

Influence of Frit Surface on the Transmittance of Transparent Dielectric in PDP

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Abstract

Producing high transparency dielectric is still one of the most important subjects in the PDP process for improving luminous efficiency. It has been reported by many workers that transparency is improved by controlling the composition of the frit, the frit size and distribution, and the firing atmosphere. To understand the mechanism of discoloration of frit, Bi₂O₃ and B₂O₃ glasses were used for a leaching test using water and alcohol solution in milling. As a result, the frit prepared by wet milling had lower chemical durability than that prepared by dry milling. The leached layer around the frit showed high stability for heat treatment because the frit surface was covered with hydroxides or hydrates which was resulted from a reaction between the frit and the solution during milling.

1. Introduction

Transparent dielectric in PDP is prepared by firing a thick film of paste containing glass frit. During the firing, frit, glass powder, is melted on a glass plate through viscous flow. When the effect of frit only is considered for attaining high transparency of the display panel, it is necessary to control the frit size and distribution. However, in spite of the proper process conditions for frit, transparent dielectric after firing is sometimes found discolored: devitrified or colored dielectric [1].

Milling is required to produce from cullet to frit with or without a solution (water, alcohol). In addition, several materials to make mills (jar and milling media) affect the product of frit. Glass surface is very different from ceramic oxides so that glass frit surface should be treated carefully during milling [2].

To understand the mechanism of frit discoloration during milling, wet and drying milling were applied to Bi₂O₃ and B₂O₃ glasses as feed materials.

2. Experimental Procedure

Glasses (BiO₂ and B₂O₃ glass systems) were prepared from Bi₂O₃, BaCO₃, B₂O₃, ZnO, SiO₂, Na₂CO₃ and Al₂O₃. After melting the glass compositions, frits were prepared by milling (Planetary mono mill, FRITSCH-pulverisette 6). Thermo gravimetric (TG) of glasses was determined on a differential thermal analyzer (TG-DTA, Rigaku, Japan) at a heating rate of 10 /min. Phase identification was performed by using an X-ray diffractometer (Rigaku DMAX 2500). Water content in the glass sample was determined by FT-IR spectroscopy (Bomem Mb - 104) in the range of 2000~5000 cm⁻¹.

The frits were prepared through wet and dry milling processes. For the wet process, different solutions (alcohol, H₂O) were used and the dry milling process was performed by using an alumina agate. Different frit sizes were prepared between the ranges of 2~5 μ m and 46~106 μ m. The dried frit was mixed with water with a ratio of 10ml of water per gram of powder [3] and leached in tightly closed Teflon containers kept at a constant temperature of 25 . Then, the initial and the final pH values of leachate with time were measured.

3. Result and discussion

The amount of physically adsorbed water in frits was different as shown in Fig. 1. The weight loss of B₂O₃ glasses complete at temperatures, 255-266°C while Bi₂O₃ at 189°C). The result of TGA suggests that Bi₂O₃ glasses are more stable than B₂O₃ glasses in terms of chemical stability under air atmosphere.

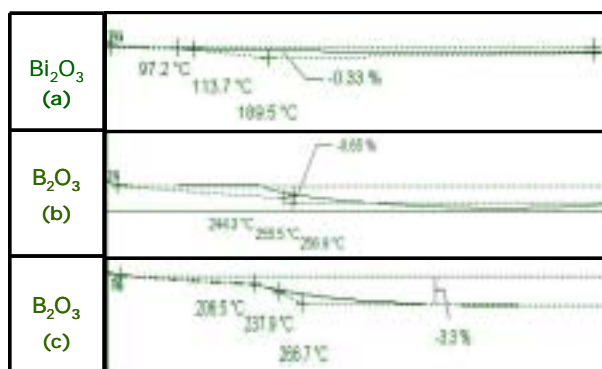


Fig. 1 TGA traces for two glasses. (a) Bi_2O_3 glass left in air 7 days (b) B_2O_3 glass after drying and (c) B_2O_3 glass left in air 7 days (milling in water for 3h).

All the frits in water increased the solution pH with increasing time as shown in Fig. 2. Leaching of mobile ions out of glass was dependent on solution types and frit compositions. It is known that alkali ions are the most mobile ions in glass. The frit from dry milling had stable surface so that pH change in water was negligible for a short time but, a little over 4 h later, the change of pH in H_2O rapidly increased because of different metal ion release rate as indicated in the changes in the leaching mechanism from a diffusion limited process to a surface dissolution rate process [4].

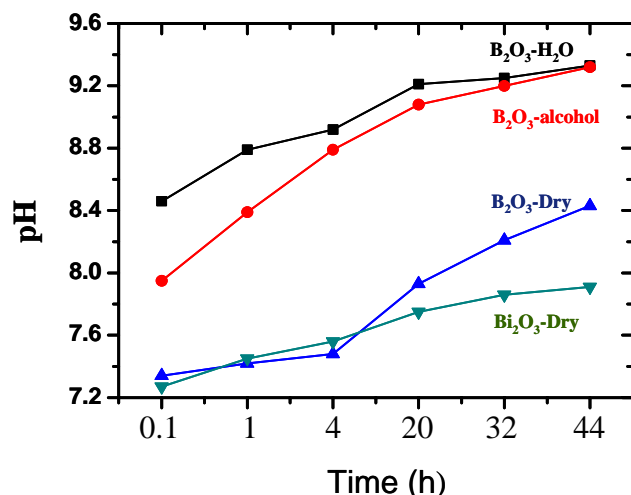


Fig. 2 Change of solution pH for frits and water suspension as a function of leaching time.

Both B_2O_3 and Bi_2O_3 glasses seem to follow the typical leaching states as a function of time as found

in other glasses [2]: the intercept parabolic region and the linear region. The large surface area of fine frits shows a large amount metal ion out of glass in water for a long leaching time (Fig. 3).

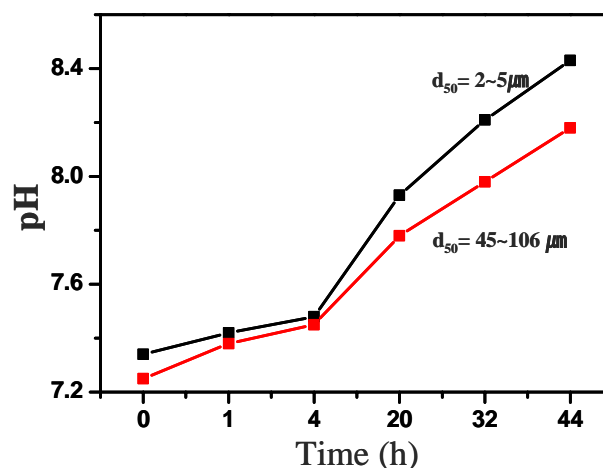


Fig. 3 Effect of frit size on the leaching.

After leaching in the solution, the frit surface formed a layer, which is one of the precipitations of hydroxides or amorphous hydrosilicates. As shown in Fig.4, the leached layer showed an amorphous phase before firing frit, while the layer after firing gave a crystalline, Zinc zirconium hydroxide (Fig. 4c). This is attributed to Zn^{+2} and Zr^{+2} , leached ions from the frit during the milling.

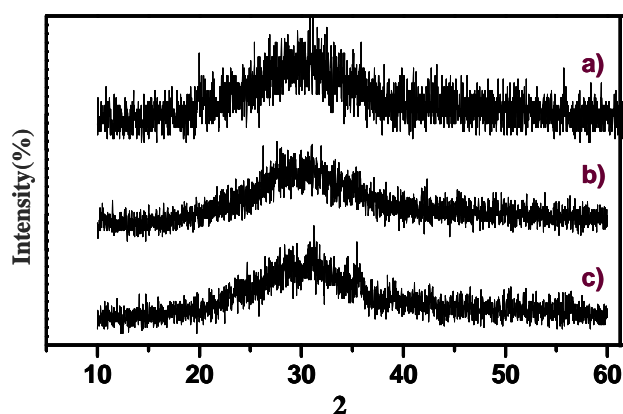


Fig. 4 Crystalline phases around frit after milling in different solutions and firing (a) Wet milling– before firing: zirconium oxide, sodium hydroxide, (b) Dry milling– after firing: Amorphous phase and (c) Wet milling– after firing (Wet- H_2O): Zinc zirconium hydroxide.

To determine the reaction of the frit to the milling solution, the frit surface (leached layer) before firing was observed with IR. The degree of reaction in the frit surface was dependent on the milling solution. The intensity of absorptions caused by water (~3450cm⁻¹(O-H band)) was clear as in Fig. 5, and the strong peak at ~2400cm⁻¹ suggests that the hydrogen bonds are an indication of alcohol media (Fig. 5) [5,6].

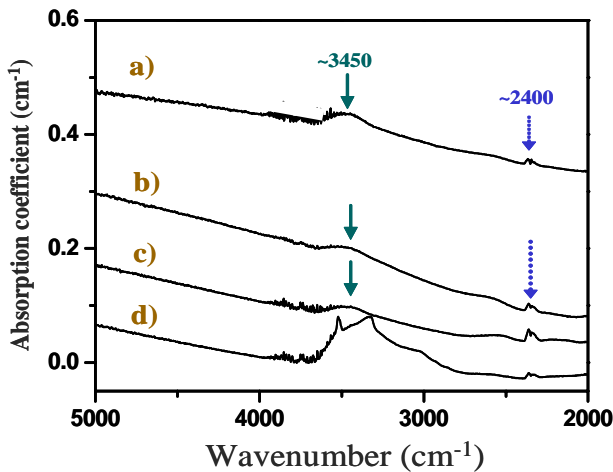
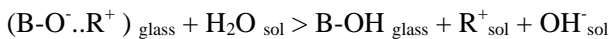


Fig. 5 Infrared spectra for frit prepared from different milling conditions (without heat treatment). (a) dry milling with a zirconia mill, (b) dry milling with an alumina agate, (c) wet milling in alcohol, and (d) wet milling in water.

The leaching result of frit presented in Figs. 2-5 is explained as the following mechanism based on glass structure of frit. B-O-B bonds are nearly inert in neutral solutions, but the B-O⁻..R⁺ and B-O⁻...R⁺⁺ bonds are highly reactive, and virtually every such site in the glass surface reacts with H₂O to form hydroxyl bonds .



H⁺ from the water penetrates the glass structure. This H⁺ replaces an alkali ion, which goes into the solution. A nonbridging oxygen is attached to the H⁺. The surface becomes depleted in alkali, alkaline earth, and other divalent species. The OH⁻ produced in the water destroys the B-O-B bonds, forming nonbridging oxygens. The nonbridging oxygens react with H₂O molecules, forming another nonbridging oxygen-H⁺

bond and another OH⁻ ion.

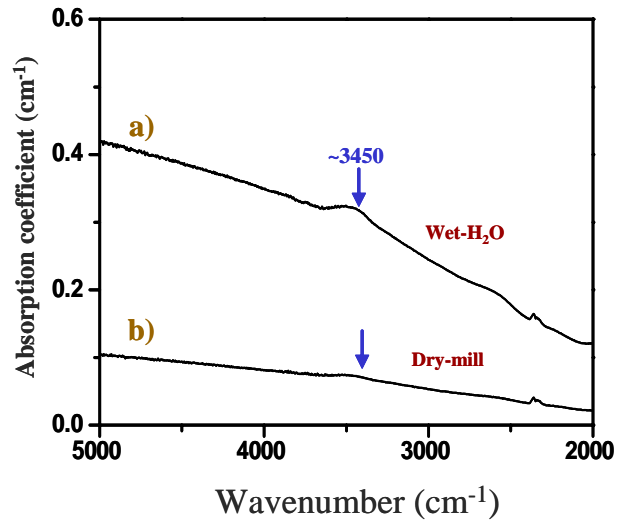
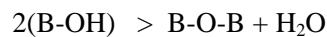


Fig. 6 Infrared spectra for frit prepared from different milling conditions (after heat treatment at 580°C for 30min). (a) wet milling in water (b) dry milling with a zirconia mill.

After firing at 580°C, the frit milled in water showed a peak at 3450 cm⁻¹ because a hydrate existed firmly on the frit surface in spite of firing at high temperature. The B-OH (Si-OH) bonds formed as a result of dealcalization were the equivalent of water since, at elevated temperature, the following reaction occurs



This reaction occurs when frit is heat treated at an elevated temperature. In some cases, the reaction proceeds at high temperature because of “self sealing”, in which individual particles are sintered by viscous flow of the surface near T_g. After the frit surfaces are sealed through sintering, the trapped water in the particles is released.

5. Conclusion

Frit prepared by dry milling showed higher chemical durability than that prepared by wet milling. Milling media and solution used for the preparation of frit affect the leached surface of frit. The degree of discoloration of the frit was different from solution and frit composition. The data obtained from the leaching tests may be useful in designing and

producing high chemical stability of frit for transparent dielectric in PDP.

6. References

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