Effect of melting temperature and additives on transparency of Bi based Transparent Dielectric Layer in Plasma Display Panel

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Abstract

We report the method of preventing the grey color of Bi based glass frits caused by reduction of Bi_2O_3. To prevent reduction of Bi_2O_3, we controlled the melting temperature. Low melting temperature reduces the reduction of Bi_2O_3 and that makes clarity transparent glass cullets. After firing, glass frits that melted at lower temperature showed better transparency. To prevent the browning, we used some additives like CuO, CeO_2, CoO and TiO_2. The colors of glass cullets were varied according to additives. After firing, dielectric layer contained additives showed better transparency than the one without additives. In the point of reaction between dielectric layer and Ag electrode, CuO was the most effective additive in preventing the yellowing.

1. Introduction

In use of materials of glass frit in Plasma display panel, lead is widely used as a raw material. Lead has many merits of controlling of low melting temperature, dielectric constant, and etc. But lead causes some problem like environmental pollution and health problem. In this reason we need other materials that can substitute lead.

Bismuth can substitute position of lead in glass frit of PDP. But when melting raw materials, bismuth shows some problem. Under reducing conditions bismuth glasses appear to be gray, brown or black. The higher the Bi_2O_3 content in the glass, the lower the temperatures are required for melting when trying to avoid the graying of glass [1]. The dark coloring is owing to dissociation of Bi_2O_3 at higher temperatures and to its conversion into the black sub-oxide BiO and then to bismuth metal. To avoid the reduction of bismuth oxide to bismuth metal, we investigated effect of control of melting temperature [1]. And we examined the influence of CeO_2, CoO, CuO and TiO_2 to control of color and transparency of Bi based glass frits of transparent dielectric layer in PDP [2, 3, 4].

Silver is widely used for electrode in PDP. When firing the transparent dielectric layers, Ag is ionized and then diffuses into the dielectric layer or glass substrate. After that ionized Ag is reduced again by the alkali ions or Sn ions contained in dielectric layers and glass substrate. These reduced Ag ions form Ag colloid and its colors change into yellow or brown in the dielectric layers and glass substrate. We called it as "yellowing" [5].

$$Ag^{+} + Sn^{2+} ? \quad Ag^{0} + Sn^{4+}$$

In some opinion, "yellowing" is caused by the reaction between the alkali ion in dielectrics and Ag or Sn. The color of dielectrics turned into yellow by Ag and into red by Sn in the glass [6]. Yellowed glass substrate absorb the light of 400~500nm wavelength, so the brightness of blue is dropped or chromaticity is changed in Plasma Display Panel. In addition to this, Ag colloid reflects the transmitted light because the colloid is bigger than ions, so the brightness of PDP can also be decreased [7]. Ag colloid also can drop the breakdown voltage of dielectric layers for it is an electric conductor,

2. Experimental

The weighed mixtures of Table 1 were melted in a platinum crucible at 900~1300℃ for 1hr.

Table 1. Compositions of glass frit

Composition	Na_2O	K_2O	BaO	ZnO	B_2O_3	Bi_2O_3	SiO_2
Contents	●	●	□	□	□	■	○

■:30~90 □:10~30 ○:1~10 ●:0~1 (wt%)

And the melt was quenched into stainless roller to make glass flakes. Each of added components was weighed by weight percent. The glass flakes were pulverized in a ball mill to obtain glass powder. After mixing the glass frit, solvent and binder, dielectric layer was coated onto soda lime silicate glass substrate by applicator.

We burned out the binder at 350℃ 1hr and heated at firing temperature for 30minutes. Thickness of coated layer measured by SEM(SM300, Topcom) and the resultant thickness was 30㎛. After that we measured transparency by V-570 UV/VIS/NIR Spectrophotometer (Jasco).

To measure the yellowing by the reaction of dielectric layer with Ag electrode, we patterned the Ag electrode onto PD200 glass substrate and firing at 550℃ for 30minutes. we coated the dielectric layers onto the specimens and burned out the binder at 350℃ 1hr and heated at firing temperature for 30min. We measured the reflectivity using the V-570 UV/VIS/NIR Spectrophotometer (Jasco) with integrating sphere.

3. Results and discussion

3.1 Effect of melting temperature

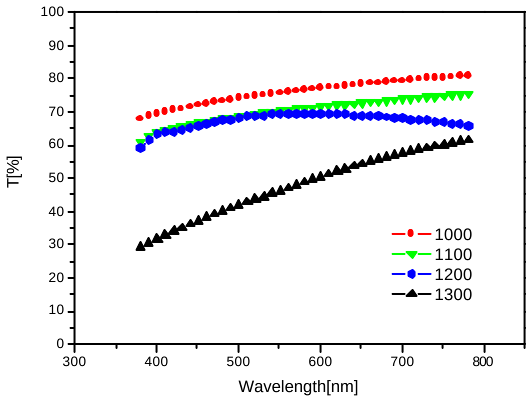
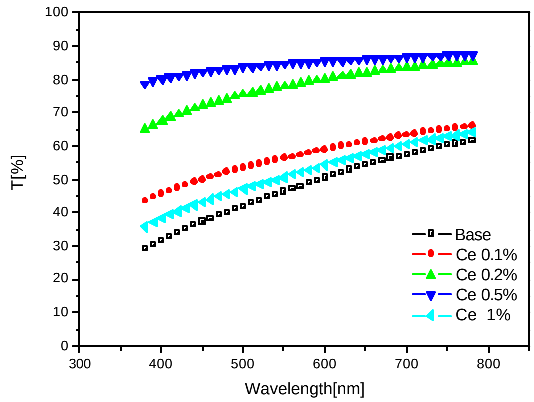


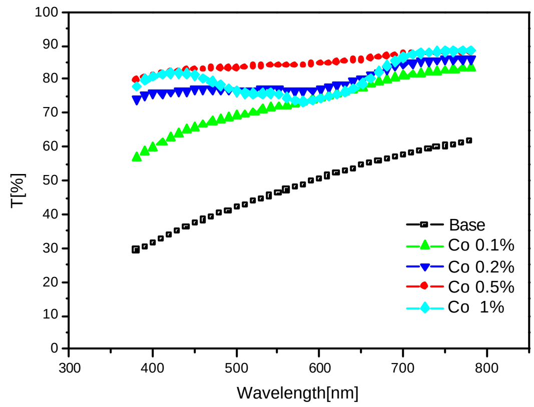
Figure 1. Transmittance of dielectric layers with the melting temperature

Figure 1 shows the transmittance of dielectric layers made from the glass frits melted at several temperatures. Highest transmittance was shown in the dielectric layer made from the glass frit which was melted at 1000℃. We also investigated the relation between melting temperature and color of bismuth glass. We melted the same composition of raw materials at 900℃, 1000℃, 1100℃, 1200℃ and 1300℃ for 1hr. As the melting temperature decreased from 1300℃ to 1000℃, the color of dielectric layer changed from dark brown to light color. But when it was melted at 900℃, the raw materials were only half-melted. The transparent dielectric layer which was coated with the glass frit melted at 1000℃, showed the highest transparency. The reason for this was diminishing the amount of Bi_2O_3 reduction as the melting temperature decreased.

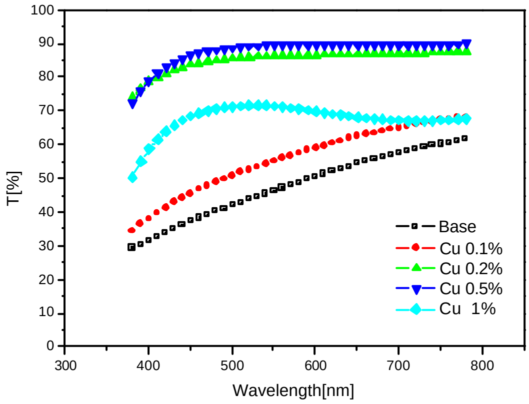
3.2 Effect of additives



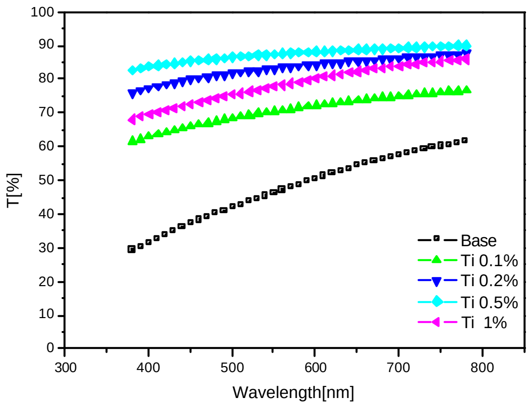
(a) Transmittance of CeO_2 added dielectrics



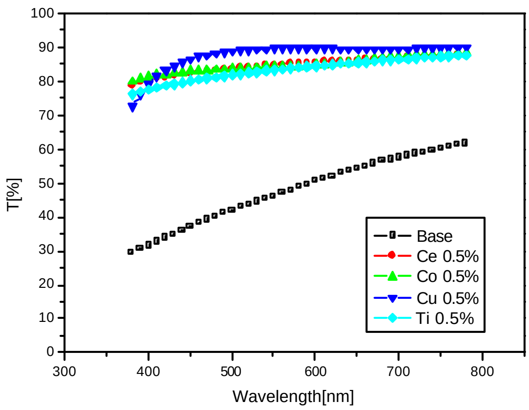
(b) Transmittance of CoO added dielectrics



(c) Transmittance of CuO added dielectrics



(d) Transmittance of TiO_2 added dielectrics



(e) Transmittance of 0.5% additive added dielectrics

Figure 2. Transmittance of dielectric layers

Figure 2 shows the transmittance of dielectric layers according to the variation of additives. In this experiment, we investigated the effect of additives on the reducing the gray color. Adding CeO_2, CoO, CuO and TiO_2 to raw materials, we examined the color of glass cullets and transparency of fired dielectric layers. After melting, the color of cullets changed according to the kind of additives. The color of cullets has changed to yellow by CeO_2 addition, blue by CoO addition and green by CuO addition. TiO_2 did not effect on the color of glass frits but it changed the color from dark brown to light one. After firing the transparent dielectric layers, the colors the layers showed same tendency. But the transparency was increased on the whole. And glass frits that contained CuO showed the best transparency. Among the results of dielectric layers with the additives of 0.1~1wt%, dielectric layers which contained 0.5wt% of additives showed the best transparency and the transparency was dropped which contained over 0.5wt%. Too much additives may decrease the transparency because of the unique color of additives themselves.

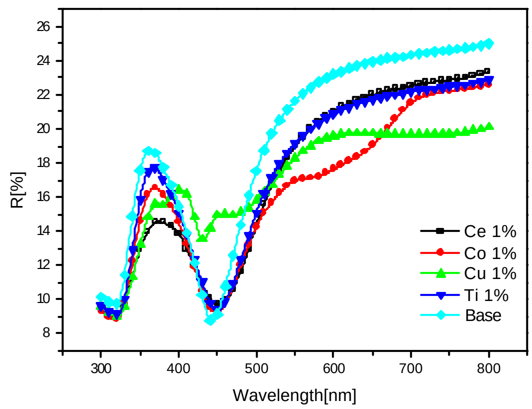


Figure 3. Reflectivity of dielectric layers

Figure 3 shows the reflectivity of dielectric layers formed onto electrode printed glass substrate. It is reported that MO_2 and CuO contained dielectric layer reduced the yellowing of Ag of electrode [7, 8]. However in this experiment, MO_2 addition couldn't reduce the yellowing but CuO addition was effective to reduce the yellowing. From the reflectivity of 400~500nm, we found that CuO contained dielectric layer has shown minimum degree of yellowing.

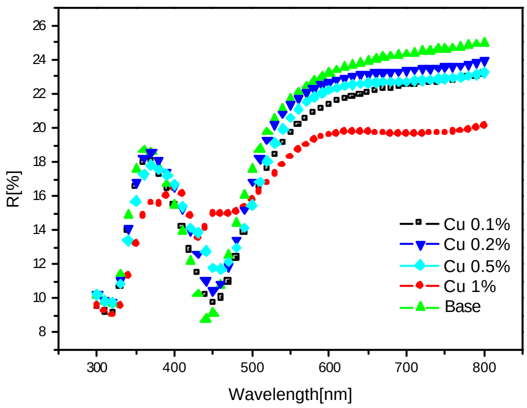


Figure 4. Reflectivity of CuO added dielectric layers

Figure 4 shows the change of reflectivity of dielectric layers with the CuO content variations. As shown in figure 3, CuO was effective additive to prevent yellowing of Ag. So we examined the effect of CuO with the variation of its contents on the preventing yellowing. In this figure we can see the more CuO contents made the less absorption of 400-500nm wavelength. CuO was useful to prevent yellowing. But too much CuO contents might fall down the other property, such as transmittance.

4. Conclusion

We investigated the effect of melting temperature and additives on Bi based glass frits. In the point of melting temperature, dielectric layer that melted at 1000℃ showed the best clarity and transparency. On the other hand, the result of glass frits melted at 1300℃ showed dark brown and the lowest transparency. When adding the additives to prevent grey color of Bi based dielectric layer, the glass cullets showed unique color of each additives and transmittance of dielectric layers were increased. Among them the dielectric layer made from 0.5wt% CuO contained glass frit showed the best transparency. And also, in the aspect of preventing the yellowing, CuO was the most effective material.

5. References

[1] Chemical Approach to Glass, Elsevier, 1984

[2] JPO 2001-139345

[3] Glass technology, Chung mun kak, 2001

[4] JPO 2002-160940

[5] J. E. Shelby and J. Vitko. Jr, Journal of non crystalline solids, vol. 50, p. 107-117 (1982).

[6] JPO 2004-327456

[7] Patent 10-2004-0007763

[8] USPT 6,635,193

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