

Feasibility of $BaO-ZnO-B_2O_3$ based Glass as a Host to Employ Various Ceramic Fillers to be applied to Barrier Ribs in Plasma Display Panels

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Abstract

Effects of additing various types of ceramic fillers to the BZB-based glass on the thermo-chemical stability, optical reflectance, and mechanical properties were investigated. The glass system demonstrated the feasibility to host various types of ceramic fillers to form micro-composites at the processing temperature suitable for PDP systems. The optical reflectance and mechanical strength of the filler-glass composites were improved as compared to the glass itself. These results demonstrate the feasibility of applying the Pb-free BZB-based glass system as a matrix for employing various types of crystalline ceramic fillers to be used as barrier rib materials in plasma display panels.

Keywords : ceramic filler, $BaO-ZnO-B_2O_3$, barrier rib

1. Introduction

Lead borosilicate glasses have been mainly used as barrier rib materials in plasma display panel systems [1-4] due to their amenable properties such as low softening temperature, comparable coefficient of thermal expansion to that of alumino-silicate glass panel for PDP (such as PD200 , 8.3×10^{-6}/K), low dielectric constant, and high reflectivity for visible lights. In addition to their basic components such as $PbO-B_2O_3-ZnO-SiO_2$, other minor components such as Al_2O_3, TiO_2, and MgO are added to modify the properties of the glass itself. Also, crystalline ceramic fillers are added to form a ceramic particulate-glass micro-composite to tailor reflectivity, dielectric constant, coefficient of thermal expansion, and fracture toughness.

Recently, great attention has been drawn to lead-free glasses [5~7] due to the hazardous effects of Pb on health and environment [8]. A notable alternative glass system to Pb-based glass system is the $BaO-ZnO-B_2O_3$ (BZB) system [9, 10], which has shown low dielectric constants of 14~18 and appropriate coefficients of thermal expansion of 7~9$\times10^{-6}$/K [10].

In the present study, the microstructure, thermo-chemical stability, optical reflectance, and mechanical strength of the ceramic filler-glass matrix system have been investigated to verify the feasibility of the BZB-based glass system as barrier rib materials in plasma display panels. Through this work, it is demonstrated that the glass system is capable of hosting various types of ceramic fillers to form micro-composites at the processing temperature suitable for PDP systems, and the resultant optical reflectance and mechanical strength can be improved.

2. Experiments

In order to prepare the glass batches, appropriate amounts of $BaCO_3$, ZnO, and B_2O_3 powders were mixed and ball milled. The batch was then melted in a platinum crucible at 1300°C for 1 h in air, followed by quenching it to room temperature. The quenched glass frits were mixed with appropriate amount of various ceramic fillers such as Al_2O_3 (corundum), MgO (periclase), SiO_2 (quartz), TiO_2 (rutile), ZrO_2 (zirconia), $2MgO-2Al_2O_3-5SiO_2$ (cordierite), and CeO_2 (cerianite) crystalline ceramic filler powders. Then, the powder mixtures were further ball milled and granulized using polyvinyl alcohol (PVA)-water solution. After uniaxially pressing the dried granules, the pressed green body was fired at 575°C for 2 h in air to

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densify.

The residual amount of crystalline ceramic fillers in densified specimens was quantified by a quantitative X-ray diffraction (XRD) method. A calibration chart (Fig. 1) was first established using 20 wt% silicon powders as internal standard in series of synthetic samples. Then, the micro-composite specimens with unknown amounts of residual ceramic filler crystal phase were pulverized and mixed with 20 wt% silicon standard. Then XRD measurement was conducted to determine the intensity ratio of ceramic fillers to the silicon standard. The amount of the residual crystalline ceramic filler phase was quantified from the intensity ratios determined using the calibration chart. The calibration charts are shown in Fig. 1. The microstructure of the residual ceramic fillers in the densified filler-glass micro-composite was investigated by scanning electron microscopy (SEM). Optical reflectance of the specimen was measured by a UV-visible optical spectrometer and their resultant mechanical strength was characterized through a compression test using specimens with a diameter of 8 mm in and a thickness of 5 mm.

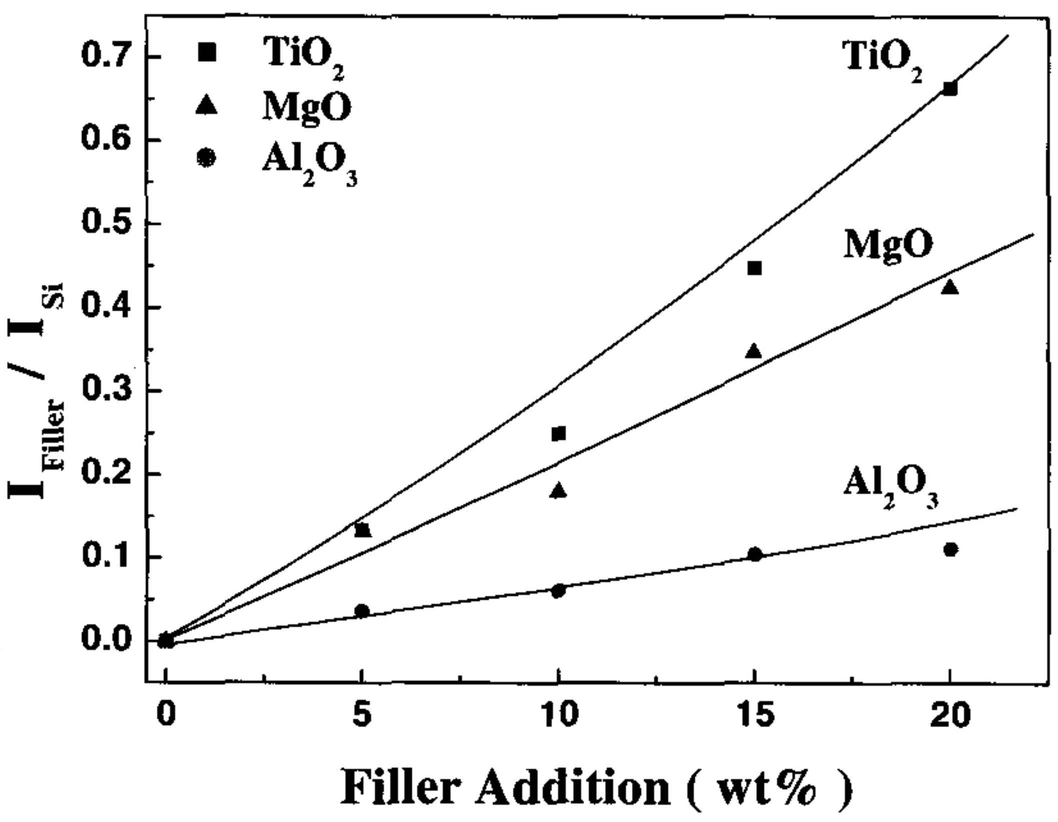


Fig. 1. Calibration charts for Al_2O_3, MgO, and TiO_2 fillers.

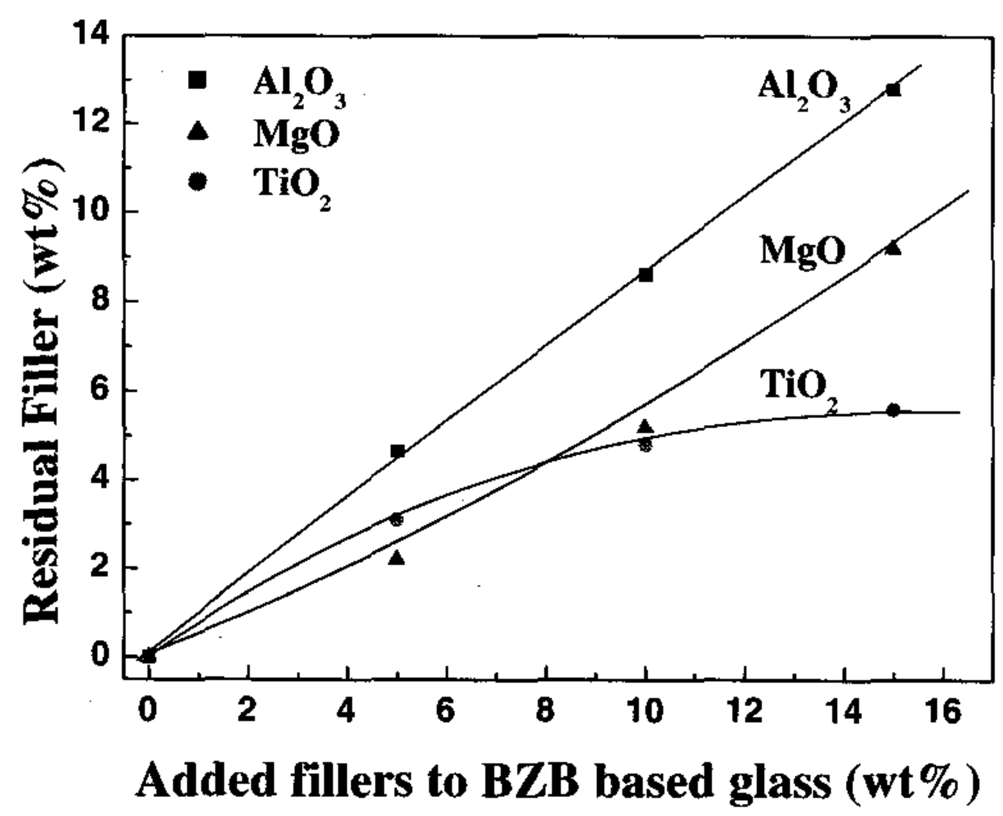


Fig. 2. Amounts of residual fillers as a function of input amount.

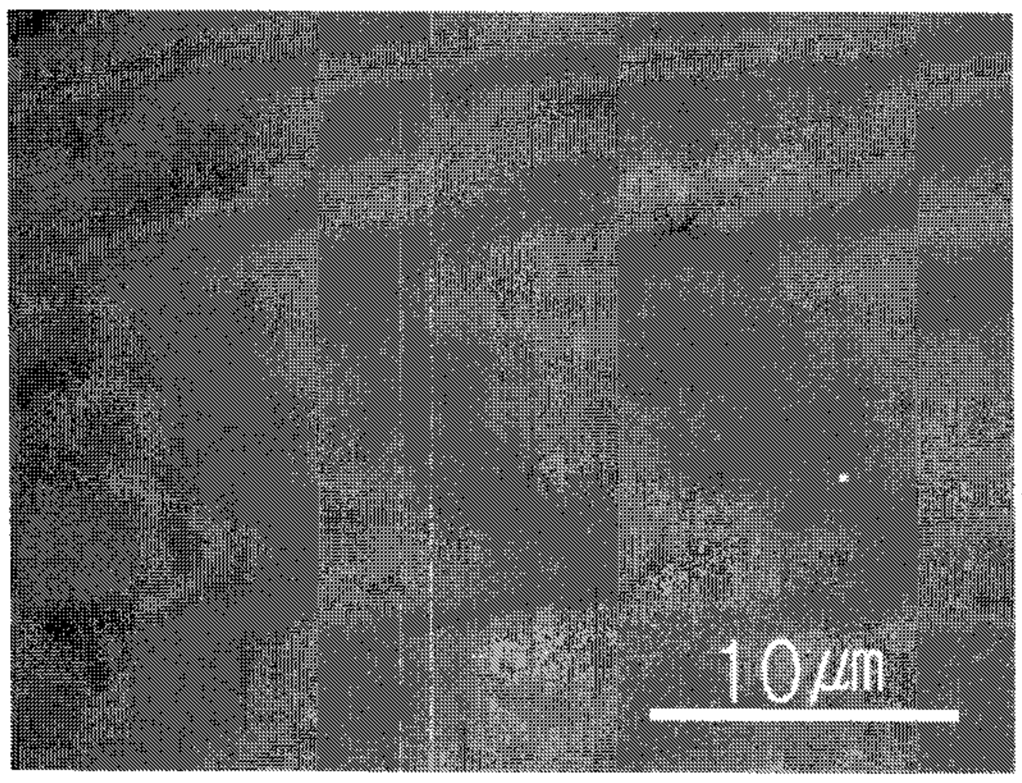
3. Results and Discussion

3.1 Thermo-chemical stability

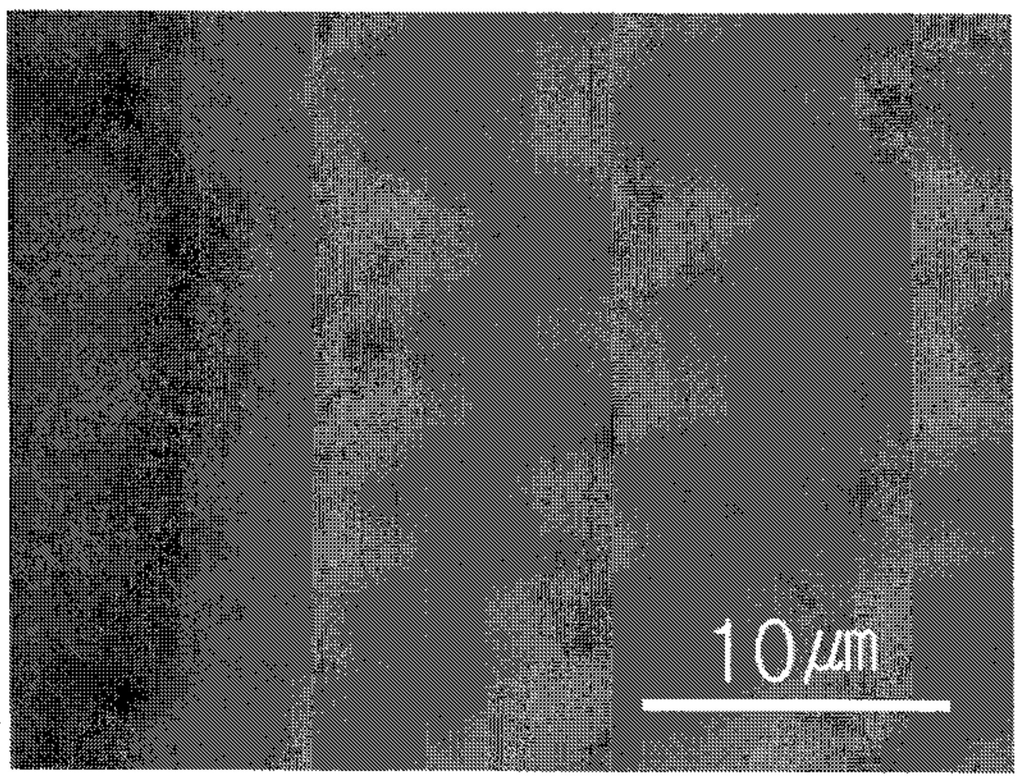
Fig. 2 shows the residual amount of crystalline ceramic fillers (Al_2O_3, MgO and TiO_2) in the densified specimen as a function of input amount, based on quantitative XRD determination. In the case where the refractory ceramic fillers inhibit the densification of the glass frits, all the added fillers will be exist in crystalline form; This means the quantitative analysis of the specimen would yield no appreciable change in the amount of crystalline filler phases. On the other hand, if the ceramic fillers are dissolved into the glass during the densification, there would be a decrease in their amounts after the densification. Thus, it is necessary to investigate how much of the added fillers have survived or been dissolved. In Fig. 2, the residual filler amount is always less than the input, indicating that the refractory ceramic fillers were partially dissolved into the glass matrix. A partial dissolution means that the fluidity of the fillers has increased to minimize the inhibition of the refractory fillers to the densification of the glass matrix. It also means that a bonding between the added filler and the glass matrix has been achieved for a suitable filler particulate-reinforcement of the glass. The partial dissolution was also observed for other types of ceramic fillers and the dissolution amount was roughly about 30~50 wt% depending on the types of the fillers.

3.2 Microstructure

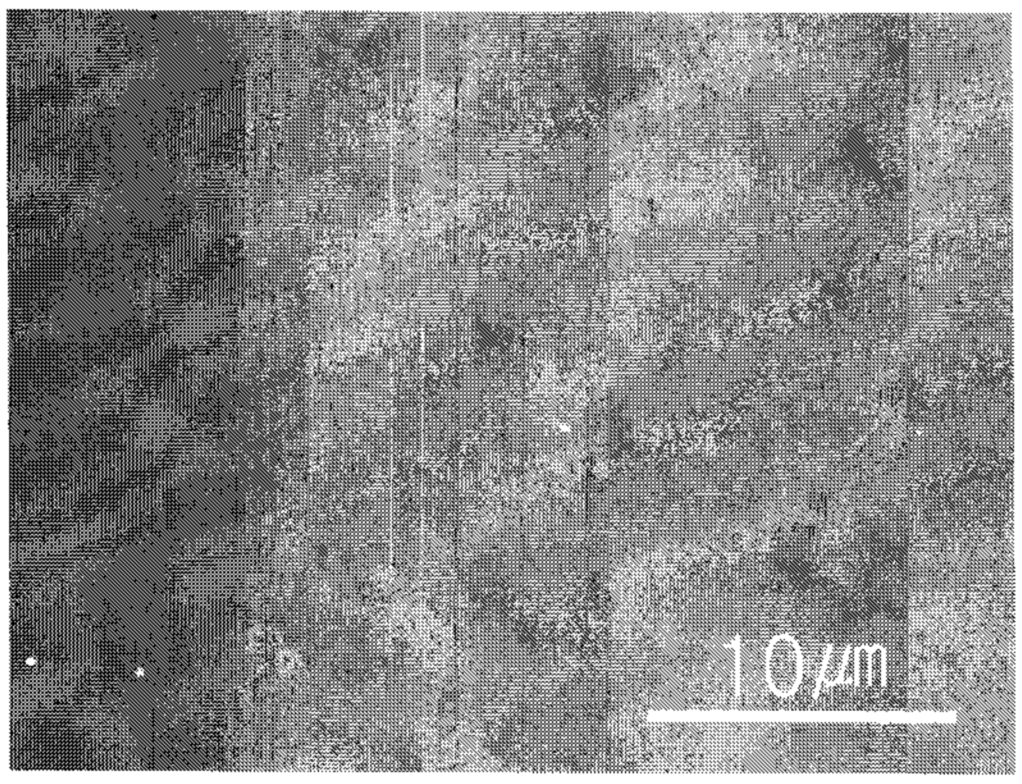
Fig. 3 shows the scanning electron micrographs of the densified specimens with 5 wt% of SiO_2, cordierite and ZrO_2 fillers, respectively. Residual fillers appear relatively dark in Fig. 3, because the ceramic fillers are composed of relatively light elements as compared to the barium- and zinc-rich glass matrix. From the locus of the relatively dark regions, the ceramic fillers are mainly located at the boundaries of the sintered glass frits and their shapes appear to be severely distorted from its original shape. The original shapes of the glass frits (Homogeneous size range was 0.1~1 μm) and filler particles (roughly about 1 μm for



(a)



(b)



(c)

Fig. 3. Scanning electron micrographs of specimens with 5 wt% of SiO_2 (a), Cordierite (b), and ZrO_2 (c) fillers.

various fillers) were more or less spherical. Such severe distortion of the filler phases could possibly arise due to the partial dissolution of the ceramic fillers into the glass, which, in turn, increases the fluidity of the filler particles to align along the boundaries of the densifying glass frits.

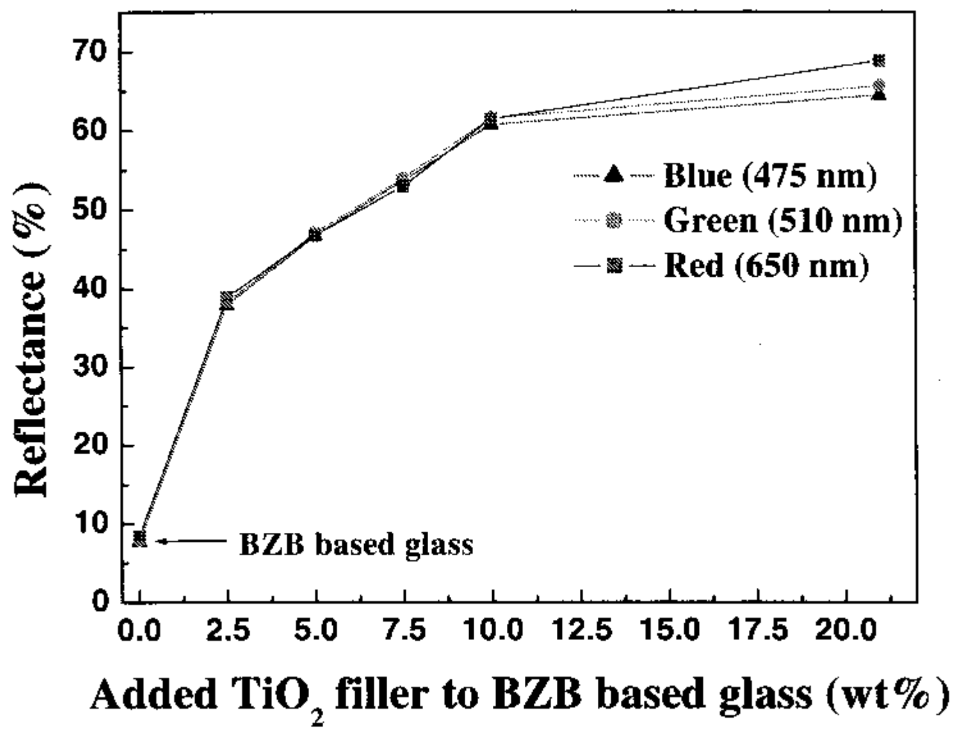


Fig. 4. Reflectance (%) of TiO_2 filler-added BZB glass at Blue (475 nm), Green (510 nm), and Red (650 nm) wavelengths.

Similar observations were made for other types of ceramic fillers as well. The density of the specimens was, in general, higher than 95 % of the theoretical one. The morphology of the residual filler together with the quantitative determination result of the residual filler amount indicates that the studied BZB-based glass system is attractive for hosting various types of ceramic fillers. It is capable of forming a bond with the refractory fillers by partially dissolving them at the processing temperature suitable for PDP systems. However, significant amounts of fillers still survive that reinforce the glass or to take the role of the optical reflectance as will be discussed in the following sub-sections.

3.3 Optical reflectance

Having shown the suitable formation of ceramic filler-glass micro-composites, the change in optical reflectance of the micro-composites in the visible wavelength range was investigated as a function of TiO_2 filler addition and the result is shown in Fig. 4. The addition of TiO_2 ceramic filler can be seen to greatly increase the reflectance and these trends are similar regardless of the investigated wave lengths in the visible range, i.e., 475 nm (blue), 510 nm (green), and 650 nm (red). The specimen with 21 wt% TiO_2 shows a reflectance of about 65 %, which value is with the suitable reflectance range (50~80 % [11]) for application to barrier ribs in the PDP system.

3.4 Mechanical strength

The ceramic filler-added micro-composites demonstrates improved mechanical strength as compared to the glass itself due to the role of residual crystalline ceramic filler phase as seen in Fig. 5. The strength (σ) and elastic modulus (E) of the crystalline ceramic fillers are much

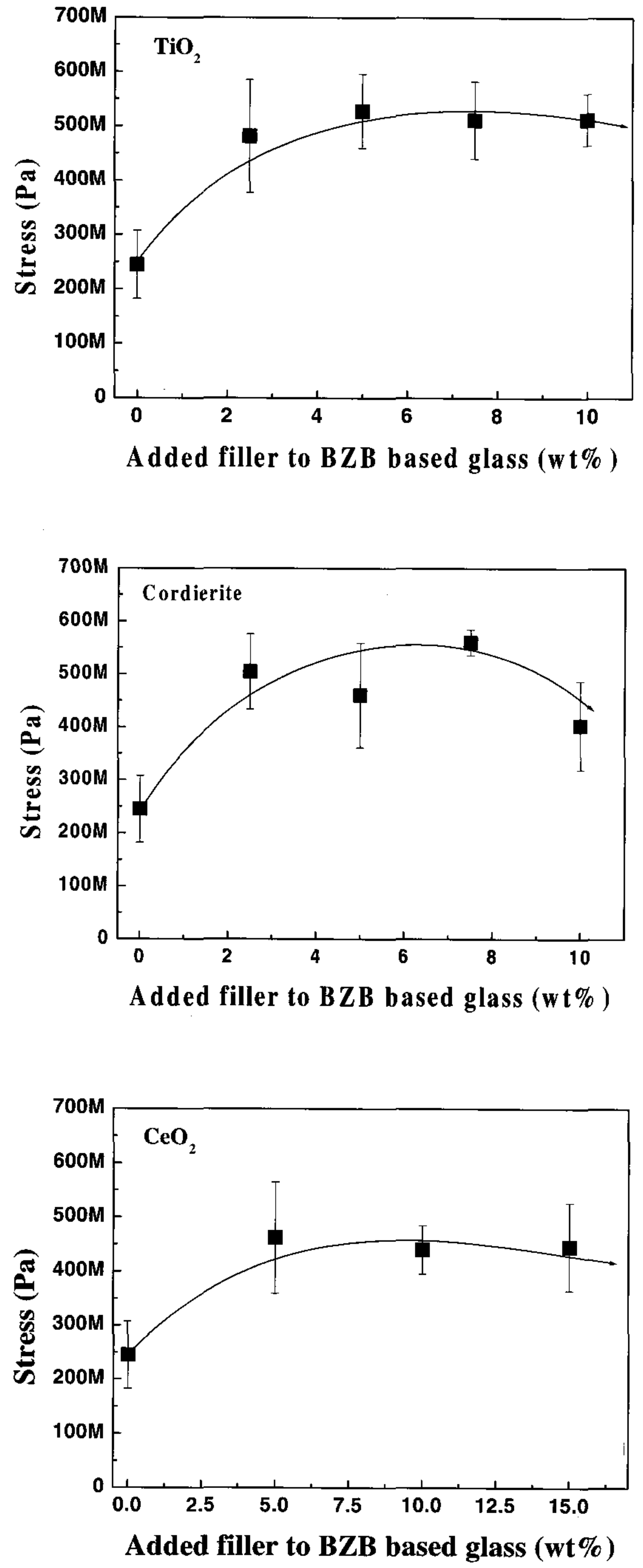


Fig. 5. Change in mechanical strength as a function of filler addition to BZB-based glass. Types of fillers are TiO_2 (top), Cordierite (middle), and CeO_2 (bottom).

Table 1. Composition of glass specimen (mol%)

Specimen	BaO	ZnO	B_2O_3
BZB	20	30	50

superior to those of oxide glasses. For instance, those of Al_2O_3 (about E=370 GPa, σ = 300 MPa) and cordierite (about E = 125 GPa, σ = 300 MPa) are much higher than the alumino-silicate glass (about E=76 GPa, 59 MPa). Therefore, the addition of the crystalline ceramic fillers can be said to improve the mechanical strengths as they take the role of particulate reinforcements, provided an appropriate bonding with the matrix is achieved. This was the case in the aforementioned studied specimens. In Fig. 5, in general, an increase in strength at about 5 wt% filler addition is pronounce while further increase in filler addition do not seem to justify the addition. In fact the addition of an excessive ceramic filler eventually decreased the mechanical strength due to the poor densification. Therefore the slight decrease or no fur ther increase in the mechanical strength beyond filler addition of 5 wt% as shown in Fig. 5 can be said to be due to the poor densification of the micro-composites as compared to the glass itself. Residual pores associated with the incomplete densification are the source of the crack generated during mechanical testing which in turn, yields a diminished strength. The elastic modulus of the filler added composites also exhibited very similar results to the trend in strength (not shown). Micro-composites with other ceramic fillers also demonstrated similar results.

Since the ceramic filler phase was mainly located at the boundaries of the former glass frits, it is suggested that the use of a more fine glass frits would result in a more evenly dispersed residual ceramic filler phase in a given specimen volume, which, in turn, would yield a more reliable glass-filler micro-composite with less scattered mechanical property data.

4. Conclusions

The BZB-based glass system showed to be an attractive method of forming filler-reinforced micro-composites (0~15 wt% fillers) by partially dissolving the crystalline filler phases. The partial dissolution (about 30~50 wt% depending on the fillers) were found to increase the fluidity of the ceramic fillers which minimized the inhibition to the rearrangement of the densifying glass frits and assisted the filler particles to align along the boundaries of the densified glass frits. The added fillers with such microstructural characteristics resulted in an increased optical reflectance in the visible rage of the spectrum (about 65 % reflectance for TiO_2 filler) and an improved mechanical properties (about 240~560 MPa depending on the fillers) as compared to the glass itself. These observations reaffirms the feasibility of the Pb-free BZB-based glass system as a host to employ various types of crystalline ceramic fillers so that it can be applied to barrier rib materials in plasma display panels.

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