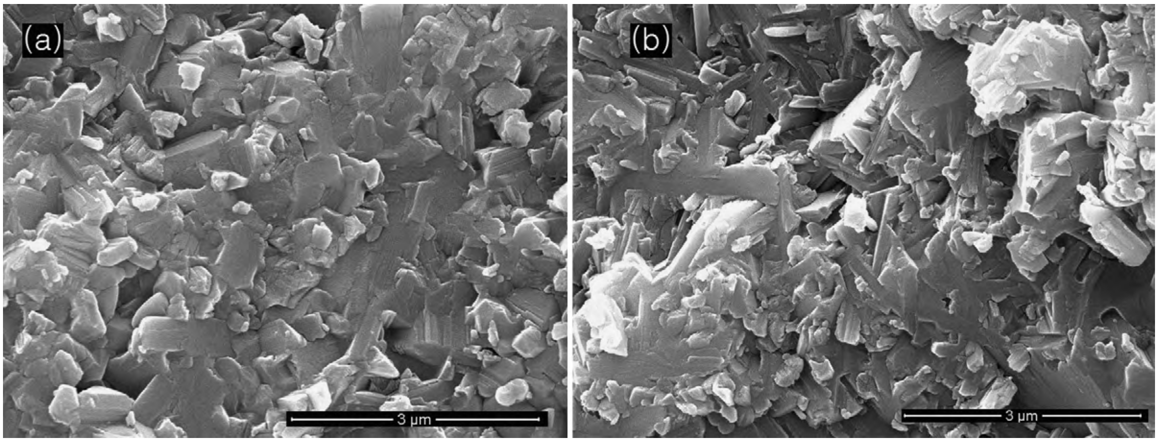

Fig. 8. The cross-section SEM images of the specimens CB4 (a) and CB5 (b).

shows the amounts of the pores. It is estimated that the remaining pores are caused by the thermal swelling of excessive melting phase during sintering. In contrast to the specimens CB1 and CB6, the specimens CB4 and CB5 with BaO and B_2O_3 in the amounts of 20 wt.% show a compacted microstructure. The optimum BaO and B_2O_3 content in the composition are important not only to fabricate the $CaSiO_3$ ceramics with a high content of β-$CaSiO_3$ phase but also to achieve a dense microstructure.

Usually, the physical properties of ceramic materials can be decided by the microstructures and their major crystal phases. In order to determine the correlation between the physical properties and the microstructures as well as the major mineral phases, Fig. 7 gives thermal, mechanical and dielectric properties of the $CaSiO_3$ ceramics. As shown on Fig. 7, the specimens CB4 and CB5 express a bending strength of about 133 MPa and 93 MPa, respectively. The specimen CB6 with a porous microstructure shows a bending strength of about 45 MPa. Therefore, the porous microstructure is disadvantage to the mechanical properties. In the case of coefficient of thermal expansion (CTE), CTE value of the specimens is totally decreasing with increasing the content of a β-$CaSiO_3$ phase in the $CaSiO_3$ ceramics. But the CTE value of the specimen CB4 is the lowest in that of all specimens, which and the CTE value of the specimen CB7 are closer to that of a pure β-$CaSiO_3$ crystal (CTE: 6.5–6.9 ppm $^\circ C^{-1}$[16]). It suggests that the CTE value could be correlative to the crystallization of a β-$CaSiO_3$ phase. According to the phase diagram of the binary system BaO–B_2O_3 and the chemical composition of the specimens in Table 1, the $B_2O_3/(BaO + B_2O_3)$ molar fraction of the specimen CB4 is located at a eutectic zone with a temperature range of 869–900 °C in the phase diagram of the binary system BaO–B_2O_3, which, thus, can help to achieve the densification sintering of the specimen CB4 at the relative low densification temperature (930 °C). Also, the appropriate content of BaO and B_2O_3 in the system CaO–SiO_2–BaO–B_2O_3 can supply a sufficient amount of a liquid phase for the crystallization of a β-$CaSiO_3$ phase. Consequently, the eutectic composition and a sufficient amount of a liquid phase can offer more possibilities to set a proper sintering behavior and achieve the better crystallization of a β-$CaSiO_3$ phase in the specimen CB4. In Fig. 8, we can see that the connection among the crystal grains in the specimen CB4 is tighter than that in the specimen CB5. The difference in the microstructures of the two specimens could be a reason that the bending strength of CB4 is higher that of specimen CB5. Furthermore, all these factors also lead to an influence on the other physical properties such as dielectric constant and loss. It can be found that, with the increase of β-$CaSiO_3$ phase content, dielectric properties of the $CaSiO_3$ ceramic are greatly improved. Therefore, the improved dielectric properties can be expected to availably achieve by the regulation of the BaO and B_2O_3 content in the composition. The best dielectric properties are shown on the specimens CB4 and CB5, whose permittivity and loss are 6.6, 7×10^{-4} and 6.5, 5×10^{-4}, respectively, meaning that a dense microstructure is equally important to the achievement of the improved dielectric properties. Consequently, the appropriate content of BaO and B_2O_3 in the quaternary system CaO–SiO_2–BaO–B_2O_3 can be referenced according to the composition of the specimen CB4 and CB5.

4. Conclusions

In summary, the dense β-$CaSiO_3$ ceramics with a densification temperature range of 930–970 °C are successfully fabricated via traditional solid-state preparation process under the sintering aid of barium borate. Thermal, mechanical and dielectric properties of the dense β-$CaSiO_3$ ceramics have been investigated in terms of the BaO and B_2O_3 content in the composition, the results show that the low temperature preparation of the dense β-$CaSiO_3$ ceramics is not only correlative with a $B_2O_3/(BaO + B_2O_3)$ molar fraction in the specimen, but also depends on an appropriate content of BaO and B_2O_3 in the quaternary system CaO–SiO_2–BaO–B_2O_3. The optimum BaO and B_2O_3 content in the $CaSiO_3$ ceramics (the specimens CB4 and CB5) can help to achieve good physical properties (bending strength: 133 MPa; ε_r: 6.5; loss: 5×10^{-4}) and decrease densification temperature (930 °C and 950 °C), indicating that the dense β-$CaSiO_3$ ceramics can be co-fired with a sliver electrode material and is promising for the application of LTCC technologies as a candidate material.

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