The Effect of Wet Milling on Transparency of Transparent Dielectric in PDP

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Abstract

We report the effect of wet ball milling conditions on the transparency of glass frit. Generally, the particle size of glass frit decreased as the milling time increased. And the transparency of glass frit changed with the particle size variation. The transparency of glass frit A increased as the milling time increased. But, the transparency of glass frit B, containing high B_2O_3 decreased as the particle size decreased. It seems to be the result of chemical reaction with water and glass frit.

1. Introduction

The transparent dielectric material for front panel in PDP is very important[1]. Many efforts are focused on the developing new glass compositions or application method such as green sheet technology for increasing the quality of transparent dielectric layer[2], but the processing factor for producing glass frit also one of the key issues for increasing the transparency of dielectric layer.

Ball milling method is still key process in producing the glass frit in spite of long processing time. But wet milling method has some problems of causing chemical reaction with glass frit and milling medium, which result in gushing out of components Pb and B from the glass frit even though it has high milling efficiency[3].

We investigate the efficiency of milling method on the glass composition of two different types. Glass frit A is composed of small amount of B_2O_3 and glass frit B is composed of a lot of B_2O_3.

We compared the results of wet milling with water (W) with IPA. The effect of wet milling was investigated with the glass frit having the same particle size made by different milling time of each wet milling. The results were studied by the transparency and FT-IR, ICP-OES analysis of glass compositions.

2. Experimental

The weighed mixtures by Table 1 were melted in a platinum crucible at 1100~1200℃ for 30min and the melt was quenched into stainless roller to make glass flakes. The glass flakes were milled in a wet ball mill with water and IPA. The glass powder was milled for 10hr, 15hr and 30hr to obtain the different particle size. In addition to this, samples were also prepared with the same particle size(D_{50} = 1.5 ~ 1.6 ㎛). The glass powder was mixed with an organic vehicle to make paste. After coating was fabricated by screen printing on a soda lime glass substrate with paste, the wet coating was dried 100℃/20min and baked 580℃/30min. But the differences of transmittances, firing at 580℃/30min[4], were so small that we couldn't compare the effect of milling conditions. So we compared the transmittances firing at 530℃/30min. Transmittance and FT-IR were measured by UV/VIS Spectrophotometer (Shimadzu UV-2401) and FT-IR Spectrometer (Shimadzu Prestage 21).

Table 1 Compositions of glass frit A and B

[Wt %]

Content	CaO	PbO	CuO	Al_2O_3	B_2O_3	SiO_2
Frit A	○	▲	○	○	○	●
Frit B	○	▲	○	○	●	○

○ : 0 ~ 10%, ● : 10 ~ 30%, △ : 30 ~ 50%, ▲ : 50 ~ 100%

3. Results and discussion

3.1 The effect of particle size on the transparency of glass frit

Figure 1 shows the milling efficiency of the milling medium for the glass frit A.

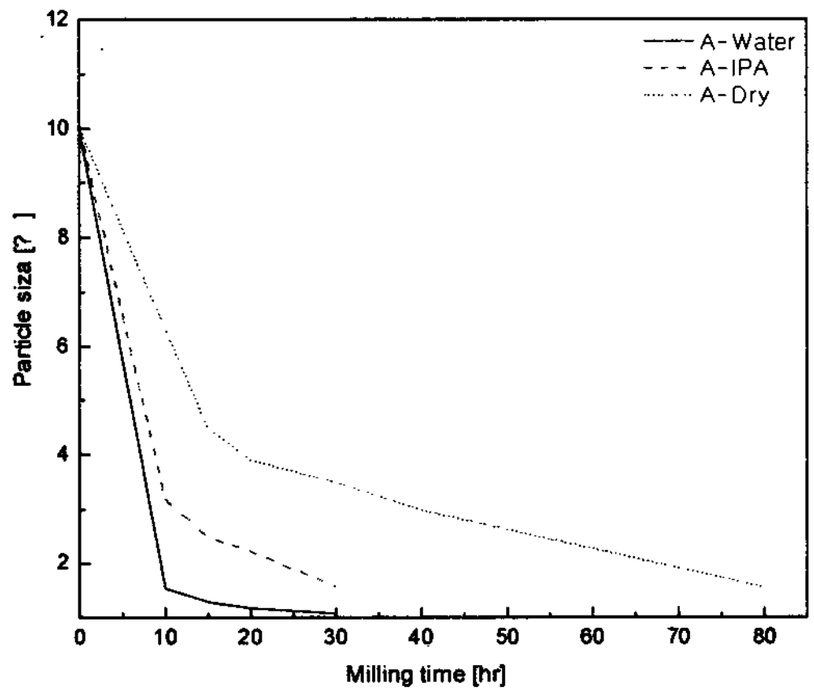

Figure 1 Milling efficiency of the milling medium

The milling efficiency was W > IPA > Dry for the same milling time. The milling efficiency of wet milling with water was better than wet milling with IPA and dry milling. For the same milling time the milling efficiency was W > IPA > Dry.

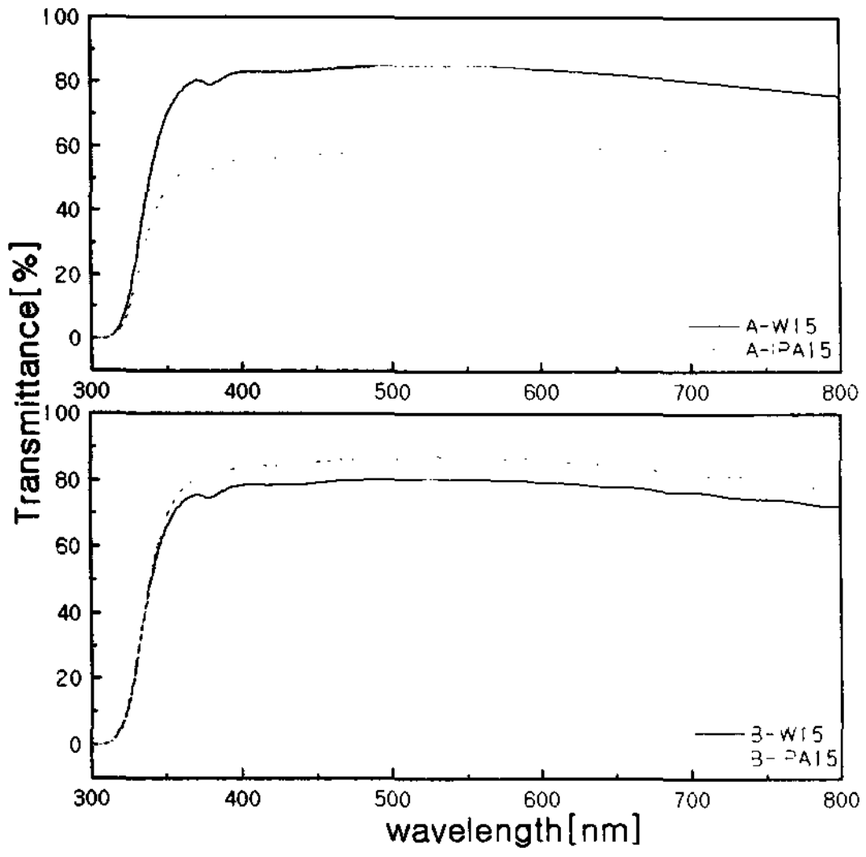

Figure 2 Transmittance of the same milling time

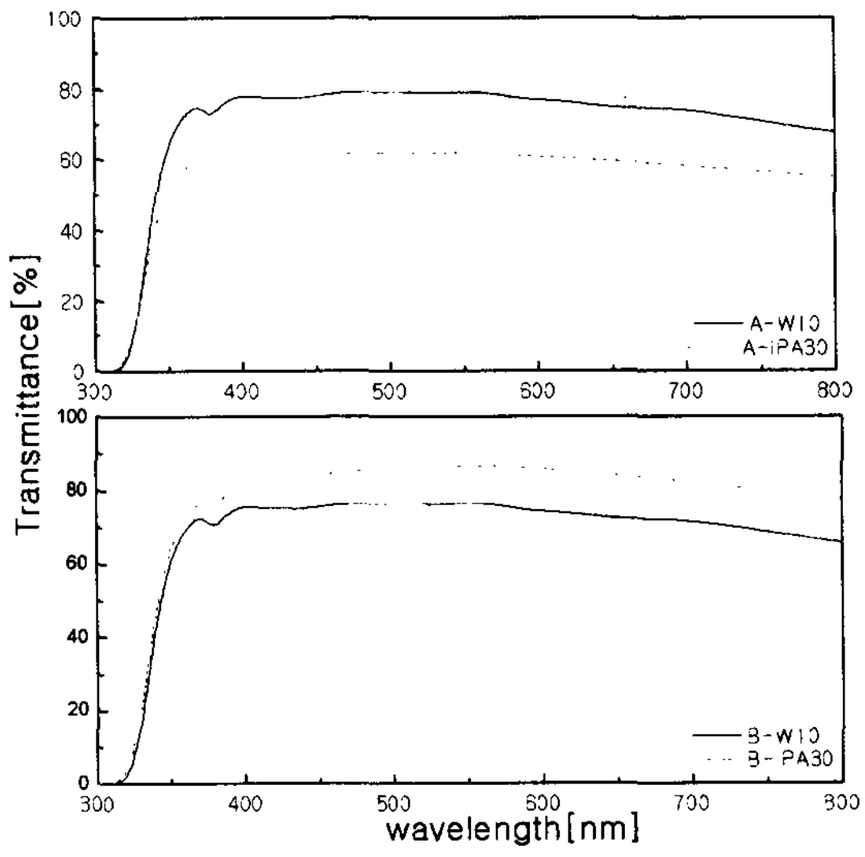

Figure 3 Transmittance of the same particle size

The glass flake was milled by wet ball milling with water and IPA for 15hr. It was prepared to compare the effect of the milling medium with the glass composition of two different types. W15 and IPA15 were pulverized by wet ball milling with water and IPA for 15hr. Then printed samples were measured the transmittance. Figure 2 shows the transmittance curve of the same milling time.

The particle size was W15 > IPA15 for the same milling time (15hr). Frit A, containing small amount of B_2O_3, showed high transparency with the increasing milling time regardless milling medium, but in case of frit B, containing high B_2O_3, the transparency did not increased with particle size reduction. These tendencies seem to be the results of positive effect of small particle in diffusion controlled sintering of powder compaction[5]. But, the transparency of frit B did not show the same tendency. The result of frit B seems to be caused by the chemical reaction between water and glass frit of high B_2O_3 content.

3.2 The effect of milling medium on the different glass composition

We examined the effect of milling medium in ball milling with the same particle size of glass frits. The milling efficiency depends on the milling medium in ball milling. So we prepared same particle size of glass frits by controlling the milling times for each milling mediums.

Figure 3 shows the transparency of the glass frits A·B, milled by difference medium to be a same particle size (D_{50} = 1.5~1.6 ㎛) by controlling milling time. Frit A showed that the transmittance was W10 > IPA30 under the same particle size. This result seems to be caused by the residual carbons, remained in glass frit during the wet milling with IPA. But, frit B showed different results according to milling medium. The transparency of Frit B was IPA20 > W10. Through this result, we verify that the milling medium has an effect on the transparency under the same particle size.

3.3 Cause of composition dependency

In the case of glass frit, it is known that residual O-H bond has influence on the physical · chemical characteristics. We conducted FT-IR analysis to compare O-H bond content of glass frit milled with different medium.

Figure 4 shows the results of the FT-IR spectrum of frit B.

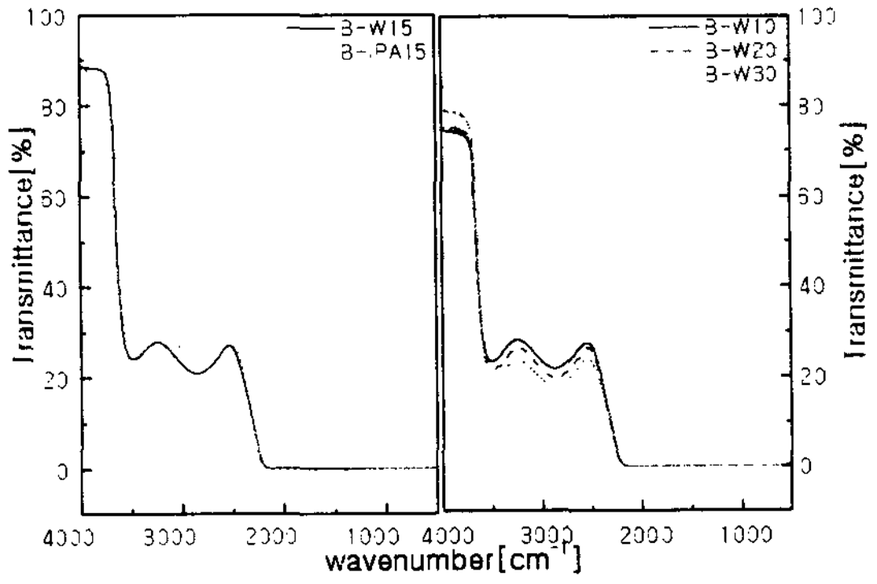

Figure 4 FT-IR spectrums of frit B

The O-H bond appeared at 3400cm^{-1} as an absorption band[6] in FT-IR spectrum. The residual -OH group remained in W15 frit was more than those of IPA15. The more the glass frits were milled with water, the more residual -OH group remains. This -OH group caused the reduction of transparency.

The wet ball milling leads to change the characteristic of glass frit for a long processing time[7]. Therefore, we analyzed the compositions of glass frit by ICP-OES (Perkin Elmer Optima 3300DV). Table 2 shows the contents of PbO and B_2O_3 after wet milling.

Table 2 Contents of PbO and B_2O_3 after wet milling

	Content	W15[wt%]	IPA15[wt%]
Frit B	PbO	66.6	67.9
	B_2O_3	25.7	25.9

The reductions of PbO and B_2O_3 contents of frit B, after wet milling with water was bigger than those of IPA. It is well known that there may be some possibility of gushing out of Pb or B from the glass frit when it milled with water[7], but the characteristic changes of glass frits caused by long processing time of wet ball milling depend not only the milling time but also the composition of glass frit. The PbO content of Frit A is similar to that of frit B. Therefore, the B_2O_3 content has a considerable effect on the transparency. We measured the transparency of glass frit to verify the influence of medium. Figure 5 shows the transmittance curve according to the medium and the milling time.

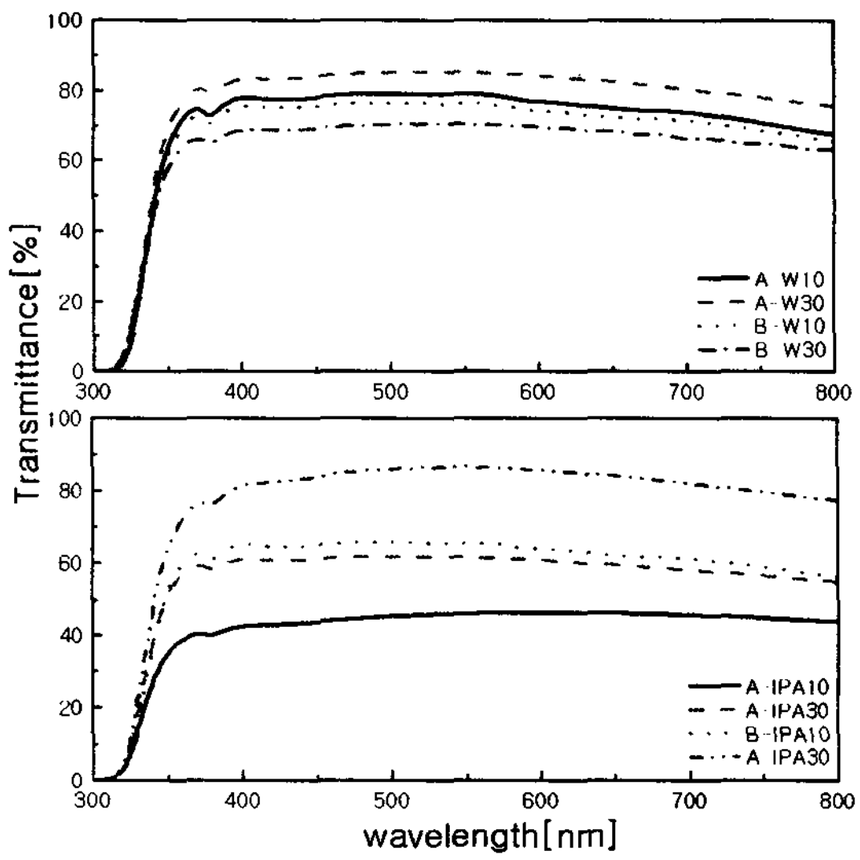

Figure 5 Transmittance of the same milling medium

Figure 1 shows that the transparency increased with the reduction of particle size of glass frit as the milling time increased. Figure 5 shows that transparency of frit A have no concern with the milling medium and composition. Frit B containing high B_2O_3 has the same tendency on wet ball milling with IPA. But, wet ball milling with water was not. The particle size of glass frit decreased as the milling time increased, but the transparency decreased on the wet ball milling with water because of the chemical reaction of with glass frit and water.
Figure 6 shows a tendency of frit A and B for the wet ball milling with water.

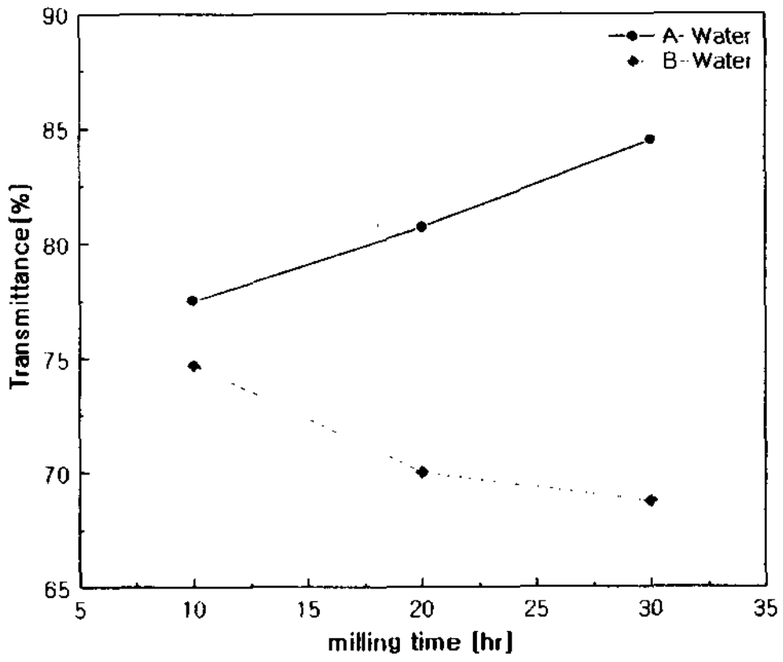

Figure 6 Transmittance of glass frit A&B milled with water

The transparency of frit A increased as the milling time increased regardless of milling medium, however, that of frit B decreased as the milling time increased.

4. Conclusion

We investigated the effect of milling medium on different glass frit composition. The effect of different milling medium on the transparency of transparent layer turned out to be dependent on the glass frit composition. Milling efficiency of wet ball milling with water was better than other milling mediums. But, water can cause the chemical reaction with glass frit, so the milling method should be chosen according to the glass compositions to be milled, especially in the glass frit of high of B2O3 content.

5. References

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