Feasibility on Fillers for Bismate Glass System Used for Etching Process in Barrier-Ribs

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Abstract

It is suggested that the bismate glass system is one of alternatives to the lead glass for barrier-ribs in PDP. Moreover it is necessary to investigate the resultant change in properties with addition of ceramic fillers. Glass frit was selected to be a Bi_2O_3-ZnO-B_2O_3-Al_2O_3 and two fillers, ZnO and Al_2O_3 were added into a glass matrix with the different content. We investigated thermal, chemical properties of bismate glass system with two different fillers. We confirmed that addition of fillers effects properties of composites such as the thermal expansion coefficient, etching mechanism.

1. Introduction

Recently, there are some environmental issues such as RoHS (Restriction of Hazardous Substances) and WEEE (Waste Electrical and Electronic Equipment) in the display industry [1]. Therefore, many studies are in progress to replace lead glasses with lead-free glasses [2,3]. One of the alternatives is bismate glasses. As the bismate glass and the lead glass have the similar atomic weight and the similar values in terms of physical properties, the properties of bismate glasses has been investigated as a material for barrier-ribs in PDP [2]. To improve thermal and mechanical properties of barrier-ribs, it is essential to conduct a study about the reaction between glass matrix and ceramic filler. It has been widely progressed to consider proper ceramic fillers to the existing compositions based on PbO system [6]. It is necessary to develop suitable ceramic fillers for PbO free glass system.

There are several methods to make barrier–ribs in PDP such as acid etching, sand-blasting, molding (lift-off), and screen printing [4]. Nowadays, the acid etching process is one of the most popular processes to form barrier-ribs in PDP. The etching process is more profitable than other processes to raise uniformity of barrier-ribs (Fig. 1). Ceramic fillers included in a glass matrix influence mechanism of etching. We need to figure out how the behavior of the ceramic fillers occurs during etching. To do it, we observed the surface morphology on a matrix etched by HNO_3 using Scanning electron microscope (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD).

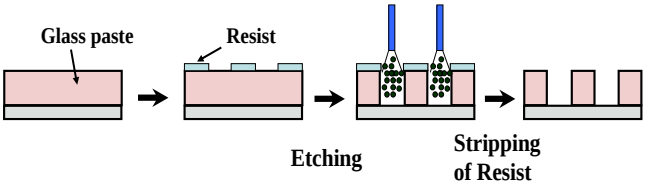


Figure 1 Diagram of etching process for barrier-ribs.

2. Experimental Procedure

Glass frit was a Bi_2O_3-ZnO-B2O3 composition as a barrier-rib to replace the current PbO system in PDP. The batch was well mixed with ball milling for 12h and was melted in an alumina crucible at 1200℃ for 1h. The melt was quenched into a stainless roller to make glass cullet. The quenched glass was pulverized to an average particle size of 2.5 ㎛ using a planetary mono mill with zirconia balls and a container. Two fillers, ZnO and Al_2O_3 were added into a glass matrix with the different content. The glass frit and ceramic fillers (ZnO, Al_2O_3) were mixed by a ball mill for 12h and dried at 130℃ for 12h. The compositions of the two fillers-added specimens are shown in Table 1. Finally, pellets were made using the pressure machine and then sintered at 550℃ for 30min.

Glass transition temperature (T_g) and crystallization peak of glass and glass-ceramic fillers were determined using a differential thermal analyzer (DTA 8120, Rigaku). Using TMA (TMA 2940, TA Instruments), thermal expansion coefficients (CTE) were measured. Samples were tested for density using the Archimedes method. The hardness and the elastic modulus of composites were evaluated by using Vickers hardness tester and a resonance method. Surface morphology was observed according to reactivity of glass and filler using Field Emission Scanning Electron Microscope (FE-SEM, S-4200,

Hitach) and Energy Dispersive Spectroscopy (EDS). Surface morphology of composite etched by 0.5%HNO_3 was observed using SEM and X-ray diffractometer (DMAX-2500, Rigaku)

Table 1. Batch of composition, the glass frit and ceramic fillers (Al_2O_3 and ZnO)

Samples (wt%)	Frit	Ceramic Fillers	
		ZnO	Al_2O_3
BF1	85	10	5
BF2	80	15	5
BF3	75	20	5
BF4	80	10	10
BF5	75	15	10
BF6	70	20	10

3. Results and discussion

According to non-isothermal DTA test, Tg was found at 465℃ for both the bismate glass and the glass composites (glass frits with fillers) and crystallization peaks were detected at 565℃ and 592℃ for glass frits with fillers. The isothermal experiment was conducted by DTA as shown in Fig. 2. Temperature increased at the rate of 10℃/min from the room temperature to 550℃ which is the firing temperature, held at 550℃ for 30min and cooled down to the room temperature.

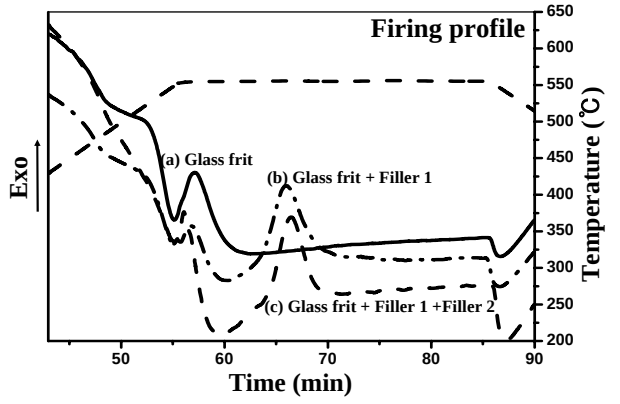


Figure 2 The isothermal experiments of glass frits and glass composites with fillers. (a) glass frit (d_{50}=2.5㎛) (b) glass frit + filler ZnO (c) glass frit + fillers (Al_2O_3, ZnO)

For frits with fillers (b and c), two exothermic peaks occurred during firing process at 550℃ for 30min. One of the peaks means the devitrification of matrix glass and the other a reaction resulted from a filler-glass. Glass composites added Al_2O_3 did not show any crystallization peak. There is no reaction between Al_2O_3 filler and bismate glass matrix as shown in Fig. 2. With only ZnO filler, the frits showed an exothermal peak indicating a reaction between the filler and frits at 10min after temperature reached at 550C.

The coefficient of thermal expansion (CTE) changes as a result of the addition of ceramic fillers (ZnO, Al_2O_3). Figure 3 shows the change in CTE as a function of fillers addition. Theoretical CTE data is calculated by the model of Turner [5].

$$\alpha_r = \frac{\alpha_1 K_1 F_1/\rho_1 + \alpha_2 K_2 F_2/\rho_2 + \cdots}{K_1 F_1/\rho_1 \quad + K_2 F_2/\rho_2 \quad + \cdots}$$

where α is the CTE, V the volume fraction, K the bulk modulus.

This discrepancy between the Turner's model and the experimental result may have arisen from the rough estimate of the provided CTE factor *pi* of the model. The results also varied depending on the type of the glass system and the number of constituents in the system. The CTE values of bismate glass composites with ceramic fillers were slightly lower than those of glass substrate such as the PD200 glass sheet (8.3×10^{-6}/K). But the CTE value can increase to be applied to barrier-rib in PDP by controlling filler size, type or changing glass composition.

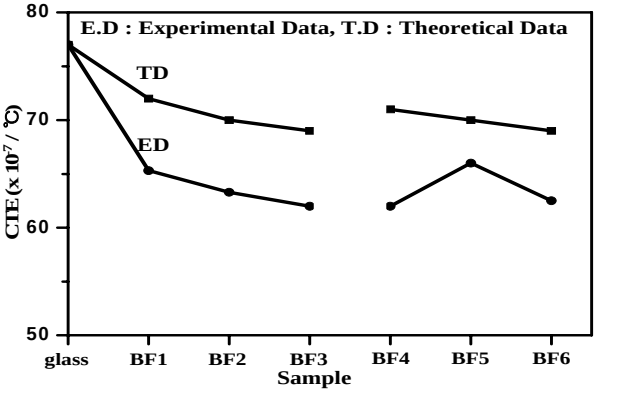
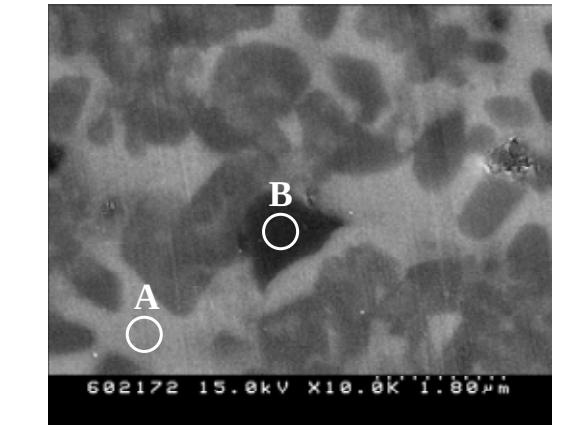
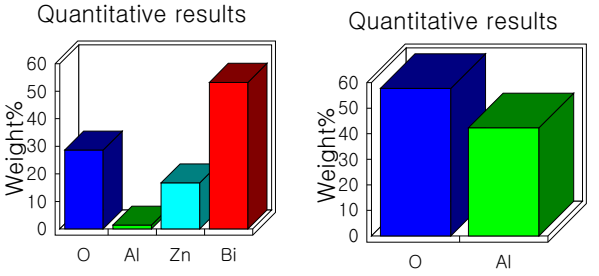


Figure 3 The change in coefficient of thermal expansion as a function of fillers added to bismate glass matrix.

XRD analysis, SEM and EDS were conducted to observe surface morphology on the glass composites with fillers as shown in Fig 4 and Fig 5. The morphology of the glass matrix after sintering was characterized by SEM as shown in Fig. 4(a). Two regions were quantitatively analyzed by the energy dispersive spectroscopy (EDS). The brighter areas (A areas in Fig 4(a)) were relatively rich in Bi, which is a glass matrix. On the other hand, the darker area (B area in Fig 4.(a)) was rich in aluminium and oxygen, implying that these regions are the Al_2O_3 filler (Fig. 4b). In the figure, the grey area is a crystal formed in the glass matrix.



(a)



(b)

Figure 4 (a) SEM image of composite(BF1) and (b) EDS in the glass matrix and the ceramic filler(Al_2O_3)

As a result of XRD analysis, two new crystal phases were found (Fig. 5) in the glass composites. One is from the reaction between the glass matrix and the ZnO filler. The other is a crystal phase from the glass matrix surface (Fig. 2b and c). The change of complex microstructure with the new crystal phases are resulted from the reaction. But there is no reaction between glass matrix and Al_2O_3 filler according to results of XRD analysis, DTA and EDS (Fig. 2c)

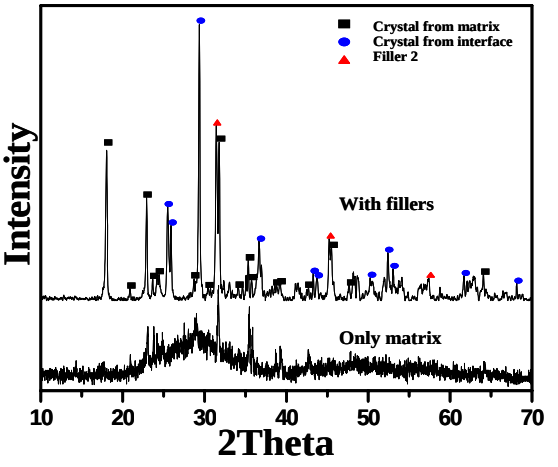


Figure 5 XRD patterns of only glass and the composite (glass frit and fillers) were sintered at 550℃ for 30min.

Figure 6 shows the surface morphology of glass composite etched by 0.5% HNO_3 at 45℃. There are many holes on the surface of composite etched by HNO_3. We consider that it is not ceramic fillers but glass matrix and new crystal phases which are dissolved by etching. In other words, the etching mechanism of barrier-ribs is to remove fillers by the acid because of the reaction phase around a filler.

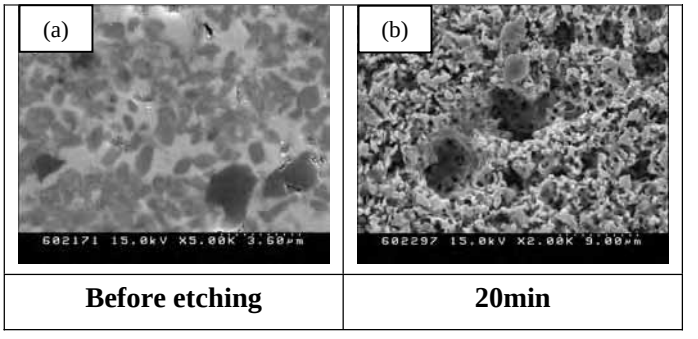


Figure 6 SEM images of glass composite (BF1) etched by 0.5% HNO_3 at 45℃ for 20min.

4. Conclusion

The effect of ceramic fillers (ZnO, Al_2O_3) addition to the Bi_2O_3-ZnO-B_2O_3 glass system was investigated from the viewpoint of its application to barrier ribs of plasma display panels. Because of crystalline ceramic fillers to the glass matrix, thermal and chemical properties such as CTE value, etching mechanism and crystalline behavior are influenced compared to the properties of glass matrix itself.

5. Acknowledgements.

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6. References

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