Thermal Properties of Phosphate Glass with Additives for Barrier-Ribs in Plasma Display Panel

Chungyong Lee[1], Dongsun Kim[1], Youngjin You[2], Sangho Lee[2] Seongjin Hwang[1] and Hyungsun Kim[1]

[1]School of Material Science Engineering, Inha University, Incheon, 402-751, Korea

TEL:82-32-860-7532, e-mail: kimhs@inha.ac.kr.

[2]Phoenix PDE Corp., Gumi-si Gyeonsangbuk-do 730-030, Korea

Keywords : Phosphate glass, Plasma Display Panel, Barrier-ribs

Abstract

Phosphate glass added the various alkali additives is one of the substitutive materials for the barrier-ribs in plasma display panel. The results of differential thermal analysis and coefficient of thermal expansion show that the alkali oxides affect the thermal properties of phosphate glass.

1. Introduction

Materials of barrier-ribs in plasma display panel (PDP) have been researching to replace the commercial materials to the new materials for low cost and harmlessness to people and environment [1-3]. Lead borosilicate glasses, the commercial components of the barrier ribs, have been used in many electronic and optical applications because it has desirable properties, such as low softening temperature and chemical durability [4-6]. However the Pb contained component is harmful to health and environmental effects [1].

Another reason for replacement of the components is cost. PD200 glass substrate, which has been using for rear substrate glass in PDP till now, needs to be substituted for its high cost. One of the candidates of the rear substrate glass is soda-lime glass. The soda-lime glass substrate is most general type of glass and cheap. However, the low-priced soda-lime glass substrate has different thermal properties from PD200. Especially, PD200 (Asahi Glass, Tokyo, Japan) has higher glass transition temperature (T_g) than T_g of the soda-lime glass (~570°C) as the rear substrate in PDP [7]. Thus, most materials, also the barrier-ribs in PDP need to be decreased its T_g by changing its composition. The coefficient of the thermal expansion (CTE) should be considered when new glass composition is deigned because the barrier-ribs are co-fired with the rear glass substrate so that it requires the similar CTE as substrate. The CTE of soda-lime glass is similar to that of PD200 [8].

Many researches have been reported about phosphate glasses such as zinc-calcium borophosphate glasses and sodium phosphate to have high CTE and low T_g and melting temperature [9-11]. P_2O_5 glasses have a potential as a new composition of barrier ribs with soda lime glass substrate because of their low melting temperature [12]. However, the low melting glasses usually exhibit poor chemical stabilities and their hygroscopic nature makes them unsuitable for many commercial applications [13]. In binary zinc phosphate glasses with X (X = Li_2O, Na_2O, K_2O, CaO, B_2O_3 and SiO_2), leachability of zinc ions has been investigated using various control agent such as X (X = Li_2O, Na_2O, K_2O, CaO, B_2O_3 and SiO_2) [14]. Alkali and alkali-earth oxides, added to phosphate glass system, are able to control the chemical durability. Furthermore, adding additives, the T_g of phosphate glass is also decreased [15].

The purpose of the present paper is to understand primary thermal properties and chemical etching rate of B_2O_3-ZnO-P_2O_5 glass system with alkali additives for the glass matrix of barrier-ribs in PDP. Thus, we investigated the B_2O_3-ZnO-P_2O_5 glass region with adding additives such as BaO, SrO, CaO. And we studied the B_2O_3-ZnO-P_2O_5 glass system with various additives such as Li_2O, BaO and SnO_2. Additionally, the etching rate was measured for the barrier ribs made of the selected B_2O_3-ZnO-P_2O_5 glass system with additives glass to select proper glass composition.

2. Experimental

All compositions of the BZP (B_2O_3-ZnO-P_2O_5) glasses were prepared from chemically pure reagents P_2O_5, ZnO, H_3BO_3, $CaCO_3$, $SrCO_3$, $BaCO_3$, SnO_2, Na_2CO_3 and

Li_2CO_3(Aldrich, USA). We determined the experiment range and measured the glass transition temperature (T_g) of B_2O_3-ZnO- xP_2O_5-(100-x) RO (R: Ca, Sr and Ba) compositions by changing contents of RO by differential thermal analyser (Thermo plus TG 8120, Rigaku, Japan). All the batches were 25g and its components were weighed to within 0.0005g. The mixed powders were melted in a platinum crucible at 1200-1300°C for 1h and then quenched it to make a cullet with the stainless ribbon roller. The quenched cullet was pulverized to make frit with 45um sieve.

Glass transition temperature (T_g) and dilatometer softening point (T_{dsp}) of the frit were determined using a differential thermal analyzer (Thermo plus TG 8120, Rigaku, Japan) at a heating rate of 10°C/min. Coefficient of thermal expansion of the B_2O_3-ZnO-P_2O_5 glasses was measured using a thermo dilatometer (Dilatometer PT-1600, Linseis Germany). Barrier ribs were made by an etching process with 0.5%NHO_3 for 240sec. The etching rate was calculated by scanning electron microscope (SEM).

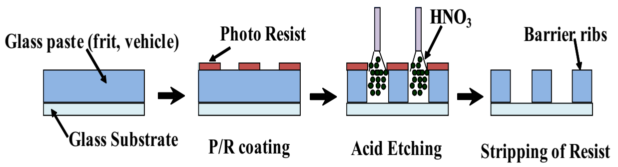

Fig. 1. Schematic diagram of etching process for barrier ribs

3. Results and discussion

Firstly, the B_2O_3-ZnO-P_2O_5 glasses with additives were investigated their T_g (Fig. 2). The T_g of B_2O_3-ZnO-P_2O_5 glasses gradually increases to the content of around BaO 15 mol%, SrO 25 mol% and CaO 30 mol% and then it was decreased by adding more additive (BaO, SrO, CaO). Each of glasses is significantly different to the slopes of their T_g. Pervious researches have reported that the various properties of phosphate glasses are conducted by the type and amount of the additives [15]. Thus, this result suggested that T_g of the phosphate glasses can be controlled by the additives (BaO, SrO and CaO) in B_2O_3-ZnO-P_2O_5 glass system as shown in Fig. 2.

We designed B_2O_3-ZnO-P_2O_5 glasses adding additives ($RO+R_2O+RO_2$) owing to have its lower Tg and its suitable CTE as shown Fig. 3 and 4. As shown in Fig. 3, the T_g and T_{dsp} of the glasses decrease with increasing additives ($RO+R_2O+RO_2$).

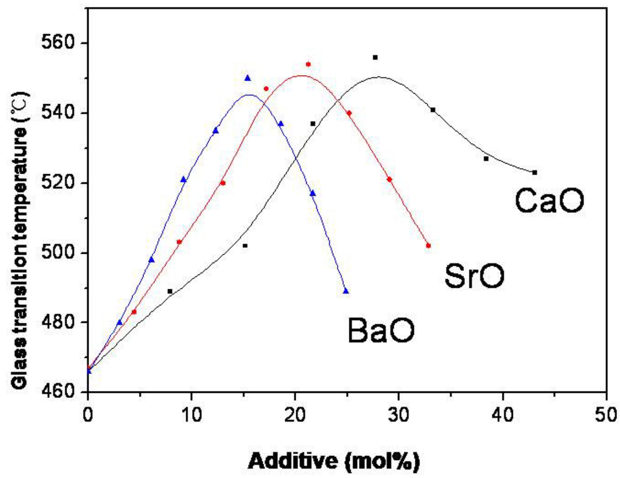

Fig. 2. Glass transition temperature (T_g) of phosphate glasses with various additives (BaO, SrO, and CaO).

However, they fluctuate at the each of composition. It can be related to the ratio of the additives. Considering that the relationship between T_g and T_{dsp} in phosphate glasses is liner, the difference between T_g and T_{dsp} will be about 24°C. The relationship can be powerful to prepare new phosphate glasses with thermal properties. Furthermore, the thermal properties (T_g and T_{dsp}) of the glasses consisted up to the 13mol% of additive in B_2O_3-ZnO-P_2O_5 glass system are sufficient of the matrix glass for barrier ribs with soda lime glass substrate.

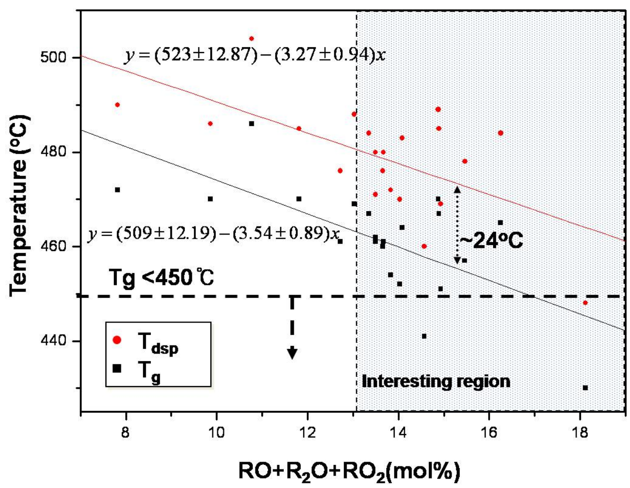

Fig. 3. Thermal properties (T_g and T_{dsp}) of phosphate glasses with increasing additives ($RO+R_2O+RO_2$).

However, some compositions are impossible to apply as the barrier rib due to its CTE. In Figure 4, it shows the CTE of each B_2O_3-ZnO-P_2O_5 glass system. The area shows the possible CTE of the glass composition similar to CTE of soda lime glass substrate (80±5 x 10^{-7}/K) and the contents of additives (13 - 19mol%) from Fig. 3. Several candidate glass compositions were able to be selected for the barrier ribs with Figs. 3 and 4.

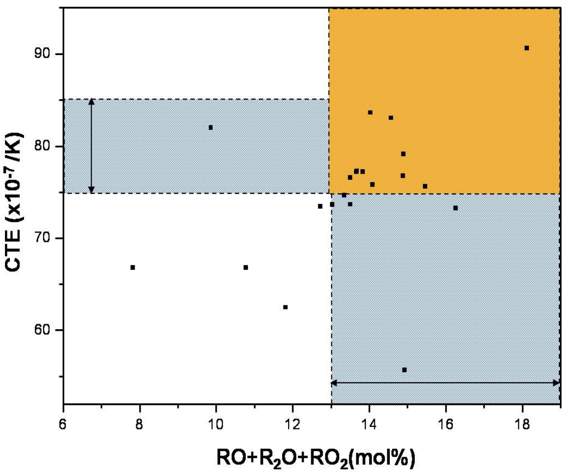

Fig. 4. Coefficient of thermal expansion of phosphate glasses with increasing additives (RO+R_2O+RO_2).

Synthetically, we consider the CTE and T_g with additives in B_2O_3-ZnO-P_2O_5 glass system. Figure 5 shows the potential compositions for matrix glass of barrier ribs with soda lime glass substrate.

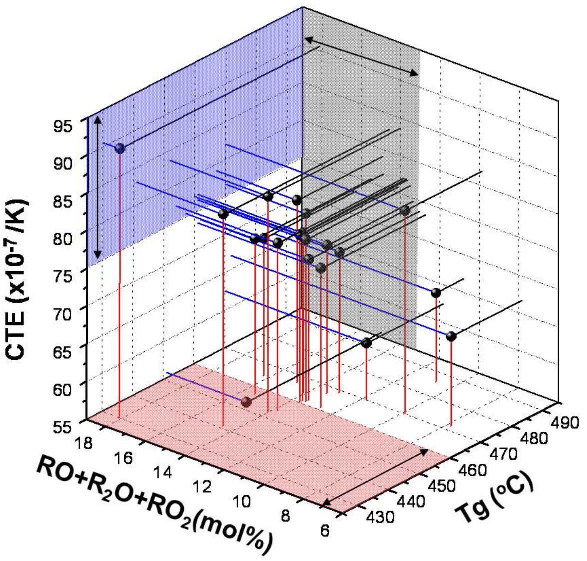

Fig. 5. Coefficient of thermal expansion (CTE) of phosphate glasses with mixed additives (RO+R_2O+RO_2).

Etching rate was determined between a selected B_2O_3-ZnO-P_2O_5 glass composition and commercial glass composition as a reference. The etching rate of the S01 is able to substitute the commercial composition of barrier ribs to the B_2O_3-ZnO-P_2O_5 glass system.

TABLE 1. Etching rate of selected B_2O_3-ZnO-P_2O_5 glass systems by 0.5%HNO_3.

Samples	Before etching(㎛)	After etching(㎛)	Etching rate
Reference	115	42	100%
S01	122	39	114%

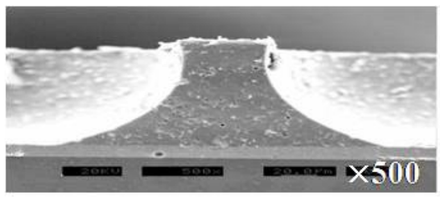

Fig. 4. SEM image of etched B_2O_3-ZnO-P_2O_5 glass.

4. Summary

We investigated the thermal properties of glasses based on the B_2O_3-ZnO-P_2O_5 glass system with RO and RO+R_2O+RO_2. It shows that Tg of B_2O_3-ZnO-P_2O_5 glass is changed by adding the various oxides. With various fillers, the thermal properties of the glasses are able to be controlled. It would be a new composition for the under 500°C sinterable barrier ribs.

5. Acknowledgements

This work was partially supported by the Ministry of Education and Human Resources Development (MOE), the Ministry of Commerce, Industry and Energy (MOCIE) and the Ministry of Labor (MOLAB) through the fostering project of the Lab of Excellency and was supported by the Ministry of Commerce, Industry and Energy (MOCIE) through the New Growth Engine Project

6. References

1. R. Morena, J. Non-Cryst. Solid, 263-264, 382-387(2000)
2. D.N. Kim, J. Y. Lee, J. S. Huh and H. S. Kim, J. Non-Cryst. Solid 306, 70,(2000)

3. S. G. Kim, J. S. Park, J. S. An, K. S. Hong, H. H. Shin and H. S. Kim, J. Am. Ceram. Soc. 89, 902(2006)
4. D. M Mattox and J. H. Robinson, J. Am. Ceram. Soc., 80 [5] 1189-92 (1997)
5. J.-H. Jean, S. C. Lin, and S.L. Yang, Jpn. J. Appl. Phys., Part *2*, 34 [4A] L422–L424 (1995)
6. N. Nair, A. Bhalla, and R. Roy, Am. Ceram. Soc. Bull., 75 [1] 77–82 (1996)
7. G. H. Hwang, H. J. Jeon, Y. S. Kim, J. Am. Ceram. Soc, 85 [12] 2956-60 (2002)
8. I. Hiroyuki, Monthly Display., 11 [11] 27-30 (2005)
9. D. G. Grossman and C.J. Phillips, J. Am. Ceram. Soc. 47, p471 (1964)
10. J. M. Clinton and W. W. Coffeen, Ceramic Bulletin 63, p1401 (1984)
11. Y. M. Moustafa and K. J. El-Egili, J. Non-Cryt. Solid 240(1-3), p144-153 (1998)
12. X. Yu, D. E. Day, G. J. Long, R. K. Brow, J. Non-Cryst. Solid 215, p21-31(1997)
13.H. Schoze, Glas-Natur, Struktur und Eigenschaften, Springer berlin, (1977)
14. R. Pyare, J. Mater. Sci. 38 2079-2086 (2003)
15. J. E. Shelby. Non-Cryst. Solid, 263&264 271-276 (2000)