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ScienceDirect

Ceramics International 36 (2010) 1473–1478

CERAMICS INTERNATIONAL

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Short communication

Different microstructure $BaO–B_2O_3–SiO_2$ glass/ceramic composites depending on high-temperature wetting affinity

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Received 15 June 2009; received in revised form 26 September 2009; accepted 18 December 2009
Available online 28 January 2010

Abstract

In this work, we propose a simple but effective method to fabricate $BaO–B_2O_3–SiO_2$ glass/ceramic composites with different microstructures that depend on the high-temperature wetting affinity. The experimental results showed that the wetting affinity between oxide ceramic and the $BaO–B_2O_3–SiO_2$ glass matrix could strongly affect the driving force of densification and crystallization and finally the microstructure of the glass/ceramic composites. It was found that suitable amounts of alumina powders could obviously increase the driving force for sintering of glass by increasing the capillary pressure. In this case, the contact angle between alumina and glass matrix is about 24° at high temperature and a densified and homogeneous microstructure of glass/alumina composite was obtained. On the contrary, rutile powders additive was found to result in higher phase separation and crystallization during the sintering of glass/rutile composites. In this case, the contact angle between rutile and glass matrix is about 124° at high temperature, and the sintered body has a lower dielectric loss than the sample with alumina additive. Therefore, the microstructure and dielectric property of glass/ceramic composites could be controlled by adjusting the ceramic composition and wetting affinity between ceramic additive and glass matrix in our study.

Keywords: Glass–ceramics; Electronic packaging; Wetting; Dielectrics

1. Introduction

Low-temperature co-fired ceramic (LTCC) is a low-cost technology for the fabrication of multi-layered ceramic materials that has been widely used for microelectronics packaging, RF filters, resonators, antennae, etc. [1–2,6–11]. A lot of materials and processes are available for blue-tooth technology, optical transceivers, sensors, satellite communication, radar systems, etc. Glass plus ceramics is a basic method for the fabrication of low-temperature co-fired ceramics [1–2,6–11]. At present, the general preparation method cannot accurately predict the dielectric performance of the glass/ceramic composites. It is well known that different microstructures, such as densified or porous structure, can strongly affect their dielectric properties of composites [3]. As a result, the applications of LTCC in high-speed circuits will be limited. Hence, it is very important to control the microstructure of the materials to obtain designable and tunable dielectric performances. Glass/ceramic is a complex multiphase system, usually including glass phase, crystalline phase and pore phase. However, with the traditional route, it is very difficult to control the sinterability of glass/ceramic composites. So it is still a great challenge to intentionally fabricate glass/ceramic with a desired structure [3–5].

In this work, the influence of alumina and rutile powders content on the densification of the $BaO–B_2O_3–SiO_2$ glass/ceramic composites was investigated. By adjusting the content of alumina or rutile additive in the glass/ceramic composite, composite materials with controllable microstructure and designable dielectric properties could be obtained. The wetting behavior of the oxide ceramic, which has a significant effect on the densification driving force, crystallization and microstructure of the glass/ceramic system, has been investigated in detail.

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doi:10.1016/j.ceramint.2010.01.005

2. Experimental procedure

First, the glass matrix was fabricated via the pre-molten method using a mixture of SiO_2, $Ba(OH)_2$ and H_3BO_3 powders with a mole ratio of $BaO/B_2O_3/SiO_2 = 0.32:0.15:0.53$. The powders were ball-milled in ethanol for 24 h, followed by a pre-molten processing at 1200 °C for 2 h in air and quenching in water. The obtained glass was then ball-milled in water for 24 h. The milled glass powders were mixed with a suitable ratio of alumina or rutile powders and pressed into pellets. The glass/ceramic powders were finally fabricated by sintering the pellets at 740–900 °C in air for 0.5 h.

The particle size distribution of pre-molten glass powders was measured with a laser granularity analyzer (Winner 2000). The wetting property between alumina (or rutile) and glass matrix was expressed by contact angles and measured using high-temperature microscopy (Union Optics). To increase measurement precision, the surface of the alumina or rutile pellets was polished, and the glass samples were cut into cubes with dimensions of 1 mm^3. The contact angle was measured by instantaneous photogrammetry when the glass was just molten and suddenly collapsed onto the alumina or rutile substrate. The initial collapsing temperature of the $BaO–B_2O_3–SiO_2$ glass system is about 1100 °C in this experiment.

An alternating current electric field always causes dielectric loss and delay in the dielectric response to the electric field when exerted onto dielectric materials. Permittivity in an alternating-current electric field is defined as complex relative permittivity (ε_r^*) (see Eq. (1)). The dielectric loss factor (D) of a dielectric material is expressed as a dielectric loss tangent (tan δ) (see Eq. (2)), which is the ratio of the imaginary component (ε_r'') to the real component (ε_r') of complex relative permittivity.

$$\varepsilon_r^* = \varepsilon_r' - j\varepsilon_r'' \tag{1}$$

$$\tan\delta = \frac{\varepsilon_r''}{\varepsilon_r'} \tag{2}$$

The relative dielectric constant ε_r and the dissipation factor (tan δ) of the sintered samples were measured on a Agilent E4991A Impedance Analyzer (Agilent Technologies Company, USA) in the frequency range of 1–1000 MHz at room temperature after being coated with silver paste.

The relative density of samples was measured by the Archimedes method. The body and surface microstructures of samples were examined by scanning electron microscope (SEM, LEO1530, Oxford Instruments). To characterize the surface crystallization of sintered glass ceramics, the samples were first polished and then etched in 0.10 M HF solutions for 15 s. The etched surface microstructure of the samples was then observed under a stereoscopic microscope. The content of glass phase on the surface was determined by the extent of etching of the sintered bodies—the more etched pits that were present, the greater the glass phase content on the sample surface.

3. Results

Fig. 1 shows the particle size distribution of glass powders that were pre-molten at 1200 °C for 2 h. It can be seen that the average particle size of the powders is around 4.5 μm and their sinterability should be much poor than fine powders. But in this study, we promote the sinterability of the coarse glass powders by adding alumina to the glass matrix. The experimental results show that high density of glass/alumina composites were obtained and the highest density of glass/alumina was formed with an alumina fraction of 5 wt% under sintering temperature of 800 °C, as shown in Fig. 2.

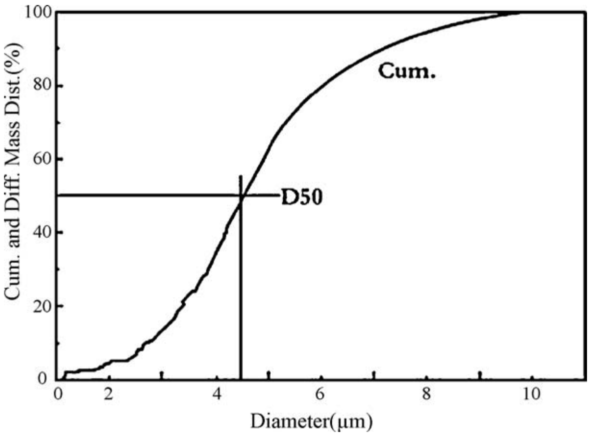

Fig. 1. The particle size distribution of $BaO–B_2O_3–SiO_2$ glass powders prepared by pre-molten method.

Usually, the highest relative density of sintered body is determined by sintering temperature when its composition is fixed. In this work, the highest relative density glass/ceramic varies with the ceramic additive fractions. The densification of glass/ceramic materials strongly depends on the fraction of ceramic additive in the composite system. Fig. 2 shows the relationship between alumina additive fraction and the highest relative density of glass/ceramics. It can be seen that the highest relative density of the glass/alumina system changes with the ceramic fraction and a maximum value of about 98% is obtained when the glass/alumina is sintered at about 800 °C with an alumina fraction of 5 wt%. However, the highest relative density of glass/rutile is about 92% when it is sintered

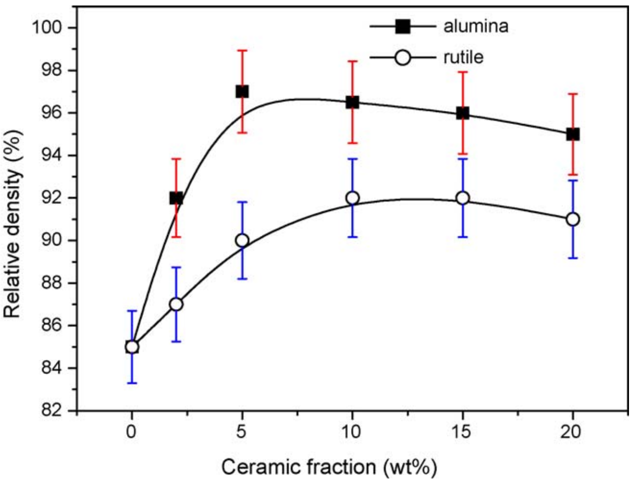

Fig. 2. The variation of relative density of the sintered sample with ceramic fraction.

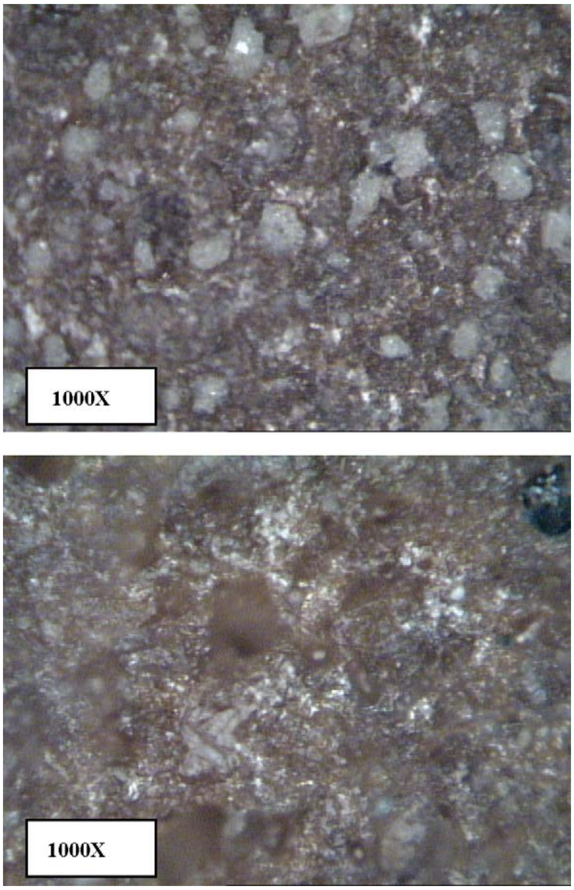

Fig. 3. SEM images of the surface microstructure of etched sample prepared by sintering: (a) BaO–B_2O_3–SiO_2 glass with 10 wt% rutile at 800 °C for 0.5 h; (b) BaO–B_2O_3–SiO_2 glass with 5 wt% alumina at 800 °C for 0.5 h.

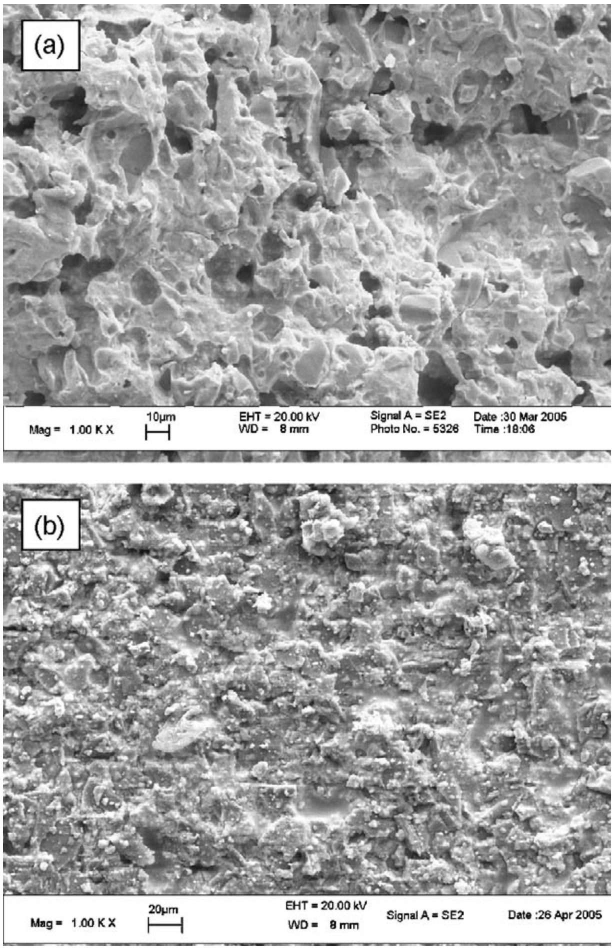

Fig. 4. (a) SEM image of the fracture morphology of the sample prepared by sintering BaO–B_2O_3–SiO_2 glass with 10 wt% TiO_2 at 800 °C; (b) SEM image of the surface microstructure of the sample prepared by sintering BaO–B_2O_3–SiO_2 glass with 10 wt% TiO_2 at 800 °C.

at about 800 °C with a rutile fraction of 10 wt%. The results show that alumina can much effectively promote the densification of the glass/ceramic system than rutile.

According Fig. 2's measured results, the sintered glass/ceramic composite samples that have the highest relative density were polished and then etched in 0.1 M HF solution for 15 s to observe their surface microstructure. It can be clearly seen that the sample with 5 wt% alumina additive (Fig. 3(b)) has more etched pits than the sample with 10 wt% rutile additive (Fig. 3(a)). The etched condition of the surface may indicate the glass phase content in the sample: the more pits present on the surface, the larger the content of glass phase in the sample. According Fig. 3's measured results, the degree of surface crystallization of sample with alumina additive is obviously lower than that of the sample with TiO_2 additive.

Although the pre-molten glass technique could decrease the sintering temperature of the glass/ceramic, a porous microstructure would easily be formed, which would result in an incomplete densification, unstable dielectric constant and metal electrode diffusion in the co-firing processes. Fig. 4(a) is a typical SEM image of a fracture surface of the glass/rutile sample obtained by sintering BaO–B_2O_3–SiO_2 glass with 10 wt% rutile, showing the formation of porous microstructures in the glass/rutile composite system sintered at 800 °C. The diameter of isolated pores can be up to several microns. In addition, both glassy and crystal phases can also be observed. This result implies that full densification of the glass with TiO_2 additive cannot be achieved at 800 °C. It is believed that TiO_2 phase in the system played a negative role during the densification process of the glass/ceramic composites. As is well known, rutile additive can accelerate the phase separation and crystallization of glass phase and therefore dramatically hinder the development of glass phase through viscous flow in the glass matrix during the sintering process [3,5]. Therefore, it usually leads to the formation of a porous structure in the glass/rutile system after sintering. Another interesting phenomenon is that the degree of crystallization on the surface of glass/rutile is much greater than in the sample's interior, as shown in Figs. 3(a) and 4(b). This will be discussed in the latter part of this report.

A porous microstructure may be beneficial for low-temperature co-fired ceramics when it is used in lower permittivity devices. However, excess pores will result in low thermal conductivity, unstable dielectric constant and metal electrode diffusion. Hence, when used as the substrate and packaging of microelectronics components, glass/ceramic materials should possess a suitable microstructure and density.

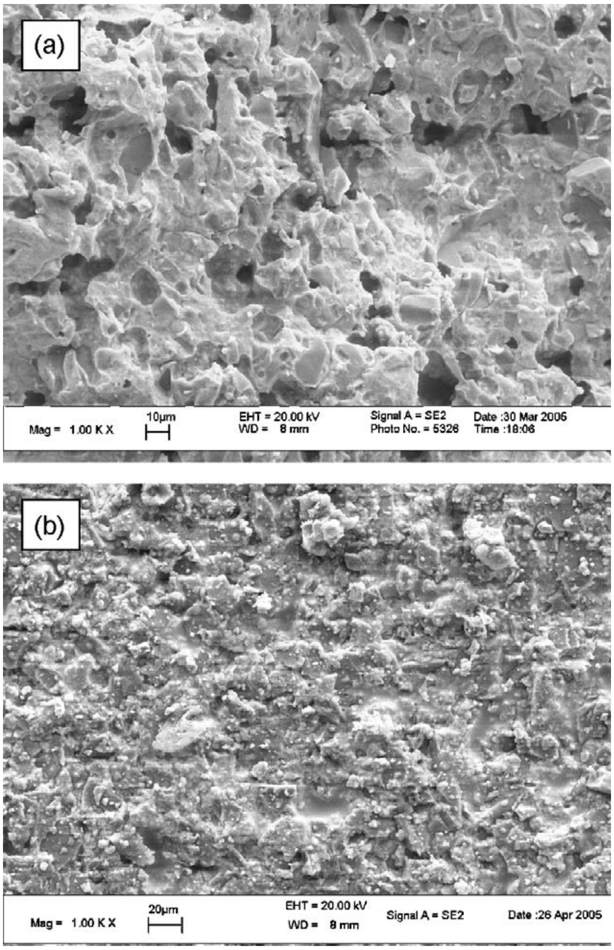

Fig. 5. (a) The fracture morphology of the sample fabricated by sintering BaO–B_2O_3–SiO_2 glass with 5 wt% alumina at 800 °C; (b) the surface morphology of the sample by sintering BaO–B_2O_3–SiO_2 glass with 5 wt% alumina at 800 °C.

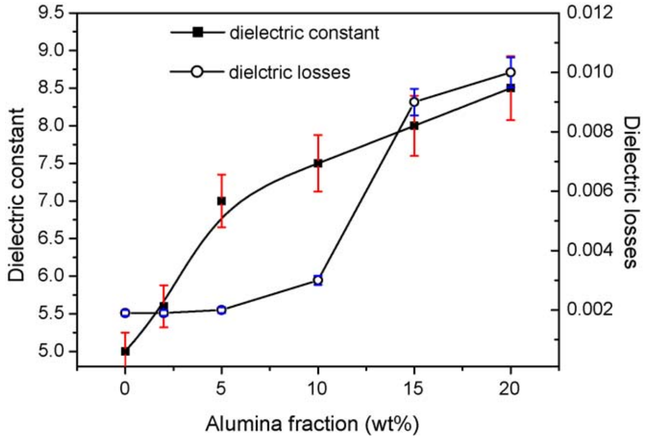

Fig. 6. The relationship between alumina fraction and dielectric performance at the largest density of sintered bodies.

Adding alumina to the glass matrix is one of the effective ways to eliminate the porous structure [9,10]. Our experimental results show that a suitable amount of Al_2O_3 could effectively eliminate gas and produce almost completely densified BaO–B_2O_3–SiO_2 glass/alumina composites. Fig. 5(a) is a SEM image of the fracture microstructure of low-temperature co-fired ceramics prepared by sintering BaO–B_2O_3–SiO_2 glass with 5 wt% alumina powders at 800 °C for 0.5 h. It can be seen that there are no apparent pores in the sample, which indicates that a high relative density (about 98%) has been achieved. In order to understand the different effects of alumina or rutile on pore elimination and the associated mechanisms during the sintering process, the high-temperature wetting properties of alumina or rutile additives on the BaO–B_2O_3–SiO_2 glass matrix are measured in this work.

On the basis of ensuring dielectric application of low-temperature co-fired ceramics, alumina should be added appropriately, because insufficient additive cannot connect the capillaries among alumina particles and promote the densification of glass/alumina, while an excess of alumina additive will result in the increase of the sintering temperature of the glass/alumina system. Fig. 6 shows the relationship between alumina fraction and dielectric performance of the sintered bodies at sintering temperature of 800 °C. The result shows that alumina additive can increase the dielectric constant and dielectric losses of the glass/alumina composites. When sintered body has the highest relative density, the dielectric constant of the glass/alumina composites increases with the alumina fraction. The reason for this is that the increased densification of glass/alumina composites could increase their dielectric constants [3]. In Fig. 6, the experimental results show that the relative dielectric constant (at 1000 MHz) increases from 5.6 to 7.0 when increasing the alumina fraction from 2 wt% to 5 wt%; the reason for this is also that the densification of the glass/alumina system was greatly improved with the addition of alumina, as shown in Fig. 2. But when the fraction of alumina exceeds 10 wt%, the dielectric constant increases because alumina has a higher dielectric constant than the glass matrix materials, and which means that higher fractions of alumina increase the dielectric constant of the glass/ceramic composites. Although high additions of alumina can decrease the densification of the glass/alumina system, itself will be the main factor to increase the dielectric constant. In addition, the results in Fig. 6 show that the dielectric losses increase with the addition of alumina, and increase rapidly when the alumina fraction exceeds 5 wt%. Hence, for densification and dielectric performance, 5 wt% is the optimal additive fraction to the BaO–B_2O_3–SiO_2 glass/alumina system sintered at 800 °C. Dielectric losses increase with the alumina fraction, although densification is also promoted with the alumina additive.

The results show that rutile additive can increase the dielectric constant of the glass/rutile composite, as shown in Fig. 7. When the highest relative density is achieved, the dielectric constant of the glass/rutile composites increases with the increase of rutile fraction. The reason for this is that the fraction of rutile is large enough to promote the dielectric constant [3]. In Fig. 7, the experimental results also show that the dielectric losses (at 1000 MHz) decrease from 0.0019 to 0.0016 when increasing the rutile content from 0 wt% to 15 wt%; the reason for this is that the crystallization of the glass/rutile system has been greatly improved with rutile addition, as shown in Fig. 4. But when the fraction of rutile

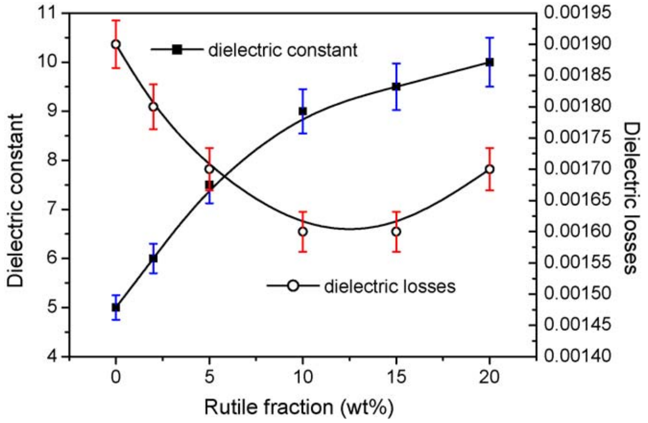

Fig. 7. The relationship between rutile fraction and dielectric performance at the largest density of sintered bodies.

exceeds 20 wt%, the dielectric losses of the glass/rutile will increase, as shown in Fig. 7.

4. Discussion

In this work, the wetting property between the alumina (or rutile) substrate and $BaO–B_2O_3–SiO_2$ glass was characterized by measuring the contact angle at a temperature of about 1100 °C. As shown in Fig. 8(a), the contact angle between alumina substrate and $BaO–B_2O_3–SiO_2$ glass is about 24°, indicating a good wetting behavior between them. The contact angle between rutile substrate and $BaO–B_2O_3–SiO_2$ glass is about 124° (Fig. 8(b)), showing non-wetting behavior between them.

The addition of oxides to glass often leads to liquid–liquid immiscibility, crystallization and phase separation, which is an important basis for forming glass–ceramics with interconnected structures. TiO_2 additive can enhance immiscibility effectively and result in spinodal decomposition or the coalescence of discrete second phase in the glass/ceramic composite system. This is one of the reasons that the interconnected structure contains crystalline and glass phases, as shown in Fig. 4. Obviously, gas cannot be completely eliminated from the sintered bodies of glass/ceramic composites and a number of factors are responsible for this phenomenon. First, the driving force created by capillarity is not large enough to densify the glass/ceramic because the content of crystal phase, the main contributory phase to capillarity, is too low (i.e. there is too much liquid). Secondly, the ability to form glass in composites is weak. The contact angle between rutile and glass matrix is larger than 120° (Fig. 8(b)), which accelerates the formation of web-like crystals and then blocks the densification of glass/ceramic composites. The crystals in the matrix and rutile phase have higher sintering temperatures than the glass phase and a larger driving force is needed to densify the crystal phase. Thirdly, the non-wetting property between rutile and the glass phase depresses the formation of glass phase in capillaries among particles during the sintering process. In addition, the liquid phase cannot flow easily and spread on the surface of the glass–ceramic and then held back the gasses being expelled from the interior of the glass–ceramic.

In the low-temperature co-fired ceramic (LTCC) system, the glass liquid phase is sufficient to fill the gaps between the solid particles so that the solid grains are separated by a liquid film, which results in the generation of capillaries among solid particles reciprocally connected and the zero dihedral angle of solid particles [3–5], as shown in Fig. 9. When alumina is added into the $BaO–B_2O_3–SiO_2$ glass matrix, the liquid phase shows good wetting behavior with the solid alumina particles at high temperatures. During the sintering process, the liquid phase fills the capillaries among the solid particles and the capillaries provide alleyways for liquid phase to flow to the exterior surface of sintered bodies, and a suitable amount of alumina additive would result in the formation of connected capillaries, which allows the expulsion of the glass liquid phase from the interior to the exterior of the glass–ceramic during the sintering process. Fig. 9(a) illustrates the flow of the gas-mingled liquid phase along the surface of the alumina particles. When the gas-

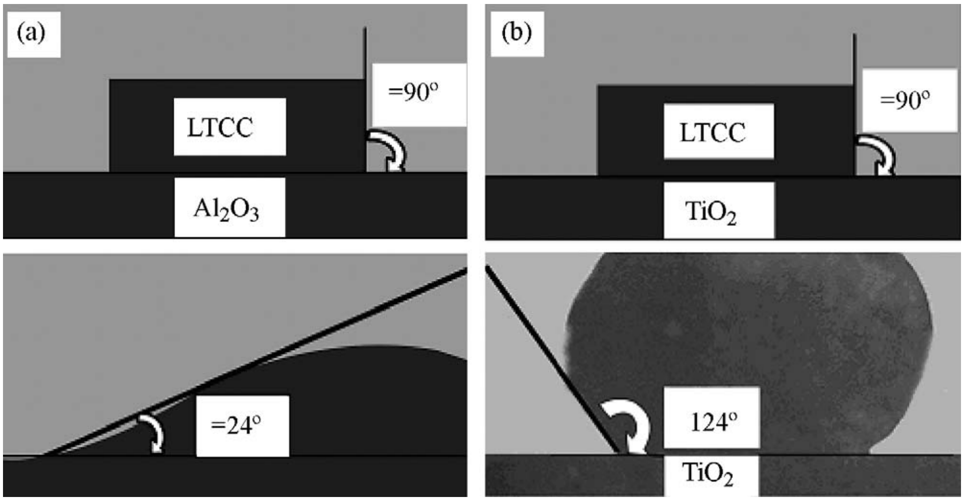

Fig. 8. The photographs of the wetting angle taken by high-temperature camera at about 1100 °C (a) between alumina and $BaO–B_2O_3–SiO_2$ glass matrix. It is about 24° (b) between rutile and $BaO–B_2O_3–SiO_2$ glass matrix. It is about 124°.

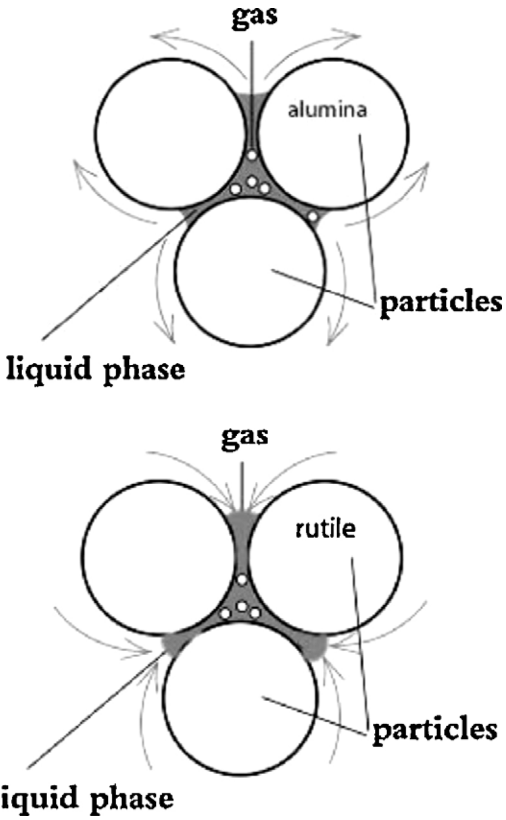

Fig. 9. The illustration of the formation of capillaries among cumulate particles under (a) wetting condition; (b) non-wetting condition.

mingled liquid phase arrives at the exterior surface of the glass–ceramic, the gasses can be expelled easily. At the same time, the crystalline phase in the interior is more abundant than glass phase because of the diffusion of the glass liquid from the interior to the exterior during the high-temperature sintering process. But on the exterior surface of the sintered body, the majority phase is glass phase with only a small amount of crystalline phase, as shown in Fig. 3(b) and Fig. 5. In the presence of alumina, the sintered body provides connected capillaries and a driving force for densification. Compared with alumina, rutile does not wet the $BaO–B_2O_3–SiO_2$ glass effectively, which will depress the formation of glass liquid phase in the connected capillaries during the sintering process and impede the gas expelling from the glass–ceramic as shown in Fig. 9(b). As a result, the glass phase content on the surface of glass/rutile composites is less than that in the interior, as is shown in Figs. 3(a) and 4.

5. Conclusions

$BaO–B_2O_3–SiO_2$ glass-based low-temperature co-fired ceramics (LTCC) was successfully performed by sintering pre-molten glass with oxide ceramics. It was found that the densification of the glass–ceramic composites strongly affected by the high-temperature wetting affinity between glass and ceramics additives by relative density measure, SEM analysis and high-temperature microscopy analysis. The experimental results showed that alumina additive could wet the glass matrix very effectively under high-temperature conditions and increase the densification driving force, giving a densified and homogeneous microstructure in prepared glass/alumina composites. On the other hand, rutile additive could not wet the glass matrix under high-temperature conditions but could accelerated the phase separation and crystallization of the glass phase during the sintering process so as to hinder the densification of glass/rutile composites.

Acknowledgements

This work is supported by Chinese“863” Program under grant 2007AA03Z449 and supported by the Research funds of The Guangxi Key Laboratory of Information Materials under grant 0710908-03-K.

References

[1] R.R. Tummala, A.H. Kumar, P.W. Mcmillan, U.S. Patent no. 4,301,324 (November, 1981).
[2] R.R. Tummala, J. Am. Ceram. Soc. 74 (1991) 895.
[3] W.D. Kingery, H.K. Bowen, D.R. Uhlmann, Introduction to Ceramics, John Wiley & Sons, Inc., 1976.
[4] A.P. Osokin1, E.N. Potapova1, Glass Ceram. 60 (2003) 296.
[5] O.P. Miguel, D.Z. Edgar, Chimie 5 (2002) 773.
[6] Y. Kobayashi, E. Kato, J. Am. Ceram. Soc. 77 (1994) 833.
[7] W. Huang, K.S. Lin, L.W. Chu, G.H. Hsiue, I.N. Lin, J. Euro. Ceram. Soc. 23 (2003) 2559.
[8] C.S. Chen, C.C. Chou, C.S. Chen, I.N. Lin, J. Euro. Ceram. Soc. 24 (2004) 1795.
[9] X.M. Cui, J. Zhou, Mater. Res. Bull. 43 (2008) 1590.
[10] C.C. Cheng, W.C.J. Wei, A. Roosen, J. Euro. Ceram. Soc. 26 (2006) 59.
[11] C.C. Cheng, T.E. Hsieh, I.N. Lin, Mater. Chem. Phys. 79 (2003) 119.