Lead free, Low temperature sealing materials for soda lime glass substrates in Plasma Display Panel (PDP)

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Abstract

New glass compositions for lead free, low temperature sealing glass frit was examined in $ZnO\text{-}V_2O_5\text{-}P_2O_5$ glass system which can be used sealing material for PDP to be made of soda lime glass substrates. Among many glass compositions, KFS-C glass showed low glass transition point (Tg) and good fluidity and adhesion characteristics when it was tested by flow button method at low temperature of 420 ℃. Its Tg was 317 ℃ and thermal expansion coefficient (CTE) was 70×10^{-7}/K. The glass frit was mixed with an organic vehicle to make a paste and it was dispensed and sealed with soda lime glass substrates at 420 ℃ for 10min. Sealed glass panels also showed good adhesion strength even sealed at low temperature of 420 ℃.

1.Introdution

Lead based glass frits have been used widely as a sealing materials for PDP. However, usage of lead will be restricted for healthy and environmental problems by such as RoHS (Restriction of Hazardous Substance). Therefore, many types of lead free glass has been developed widely[1]. One of the powerful candidates was Bi-based glasses, which has similar atomic weight and similar values in terms of physical properties with lead. But the cost of bismuth has raised sharply recently and its effect on healthy and environmental problems might be the same as lead[2]. So we developed Pb & Bi free sealing glass composition. In addition to this, we have to reduce the sealing temperature to replace PD-200 to soda-lime glass as a substrate of PDP for the cost competitiveness of PDP as for the strain point of soda lime (about 511℃) is lower than that of PD-200 glass (about 570℃). As Pb free, Bi free sealing glasses, there have been known $SnO\text{-}P_2O_5$ system [3], Mn-Sn-P system[4], and $BaO\text{-}B_2O_3\text{-}ZnO$ systems[5]. $SnO\text{-}P_2O_5$ system has poor water resistance and easily crystallized before sealing. $BaO\text{-}B_2O_3\text{-}ZnO$ system is incongruent for low temperature firing. Therefore, we developed new glass composition in $ZnO\text{-}V_2O_5\text{-}P_2O_5$ systems which have low Tg and good fluidity even fired at low temperature of 420℃. Previous works were introduced on the same composition system[6], but it was adequate for normal sealing temperature of 470℃.

2.Experimental

Fig.1 shows the whole process of sealing. The glass batches were dry mixed and melted in an alumina crucible in an electric furnace for 10~30 minutes in air at temperature between 1100~1200℃. Molten glass was quenched by 2-Roll quenching machine. The glasses were dry milled to give the frit with a mean particle size (d50) about 10 um. The thermal properties of glass frits were analyzed by TMA(Q-400, TA, USA) and DSC(Q-10, TA, USA). Fluidity of glass frits were tested by Flow button method being pressed into a pellet by mold(12.6Φ) and fired at 420℃, 10 min.

Glass frits were mixed with two types of organic vehicles based on NC (Nitrocellulose) and AC (Acrylates) binder. Pastes properties were tested by FOG (fineness of gauge) and viscometer (HB DV II+ pro, Brookfield)

Pastes were dispensed on the soda lime glass substrates by dispenser and dried for 10~30 minutes in air at temperature 100℃ and then it was pre-baked at 450℃ for 10 min. and finally fired at 420℃ for 10~30min.

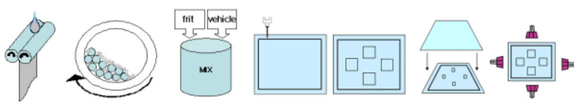


Fig. 1. Diagram of sealing process.

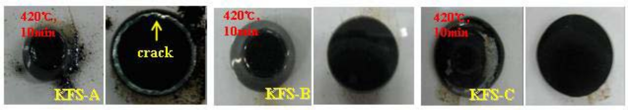
3. Results and Discussion

3.1. Glass composition and their properties

Table 1 shows some compositions and properties of glass frits. These glasses showed good fluidity even at fired 420℃. Among them, KFS-C showed best fluidity and adhesion property. As shown in Fig.2, KFS-A induced crack to glass substrate under the flow button. In case of KFS-B, its size of flow button was too small to be used even though its Tg (glass transition point) was low enough. The Tg and CTE of KFS-C was 317℃ and 70×10^{-7}/K.

Table 1. Compositions and properties of glasses in ZnO-V_2O_5-P_2O_5 system

	mol%				Glass transition point(℃)	Flow button (mm)	adhesive property
	RO	RO_2	R_2O	$P_2O_5+V_2O_5$			
KFS-A	17	5	-	85	318	20.0	Crack
KFS-B	15	5	-	85	319	16.0	Good
KFS-C	15	2	3.8	85	310	20.9	Good



Front view Rear view Front view Rear view Front view Rear view

(a) KFS-A (b) KFS-B (c) KFS-C

Fig. 2. Flow button image of KFS series

3.2. Paste characteristics

Table.2 shows the result of FOG test of the paste made with KFS-C. Two kinds of pastes also showed similar dispersion of glass frits to Pb reference paste.

Table 2. Fineness of gauge of sealing pastes

Pb Reference		AC-Binder		NC-Binder	
µm	Hegman	µm	Hegman	µm	Hegman
72	2.3	68	2.6	72	2.3
82	1.8	74	2.2	74	2.2

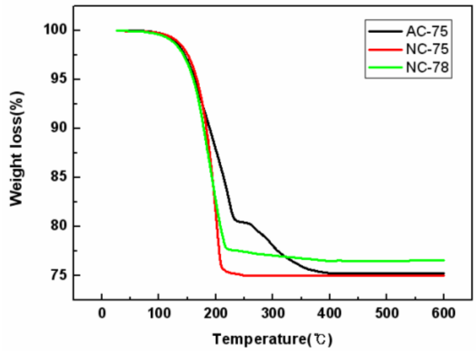


Fig. 3. TG-DTA curves of pastes

Fig. 3 shows the results of TG-DTA analysis. Paste with AC binder decomposed much higher temperature of 350~400℃ than paste with NC binder regardless of solid contents. So the paste with AC binder might remain much residual carbon in sealing materials after sealing for its high decomposition temperature. Fig. 4 shows the optical microscope images of seal line. (a) shows dispensed line of dried glass paste. It showed very good linearity and adequate line height. (b), (c) shows fired seal line between the front & rear glass substrates. These fired seal line also showed good linearity and good adhesion characteristic.

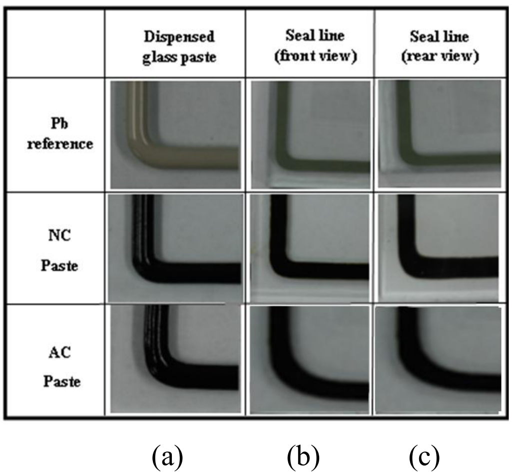


Fig. 4. Optical image of seal line

3.3. Sealing properties

3.3.1. Nondestructive x-ray test

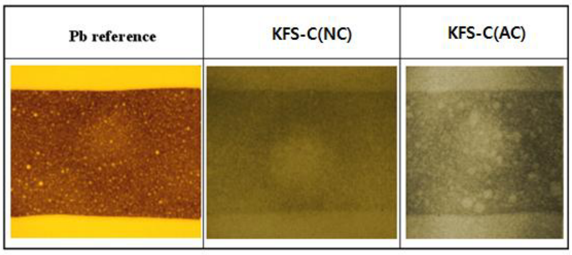


Fig. 5. Nondestructive X–ray of seal line

Fig.5 shows the pore distribution within the seal line by nondestructive X-ray. As predicted in 3.2, panel sealed with KFS-C(AC) paste showed many large size pore compared to that of others. Panel sealed with KFS-C(NC) paste also showed many pores compared with Pb reference, but the size of pore was similar to Pb reference.

3.3.2. Residual stress distribution

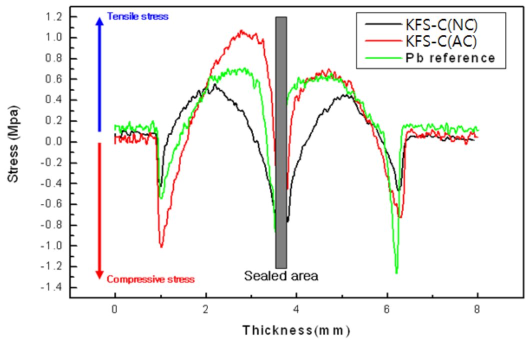


Fig. 6. Residual stress of sealed panels

In Fig. 6, Panel sealed with KFS-C(AC) paste showed most uneven stress distributions. That of panel sealed with KFS-C(NC) paste showed smaller stress than Pb reference.

3.3.3. Sealing strength

Table 3. Sealing strength of sealed panels

	1st	2nd	3rd	4th	Aver.
NC	36.78	35.44	10.74	5.90	17.36
AC	17.45	6.98	13.29	11.95	11.86
Pb reference	28.59	18.52	25.77	15.44	22.08

Table 3 shows the bonding strength of sealed panels. Panels sealed with KFS-C(NC) paste showed better strength than those sealed with KFS-C(AC). These results may have close relation with the results of non-destructive X-ray and residual stress distribution shown in 3.3.1 and 3.3.2.

3.3.4. Optical microscope of fractured surface

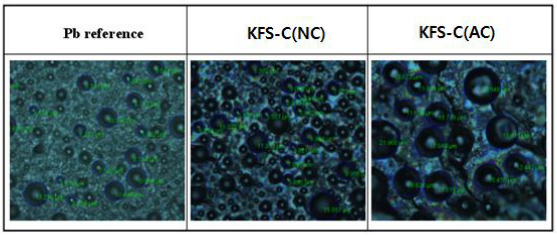


Fig. 7. Optical microscope of fractured surface

Fig.7 shows the surface of fractured sealing glass frit. It also showed similar pore distribution of the result of nondestructive x-ray test. Lower sealing strength of panels using the paste with AC binder might be caused by large size pores.

4. Summary

Sealing glass frit, KFS-C in ZnO-V_2O_5-P_2O_5 glass system showed potential characteristics as a Pb free, Bi free low temperature sealing material for PDP. It has a low Tg and good fluidity even at the low firing temperature of 420℃. So it can give the cost competitive of PDP by allowing the usage of low cost soda lime glass substrate and reducing the energy consumption by lowering the firing temperature of PDP.

5. References

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