Application of Fusion Behavior of Frits to Control of Transmittance in Transparent Dielectric

Seung Bo Shim*, Seong Jin Hwang, Hyung Sun Kim
School of Material Engineering, Inha University, 253 Yonghyun-dong, Namgu, Incheon, 402-750, Korea
Phone: 82-032-860-7545 E-mail:kimhs@inha.ac.kr.

Abstract

It is important to keep a constant transmittance of dielectric during firing. To control the shrinkage and fusion stage of frits in firing, we used a hot stage microscope (HSM) to analyze the thermal properties of the lead and bismate glass frits by the in-situ method. This research would be useful for improving the reliability of transmittance of dielectric during firing in industry using a large furnace with temperature deviation.

1. Introduction

Plasma display panel (PDP) has been adopted in commercial display market. It has advantages over display devices in its large size, simple structure, high resolution and wide viewing angle compared to other flat panel displays. In PDP, lead oxide is widely used for the transparent dielectric, barrier rib and sealing material [1]. However, to prevent the generation of hazardous waste, European Union (EU) have enacted Restriction on Hazardous Substance (RoHS) [2]. From this reason, it is necessary to develop other materials. Recently, the bismate glass is interested in for replacing materials and many researches are reported for the application in PDP [1,3]. However, the bismate glass is found not to be satisfactory as compared with the commercial lead glass system because of different thermal characteristics [3-4].

To determine the thermal properties of glass frits are an important factor for the controlling and improving the transparent dielectric materials. Many kinds of the thermal analyzers were in existence for analyzing thermal properties of frits. Those methods for analyzing thermal properties of glass are time consuming and expensive. However, the hot stage microscope can easily determine the thermal properties about glass frits at elevated temperatures [5-6]. In this work, we studied the shrinkage, fusion and melting rate, and viscosity of bismate glass for improving the transmittance of transparent dielectric in PDP.

2. Experimental procedure

The lead glass (commercialized composition of transparent dielectric) was prepared by mixing powders over 99% pure of PbO, SiO_2, B_2O_3, Al_2O_3 and TiO_2 (Aldrich, USA) and the bismate glass (developed compositions) was prepared by mixing powders over 99%of Bi_2O_3, B_2O_3, ZnO, BaO, Al_2O_3 SiO_2 and CeO_2 (Aldrich, USA). The batches were melted in an alumina crucible at 1000-1300℃ for 1h. The glasses were crushed and milled in dry conditions in a zet mill.

The particle sizes were analyzed by a particle size analyzer (LS230 & N4PUS, Coulter, USA). The glass transition temperature (T_g) was determined with a thermogravimetry-differential thermal analysis (TG-DTA, Rigaku, Japan) at a heating rate 10℃/min with alumina as the reference. The Littleton softening point (Ts) was measured by Ts equipment (Orton, USA)

Two glasses, $PbO-SiO_2-B_2O_3$ system, $Bi_2O_3-B_2O_3-ZnO$ system were analyzed using the automatic hot stage microscope (HSM, Ajeon Co. Korea) for thermal behaviors of frits. The measurement method was conducted in air environment at heating rates of 10℃/min on cylinder typed samples (3x3 mm), is normally placed on an alumina plate at the end of a thermocouple (Pt/Rh). The microscope projects the sample image through a glass window and onto the recording device. The computerized image analysis system automatically records and analyses the sample geometry during heating. HSM software calculates the percentage decreasing angle and area of the sample images relative to the initial shape of the sample. The surface tension was measured by a sessile drop method [7].

3. Result and discussion

The particle size distributions of frits for the lead and the bismate glasses are shown in Figure 1. Each of glass frits has the similar particle sizes and distributions. The frits can be used in a transparent dielectric for PDP industries.

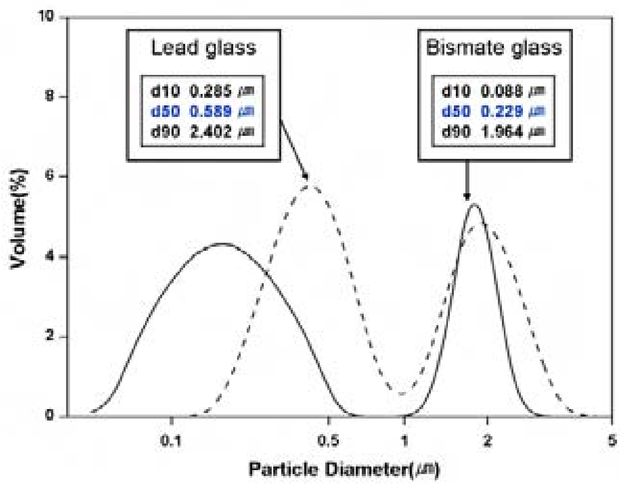

Figure 1 Particle size distributions of the glass frits (the lead and the bismate frits)

As shown in Fig. 2, the lead glass has lower Tg and Ts than bismate glass. In terms of the viscosity of glass, in fact, the range of Ts has an impact on the behavior of shrinkage and the fusion of frits during firing with counting that the frits size of two glasses is the same distribution (Fig. 1).

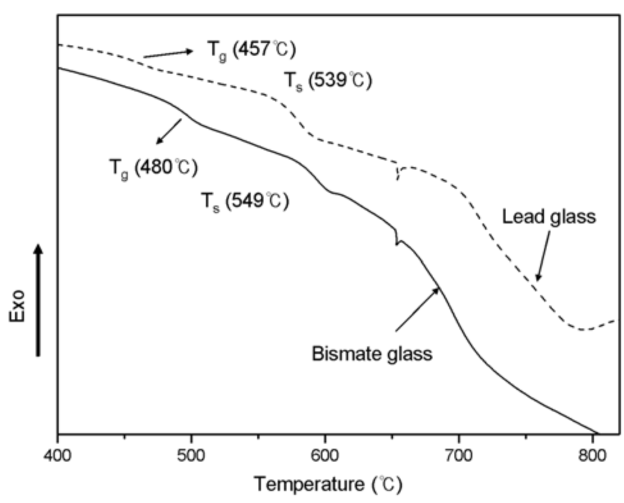

Figure 2 DTA curves of the lead and the bismate glass frit

Figure 3 shows the change of angle with the lead and the bismate glass pellets at elevated temperatures. The starting point of deformation pellet was 540℃ for the lead glass, while the bismate one at 570℃. On the other hand, the rate of angle change for the lead glass pellet was faster than that of the bismate one in the range of deformation showing a narrow curve as shown in Fig. 3. Considering an industry process in the firing temperature of the transparent dielectric, the range of 560-600℃ is the practical condition. The lead glass has more thermal stability than the bismate glass in the firing. Therefore it is necessary to control the shrinkage rate and the fusion rate of frits in the range of firing temperature to get a high reliability of transmittance.

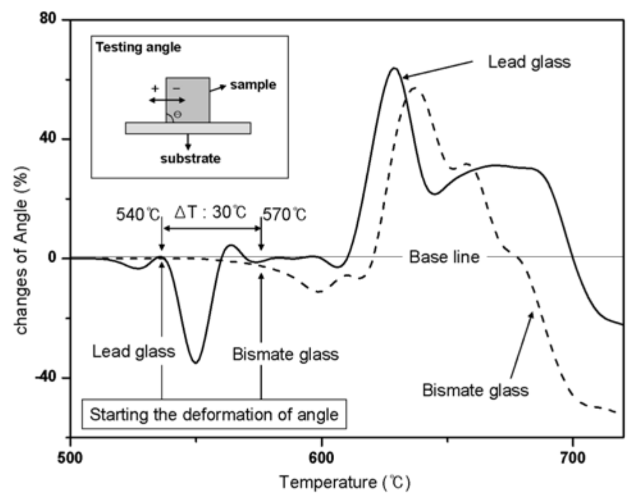

Figure 3 Change of angle with the lead and the bismate glass pellets by the HSM

In Table 1, the surface tension of the lead and the bismate glass is 0.39 and 0.38 (N/m), respectively at 690℃. From the results of HSM, the viscosity of the lead and the bismate glass is 6.42 and 6.54 (dPas), respectively at 580℃. Based on the glass sintering, we assumed that the lead glass frit size and the firing time are the same as the bismate frit [8] and the glass viscosity at 690℃ is equal to that at 580℃ based on the earlier research [9]. The shrinkage is determined by the surface tension and the viscosity obtained by HSM for the lead and the bismate glass frit. The shrinkage of lead glass frit may be higher than that of bismate glass frit at the same temperature. Furthermore, assuming that the shrinkage is related to the fusion rate of glass frit, the lead glass frit would have a faster fusion rate than the bismate glass frit.

Table 1 Thermal properties comparison of the lead and the bismate glass

Factor for glass sintering	Lead glass	Bismate glass
Surface tension (γ : N/m) at 690℃	0.39	0.38
Viscosity (η : dPas) at 580℃	6.42	6.54
$\frac{\gamma}{\eta}$	6.07x10^{-2}	5.81x10^{-2}

Considered the result of Fig. 3 and Table 1, we suggest that the lead glass may be reached the fusion temperature earlier than the bismate glass frit. Therefore, a schematic diagram presents the difference of fusion temperature for dielectric thick films (green sheet or printed layer) of two different compositions to be melted down on the bus electrodes (Fig. 4). The fusion rate of thick films on a substrate is strongly related to the transmittance of dielectric. With the heating rate (10℃/min) and the starting fusion temperature, the fusion rate of lead glass with earlier fusion affects the different transmittance compared to the bismate glass.

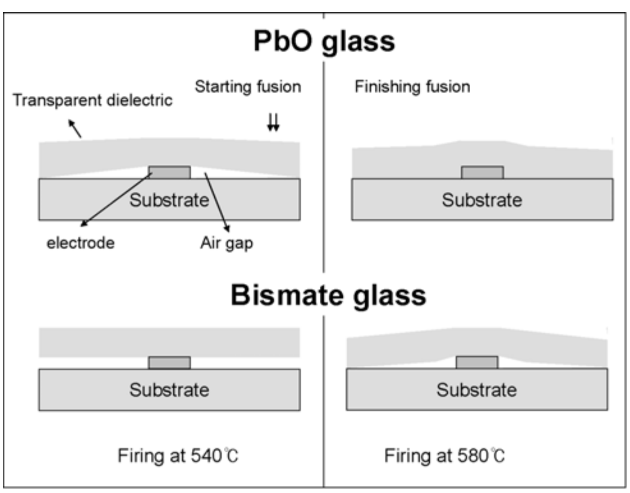

Figure 4 Schematic diagram for the fusion rate of transparent dielectric (the lead and the bismate glass frit) fired at 540 and 580℃.

4. Conclusion

We analyzed the shrinkage, fusion and melting rate, and viscosity of the lead and the bismate glass frits. The bismate glass has the slight difference of thermal properties monitored by a hot stage microscope (HSM) compared with the lead glass. The control of fusion behavior of frits during firing using HSM is useful for improving the high transmittance and the reliability of transmittance of dielectric.

5. Acknowledgements

This work is financially 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.

6. References

[1] J. S. Jeon, M.L. Cha, H.S. Kim, Mat. Science Forum, 486-487 (2005), p.321

[2] J. Fu, H Yatsuda, Phys. Chem. Glasses. 36 (1995), p.211

[3] M. L. Cha, J.S. Jeon, H.S. Kim, Mat. Science Forum, 486-487 (2005), p.325

[4] H. Scholze, Ver. Dtsch. Keram. Ges., 391, 63-8 (1962).

[5] D. A. Earl, M. Ahmed, Ceramic Engineering and Proceedings, 24[2], 3-12 (2003).

[6] M. J. Pascual, L. Pascual, A. Duran. Phys. Chem. Glasses, 42(1), 61-6 (2001)

[7] F.S. Shyr,. Mat. Sci. Letter, 10, p.946-948 (1991)

[8] J. S Park, S. M. Han, J.H. Hwang, C.Y. Kim, in Proceedings of The 5th International Meeting on International Display (Seoul, Korea, July. 2005), Korean Information Display Society, p.1229.

[9] S. Fuijino, C. Hwang, K. Morinaga, J. Am. Ceram. Soc. 87, 1, 10 (2004)