13-2: Thermochemical Stability and Mechanical Properties of Ceramic-Filler Added BaO-ZnO-B_2O_3 Based Glass for Application to Barrier Rib in Plasma Display Panels

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Abstract

Feasibility of BaO-ZnO-B_2O_3 (BZB) based glass system in the light of dielectric and thermal expansion properties are reported in the literature. Effects of addition of various types of ceramic fillers to the BZB-based glass on the thermochemical stability and mechanical properties were investigated in the present work. The studied filler-glass system demonstrated a capability to host various types of ceramic fillers to form thermochemically stable microcomposites at the processing temperature suitable for PDP systems. At the same time, mechanical strength of the filler-glass composites was much improved as compared to the glass itself. These observations brighten 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 material in plasma display panels.

1. Introduction

Lead borosilicate glasses have been mostly used as barrier rib in plasma display panel systems [1-3] due to their amenable properties for the application such as low softening temperature, comparable coefficient of thermal expansion to the soda lime silicate glass panels, low dielectric constants, and high reflectivity. In addition to the basic components such as PbO-B_2O_3-ZnO-SiO_2, several minor components such as Al_2O_3, TiO_2, and MgO are added to adjust the properties of the glass. In general, the glass frits are densified with the ceramic fillers to mechanically reinforce the glass by the ceramic particles.

Recently, interest in lead-free glasses [4-6] is highly increasing considering the deleterious effect of Pb on health and environment [7]. A notable alternative glass system to Pb-based system is the recently reported BaO-ZnO-B_2O_3 (BZB) system [8-9], which has been shown to have low dielectric constants of 14~18 and appropriate coefficients of thermal expansion of $7\sim9\times10^{-6}$/K [9].

In order to utilize the BZB system, further researches, e.g., its capability to form a stable microcomposite system when ceramic filler particles are embedded to the glass. In the present study, the effects of addition of various types of ceramic fillers on the microstructure and mechanical properties of the BaO-ZnO-B_2O_3 (BZB) based glass have been investigated. Microstructure, thermochemical stability of the ceramic filler-glass microcomposite system, and the resultant mechanical properties have been studied to check the feasibility of applying the non-Pb based glass system to barrier rib in plasma display panels. This work demonstrates that the studied glass system has a capability to host various types of ceramic fillers to form thermo-chemically stable microcomposites at the processing temperature suitable for PDP systems.

2. Experimental

In order to prepare the glass batches, an appropriate amount of $BaCO_3$, ZnO, and B_2O_3 powders was mixed and ball milled. The batch was then melted in a platinum crucible at 1300℃ for 1 h in air, followed by quenching to room temperature. The quenched glass was pulverized to average particle size of 1.0 m and the 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) 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℃ for 2 h in air for densification.

The residual amount of crystalline ceramic fillers in densified specimens was quantified by a quantitative X-ray diffraction (XRD). A calibration chart (Fig. 1) was first established using 20 wt% silicon powder as internal standard in series of synthetic samples.

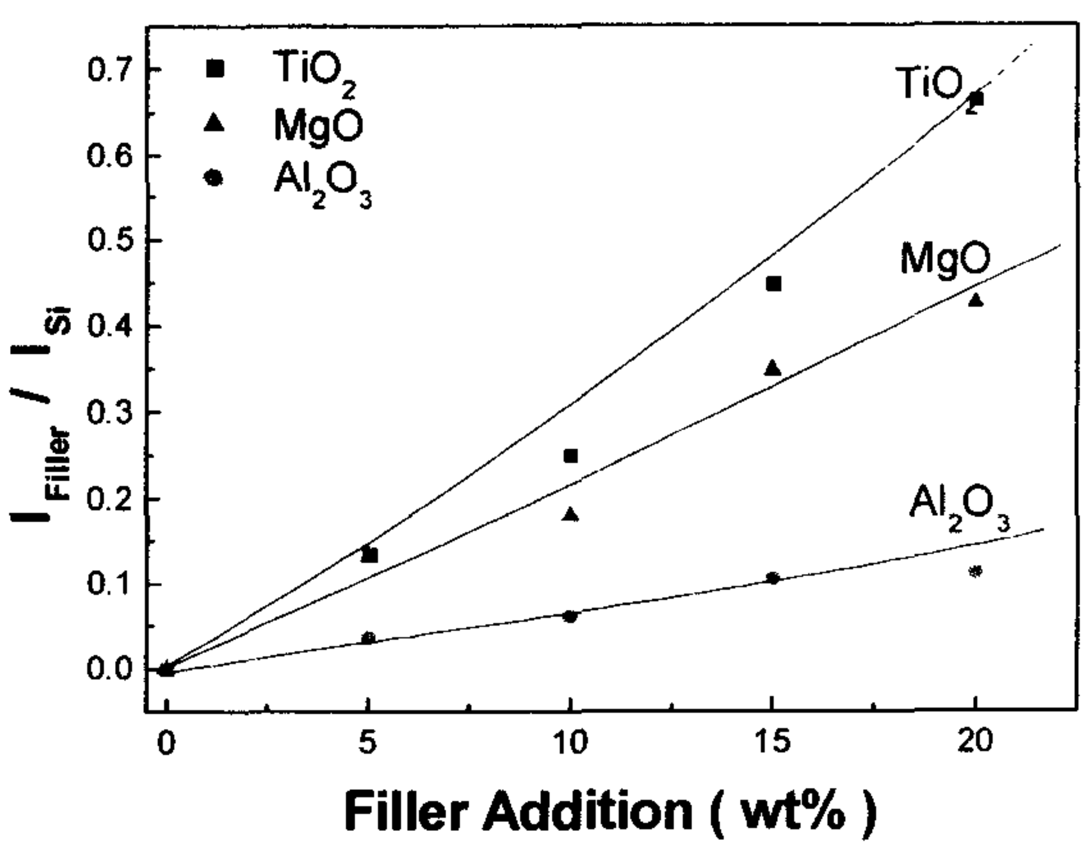

Fig. 1. Calibration charts for Al_2O_3, MgO, and TiO_2 fillers.

Then, the microcomposite specimens with unknown amounts of residual ceramic filler crystal phase were pulverized and mixed with 20 wt% silicon standard, followed by XRD measurement 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 determined intensity ratios using the calibration chart shown in Fig. 1. The shape of the residual ceramic fillers in the densified filler-glass micro-composite was investigated using scanning electron microscopy (SEM) and the resultant mechanical strength of the specimen was characterized by a compression test using specimens with about 8 mm in diameter and about 5 mm in thickness.

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 Fig. 2, residual amount is always less than the input, indicating that partial dissolution of the added ceramic fillers into the studied non-Pb based glass system has occurred. The same result was also yielded for other types of ceramic fillers. The density of the densified specimens was in general higher than 95% of the theoretical value. These phenomena indicate the fact that the studied BZB based glass system has a capability to host various types of ceramic fillers to form thermo-chemically stable microcomposites at the processing temperature suitable for PDP systems.

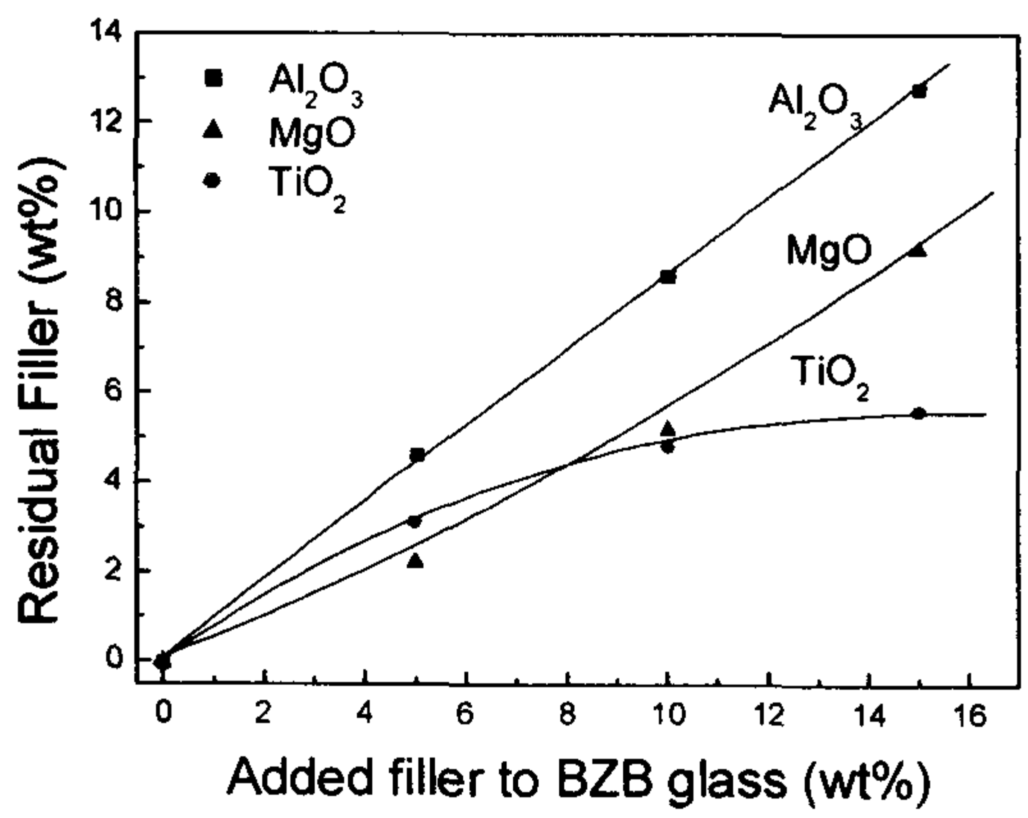

Fig. 2. Amount of residual filler as a function of input amount.

3.2 Microstructure

Fig. 3 shows scanning electron micrograph of the densified specimens with 5 wt% of SiO_2, Cordierite, and ZrO_2 fillers, respectively. Residual fillers appear relatively dark in Fig. 3 in secondary electron mode 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 noted to be located mainly at the boundaries of the formerly glass frits and their shape was severely distorted from the initial shape, possibly due to the partial dissolution of the ceramic fillers into the glass. The same phenomenology was observed for other types of ceramic fillers as well.

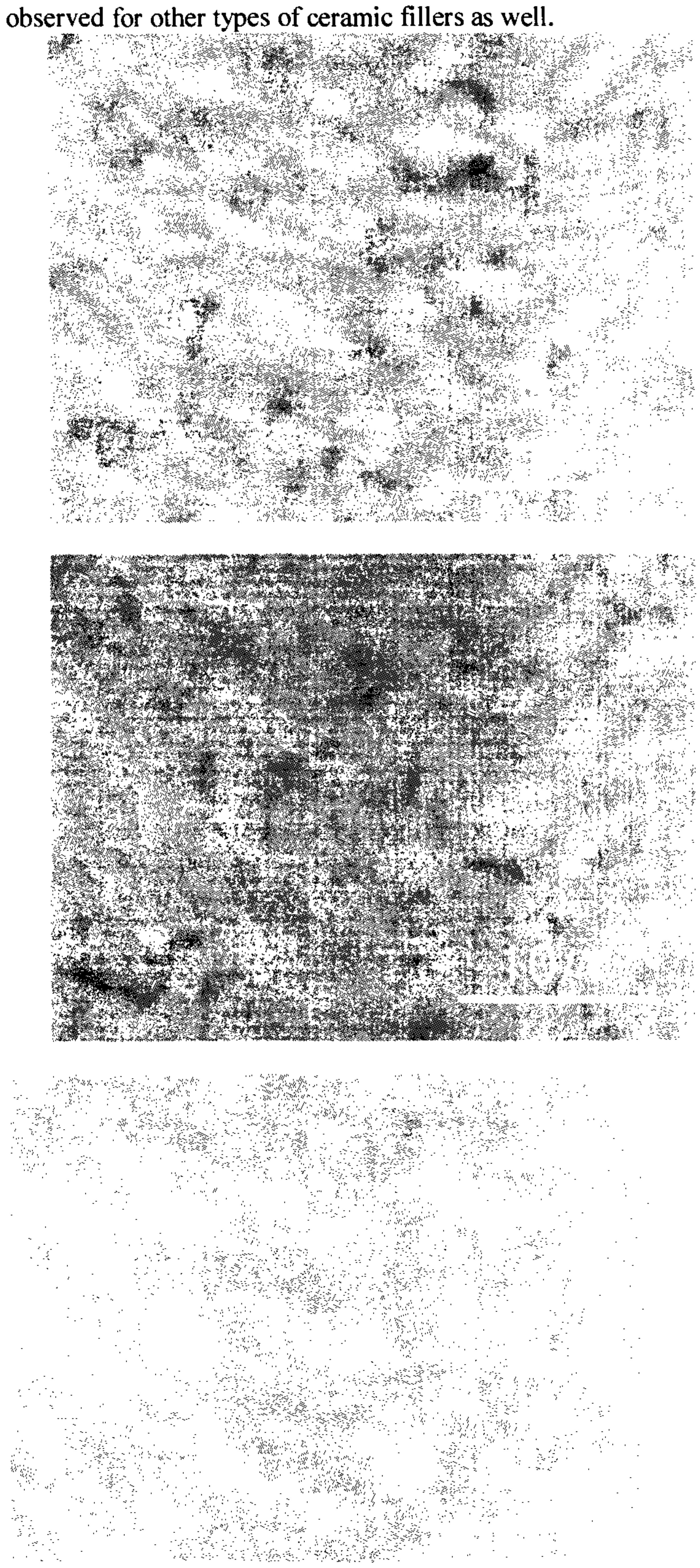

Fig. 3. Scanning electron micrographs of specimens with 5 wt% of SiO_2 (top), Cordierite (middle), and ZrO_2 fillers (bottom).

3.3 Mechanical strength

The ceramic filler-added microcomposites demonstrated improved mechanical strengths as compared to the glass itself due to the role of residual crystalline ceramic filler phases as seen in Fig. 4. In Fig. 4, increase in strength at 5 wt% filler addition is pronounced while further increase in filler addition does not seem to justify the addition from the viewpoint of mechanical strength improvement. Actually, the addition of too much ceramic fillers

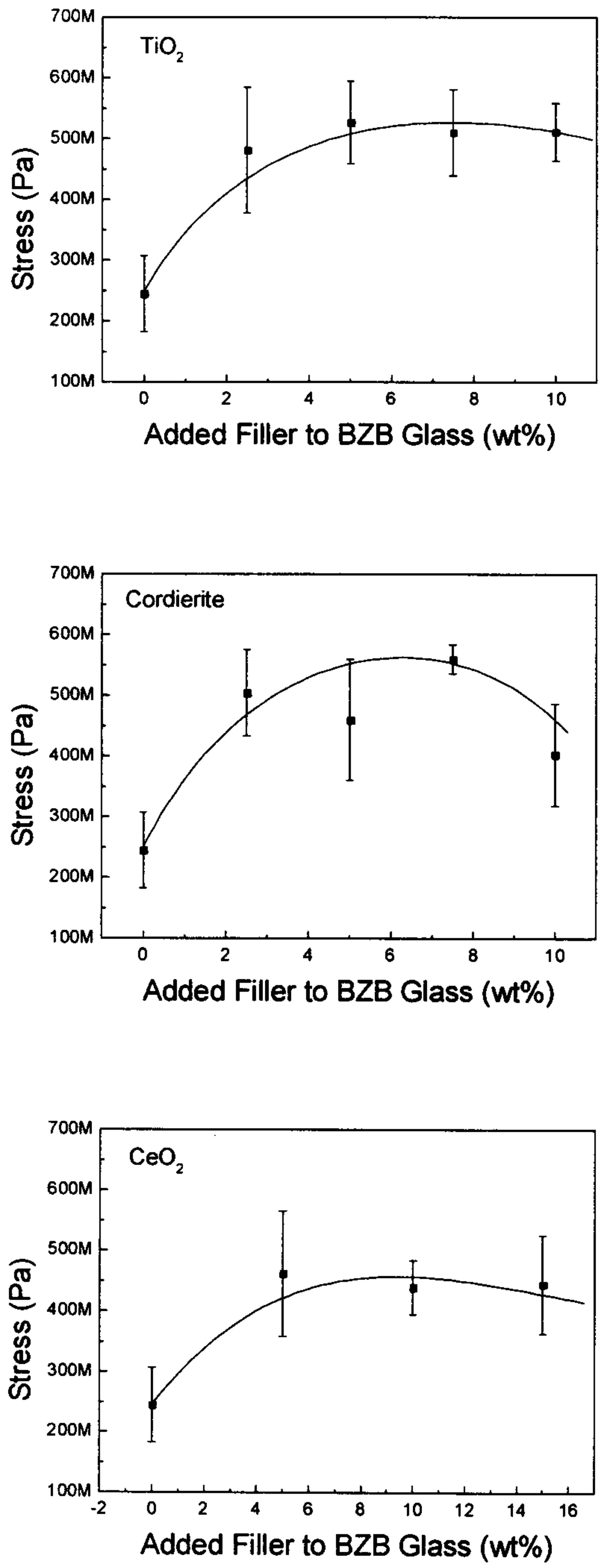

Fig. 4. Change in mechanical strength as a function of filler addition to BZB-based glass. Types of fillers are TiO_2 (top), Cordierite (middle), and CeO_2 (bottom).

would eventually decrease the mechanical strength because of the poor densification. Thus, no further increase or slightly decreasing trend in mechanical strength beyond 5 wt% filler addition in Fig. 4 would be due to the inferior densification of the microcomposites as compared to the glass itself. Residual pores associated with the incomplete densification are the source of crack growth and thus diminished strength. Elastic modulus of the filler -added composites also exhibited very similar results to the trend in strength. Microcomposites with other ceramic fillers also demonstrated similar results.

Since the ceramic filler phases were located mainly at boundaries of the formerly glass frits, it is suggested that the use of the more fine glass frits would result in a more evenly dispersed residual ceramic filler phases, which, in turn, would yield a more reliable glass-filler microcomposite with less-scattered mechanical properties.

4. Conclusion

The studied BZB-based glass system three distinctive features as follows. (1) Its thermochemical stability to form stable filler-glass microcomposites, (2) well-dispersed ceramic filler phases at boundaries of formerly glass frits, and (3) improved mechanical properties as compared to the glass itself. These features brighten the feasibility of a 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 material in plasma display panels.

5. References

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