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Research on the High Strength Glass Ceramics/Mullite Ceramics Composites

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ABSTRACT

In order to improve the bending strength of mullite ceramic thin tiles, SiO_2-ZnO-Na_2O-Y_2O_3 glass was prepared on the surface of the tiles. The influences of the thermal properties and thermal expansion coefficient of the glass and the sintering temperature on the structure and the property of the composites were investigated by differential thermal analysis (DTA), X-Ray Diffraction (XRD), Raman and scanning electron microscopy (SEM). The bending strength of the composites was measured with an universal testing machine. Results show that the crystallization temperature of the SiO_2-ZnO-Na_2O-Y_2O_3 glass is higher than that of SiO_2-ZnO-Na_2O glass. The corresponding crystallites show more complex structure for the SiO_2-ZnO-Na_2O-Y_2O_3 glass. The thermal expansion coefficients of both glasses are lower than the mullite ceramic tiles. The bending strength of the composites after sintering at 1150℃ *was obviously improved by* 10.7% *to* 106.2 *MPa, compared with the mullite ceramic tiles.*

Keywords**:** *Glass Ceramics, Mullite Ceramics Thin Tile, Composites, Bending Strength*

1. Introduction

Large ultra-thin dry-pressing thin ceramic tiles have many excellent properties, such as thinness, large size (900 mm × 1800 mm × 5.5 mm), lower weight (only 1/3 - 1/2 of regular ceramic wall and floor tile) and saving of source material and energy and reducing of dust and gas. It is becoming one of developing low-carbon green environmental new product advocated by all the countries in the world [1]. However, the large ceramic thin tiles still have many problems during the course of processing and application due to their large size and thinness, especially the poor mechanical strength of the product [2,3]. In order to solve this problem, thin mullite ceramic tiles are developed to increase their strength greatly [4]. To improve the strength of the mullite ceramics thin tile further and get a good decoration effect, a kind of microcrystal glass is prepared on the surface of the mullite ceramics and a better result is achieved. Recently, the theory analysis and practical application of microcrystal glass composited to ceramic board has made rapid progress [5]. Usually, ceramic tile is used as a matrix and about 5 - 10 mm microcrystal glass frit is added on its surface. Then, it is sintered at high temperature and finally the glass/ceramic composites are obtained. It is widely used as a decorating material on vestibule, post, internal and external walls of stations, hotels, halls and entertainment facilities [6].

In the present work, the following method to combine microcrystal glass with ceramic board is used. On the surface of the large-size ultra-thin mullite ceramic tile (900 mm × 1800 mm × 5.5 mm), ceramic glass of 1 mm thickness is prepared. The strength of the ceramic tile is greatly raised according to optimizing processing. The influences of the thermal properties and thermal expansion coefficient of the glasses and the sintering temperature of the composites on the structure and the property of the composites were investigated.

2. Experimental

Details for the preparation of the mullite ceramic tile (900 mm × 1800 mm × 5.5 mm) were reported in [4]. The raw materials were as follows: 50 wt% - 55 wt% fly ash, 30 wt% - 35 wt% pyrophyllite, 10 wt% - 15 wt% bauxite and 4 wt% AlF_3.

Microcrystal glass was a sort of borosilicate glass and

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the composition is shown in **Table 1**.

High purity silica, reagent grade boric acid, zinc oxide, sodium carbonate and yttrium oxide were used as source materials and mixed in the above ratios, ball milled and dried. Then, the mixture was ground in a platinum crucible and kept it at 1500˚C for 3 h. The molten glass transformed from the mixture at high temperature and underwent water quenching and a course of drying and ball milling to produce a glass power with an average size about 1 - 3 μm. These glass powder was distributed uniformly by distributor on the surface of mullite ceramic tile and its thickness was kept at 1.2 mm. Next, the covered tile was placed in a furnace for a second sintering at 1000˚C - 1200˚C, causing the glass powder to remelt, nucleate, crystallize and combinesolidly with the ceramic base. After cooling down to the room temperature, the large-size ultra-thin mullite glass ceramic tile was prepared finally.

3. Characterization

Subsequently, the phase composition of the sample was characterized by a Rigaku D/max-3C X-ray diffractometer (XRD) and Raman spectroscopy. The thermal stability and morphologies of the sample were analyzed by a NETZSCH STA 409 PC/PG (DTA) and JSM-6390A (JEOL) scanning electronic microscope (SEM) respectively. The characterization of the mechanical property of the sample was measured by a universal material testing machine (Taiwan Baoda Co. Ltd) and the testing of the bulk density of the sintered sample was carried out by the underwater weighing method and then the porosity of the sample was calculated.

4. Results and Discussion

4.1. The Sintering Behaviors of the Ceramic Glass Mullite Board

Most research about microcrystal ceramic board show that the range of the mullite crystallization temperature of the ceramic thin tile is about 900˚C - 1200˚C with the content of mullite crystal increasing as the temperature rise. The property of the sample is mainly dependent upon the range of crystallization of ceramic glass and the effective controlling. If the ceramic tile base and the glass produce many more crystals, the mechanical property of the composite tile would be greatly improved.

Table 1. The composition of SiO_2-ZnO-Na_2O-Y_2O_3 glasses/ mol%.

No.	SiO_2	B_2O_3	ZnO	Na_2O	Y_2O_3
1	37	18	20	25	-
2	37	18	20	20	5

Figure 1 shows the DTA curves of the as-prepared glasses. The endothermic peak observed at nearly 740˚C is when Y_2O_3 was added into the glass, which might be caused by the rebuliding of the structure in the course of melting the glass. The exothermic peak at 880˚C might have been caused by the crystallization of the glass phase. The crystallization of glass can decrease the content of the glass phase which is not helpful to the densification of the composites, so increasing the crystallizaion tempe- rature of the glass can improve the sintering of the composites. It is proved that the addition of Y_2O_3 can increase the crystallization temperature of glass to 950˚C nearly the crystallization temperature of mullite ceramic, which is very beneficial to the optimization of its structure.

The porosity of the as-prepared glass/ceramic composites sintered at different temperatures was showed in **Figure 2**. The addition of different glass on the surface

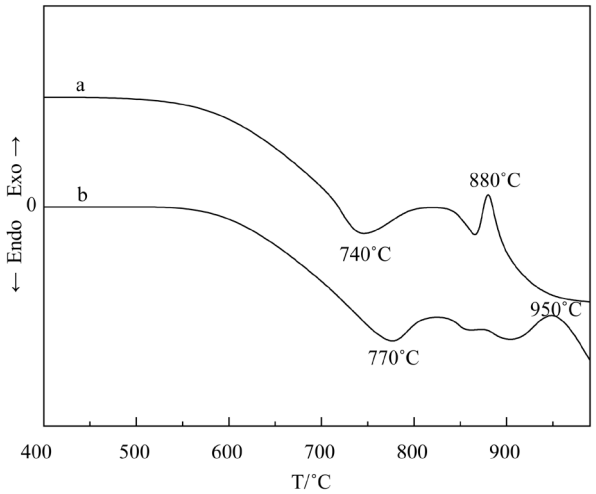

Figure 1. DTA curves of the as-prepared glasses (a. SiO_2-ZnO-Na_2O; b. SiO_2-ZnO-Na_2O-Y_2O_3).

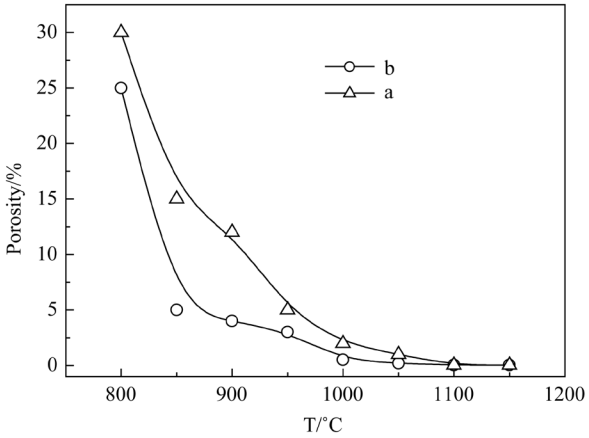

Figure 2. Porosity of the as-prepared glasses/ceramics composites sintered at different temperatures (a. SiO_2-ZnO-Na_2O; b. SiO_2-ZnO-Na_2O-Y_2O_3).

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of ceramic board had a great impact on the property of the composites. When the SiO_2-ZnO-Na_2O-Y_2O_3 glass was added on the surface of ceramic board, the density of the composites reached its highest at 1050˚C with a corresponding porosity of less than 0.3%. Comparatively, when the SiO_2-ZnO-Na_2O glass was used as the glass coating, a temperature of 1100°C was required to make the composites so dense. The higher crystallization temperature of the SiO_2-ZnO-Na_2O-Y_2O_3 glass relative to the SiO_2-ZnO-Na_2O glass might be the reason for this.

4.2. The Structure and Property of the Glass/Ceramic Composites Board

Figure 3 shows the surface XRD patterns of the as-prepared glasses. A weak bun peak can be observed on the surface of the glass after sintering, which proves that the crystal of the surface was either amorphous or the crystal is was too small to generate the peak.

There were ZnB_4O_7 and $ZnSiO_4$ peaks in the SiO_2-ZnO-Na_2O-Y_2O_3 glass, which indicate the existence of the crystal. In order to confirm the structure of the crystal, the sample was analyzed by Raman spectroscopy. The crystallization of B_2O_3 and SiO_2 was found in the SiO_2- ZnO-Na_2O glass through the testing (**Figure 4**), though the intensity of those peaks decreases with the increasing of the temperature. Additionally, the Raman testing of the SiO_2-ZnO-Na_2O-Y_2O_3 glass showed that the presence Y_2O_3 crystals and the silicate melting structure of [Si_2O_7] and [SiO_4] (**Figure 5**), proving that the crystallites structure of SiO_2-ZnO-Na_2O-Y_2O_3 glass was more complex and the addition of Y_2O_3 promotes the crystallization of the galss.

Figure 6 shows the cross-section SEM images of the glass/ceramic composites. Obviously, a well bonded and

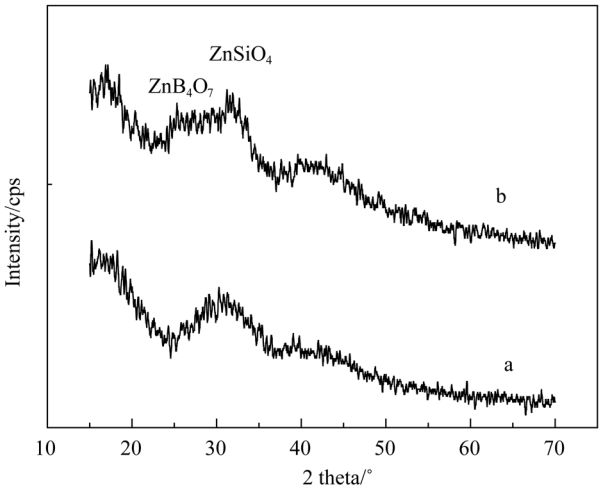

Figure 3. Surface XRD patterns of the as-prepared glasses (a. SiO_2-ZnO-Na_2O; b. SiO_2-ZnO-Na_2O-Y_2O_3).

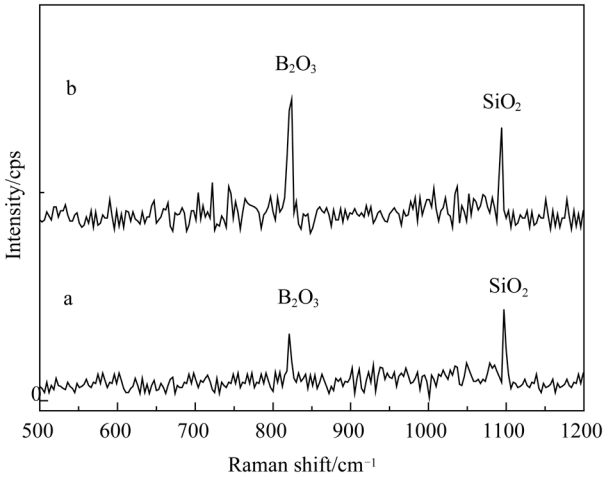

Figure 4. Raman patterns of the as-prepared SiO_2-ZnO-Na_2O glasses (a. 1200˚C; b. 1100˚C).

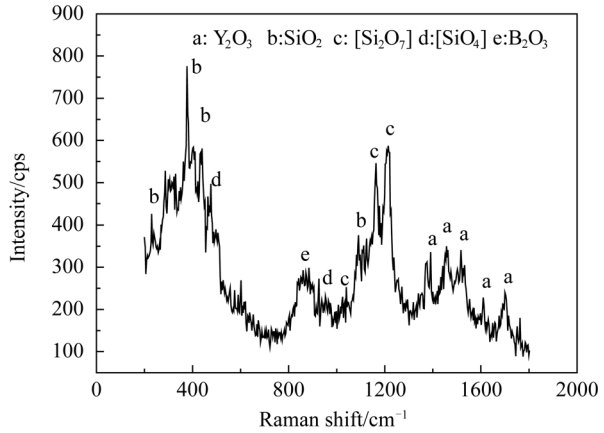

Figure 5. Raman pattern of the as-prepared SiO_2-ZnO-Na_2O-Y_2O_3 glasses.

condensed glass layer on the surface of ceramic substrate without holes and cracks was achieved, which indicated the good match of the physical and chemical compatibility between the glass layer and ceramic base and that the use of the glass and adoption of processing were reasonable.

The thermal expansion coefficients of the ceramic substrate and the glasses are displayed in **Table 2**. Thermal expansion coefficient of both SiO_2-ZnO-Na_2O glass and SiO_2-ZnO-Na_2O-Y_2O_3 glass were less than that of ceramic tile. Comparatively, the thermal expansion coefficient of SiO_2-ZnO-Na_2O glass was closer to that ceramic tile which is crucial to promote the strength of the composites. During the course of cooling down, compressive stress can be formed in glass layer and the wider the difference in thermal expansion coefficient between the glass and the ceramic tile is, the higher the compressive stress is; too much compressive stress can lead to

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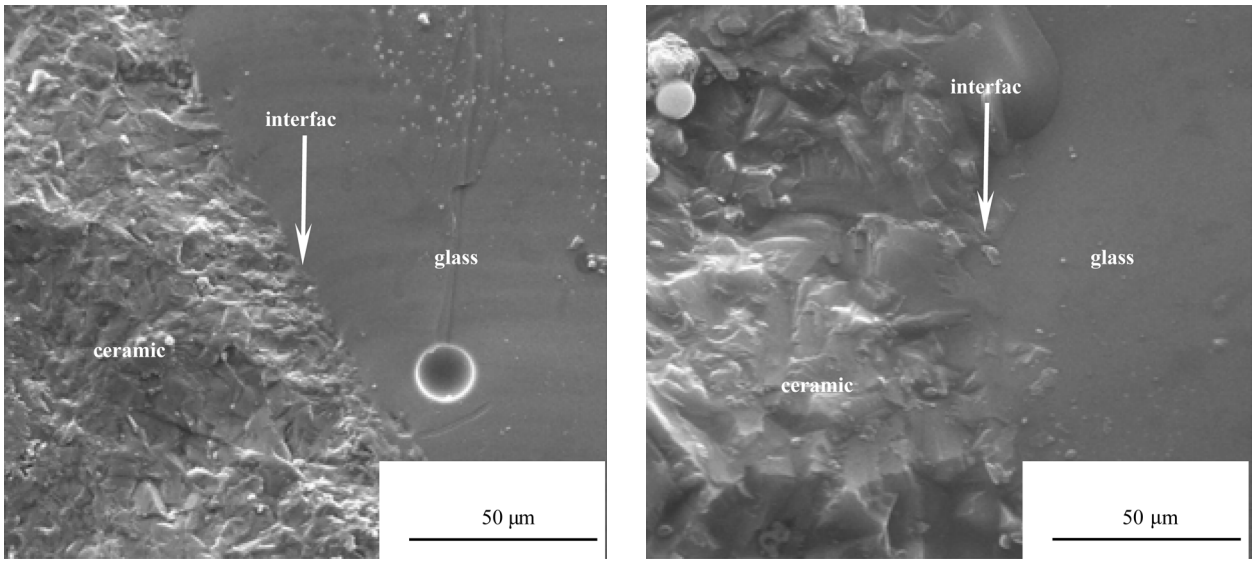

Figure 6. The cross-section SEM images of the glass/ceramic composites (a. SiO_2-ZnO-Na_2O/ceramics; b. SiO_2-ZnO-Na_2O-Y_2O_3/ceramics).

Table 2. Thermal expansion coefficient of the ceramics substrate and the glasses (× 10^{-6}/K).

Temperature	40˚C - 400˚C	40˚C - 500˚C	40˚C - 600˚C	40˚C - 700˚C
SiO_2-ZnO-Na_2O-Y_2O_3	5.9885	5.9959	6.1207	6.5781
SiO_2-ZnO-Na_2O	6.2133	6.3438	6.8154	7.1873
Ceramic tile	6.7091	6.9815	7.6889	7.3512

cracks of the glass layer and deformation of the composites. Thus, it is necessary to control the difference in the thermal expansion coefficients.

Figure 7 shows the relationship between the bending strength of glass/ceramics composites and the sintering temperature. The bending strength of the composites increases with the sintering temperature, and when the temperature was about 1180˚C, the bending strength of the mullite ceramic tile reached the highest value of 95.9 MPa. After covering with the SiO_2-ZnO-Na_2O glass, the bending strength was greatly improved to about 101.3 MPa and 5.2% enhanced. By comparison, when the SiO_2-ZnO-Na_2O-Y_2O_3 glass is coated on the surface of the ceramic tile and sintered at the temperature of 1100˚C, the bending strength peaked at 106.3 MPa and 10.7% enhanced. This was not only caused by massive microcrystals of the glass layer, but also the lower compressive stress formed in the glass layer. In addition, the crystal structure of SiO_2-ZnO-Na_2O-Y_2O_3 glass was more complicated and its high crystallization temperature was helpful to improve the density of the composites during the course of sintering, which reduced the sintering temperature and sharply improved the strength of the composites.

5. Conclusions

SiO_2-ZnO-Na_2O glass and SiO_2-ZnO-Na_2O-Y_2O_3 glass on the surface of large-size ultra-thin mullite ceramic tile was successfully prepared by a distributing sintering

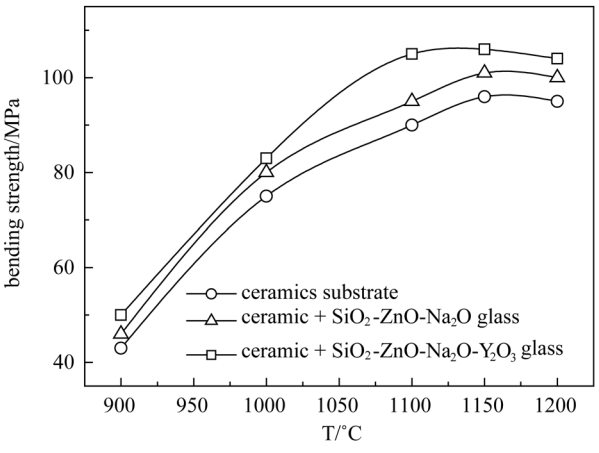

Figure 7. Relationship between the bending strength of glass/ceramics composites and the sintering temperature.

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method. The crystallization temperature of SiO_2-ZnO-Na_2O-Y_2O_3 glass was higher according to DTA analysis, and the XRD and Raman analysis indicateed that the crystallite structure of SiO_2-ZnO-Na_2O-Y_2O_3 glass was more complicated with ZnB_4O_7, $ZnSiO_4$, B_2O_3, Y_2O_3 and SiO_2 crystal structures in the glass. The thermal expansion coefficients of the SiO_2-ZnO-Na_2O-Y_2O_3 glass were lower than the mullite ceramics tile, and the bending strength of the composites after sintering at 1150°C was obviously improved and reached 106.2 MPa and 10.7% enhanced when compared with the mullite ceramic substrate.

6. Acknowledgements

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