

Dispersion stability and characterization of lead-free transparent dielectric glass frit

Young-Jei Oh* and Jin-Won Lee

Thin Film Materials Research Center, Korea Institute of Science and Technology, Seoul 136-791, Korea

The effect of solvents and dispersants on the slurry dispersion stability in tape castings of lead-free transparent $\text{Bi}_2\text{O}_3\text{-ZnO-BaO-Al}_2\text{O}_3$ dielectric layers for plasma display panel (PDP) were studied. A comparative study of mechanical and optical properties of the green sheets fabricated with and without dispersion stabilizers was performed. The optimum dispersion stability, which was due to steric stabilization, was observed for a 1.5 wt% polyethylene glycol solution in methanol with 33.3% solid loading; the corresponding green sheet demonstrated the best mechanical and optical performance after firing. The green sheet prepared by dispersion stability had a stronger tensile strength of 6.6 kg/cm^2 (6.47 MPa) and more uniform microstructure than the green sheet prepared without dispersion stability (tensile strength of 4.6 kg/cm^2 (4.51 MPa)). The optimum result was obtained by fire processing a green sheet at 505°C for 30 minutes; the dielectric layer obtained with $30 \mu\text{m}$ thickness on soda-lime glass substrate had a transmittance of 81% at a reference wavelength of 550 nm without a yellowing phenomenon.

Key words: Dispersant, Slurry, Green sheet, Lead-free transparent dielectrics, PDP.

Introduction

A plasma display panel (PDP) is a gas discharge display device which displays an image using visible rays emitted by an energy gap generated when ultraviolet rays generated upon discharge of a gas between two sheets of glass substrates excite a fluorescent material and electrons of the fluorescent material return from an excited state to a ground state. Due to its simple structure and easiness to increase its size, the PDP has been much studied in the field of display devices such as wall mounted TVs and high-definition (HD) TVs. In particular, a transparent dielectric is a crucial part that serves as a capacitor during discharge, limits the electric current, and provides a memory function.

To form the transparent dielectric, a screen printing method has been widely used until now. However, this method requires film formation by several repetitions for a desired thickness, resulting in some defects such as easy bubble generation and non-uniform dielectric characteristics due to surface non-uniformity. Consequently, there is a need for a new manufacturing process capable of substituting for the screen printing method. To solve these problems, this paper suggests formation of a lead-free transparent dielectric using a tape casting method. The tape casting method is a low-cost process for manufacturing thin, high-quality, and large-size ceramic sheets [1, 2].

In general, the tape casting method requires adequate dispersion of ceramic powders in a liquid medium for

optimization of properties. Since voluntary aggregation of particles occurring in the slurry due to collision caused by the large specific surface area of the powders, van der Waals' attraction, and Brownian motion during a ceramic process may result in defects in shape, a uniform dispersion of the slurry has to be performed first to prevent such aggregation for the purpose of optimizing the casting. The dispersion of a ceramic slurry can be controlled by applying an electrostatic repulsion or steric stabilization mechanism by adding a dispersing agent capable of changing the surface potential of the aggregated particles or stabilizing the aggregated particles in the dispersion medium [3].

Therefore, in this study, the optimal slurry composition and conditions for forming a transparent dielectric by a tape casting method using a lead-free transparent dielectric material of the $\text{Bi}_2\text{O}_3\text{-ZnO-BaO-Al}_2\text{O}_3$ system was established and the influences of the dispersion stability upon the rheological characteristics of the slurry, the mechanical characteristics of a green sheet, and the fine structure and optical characteristics of the lead-free transparent dielectric were studied.

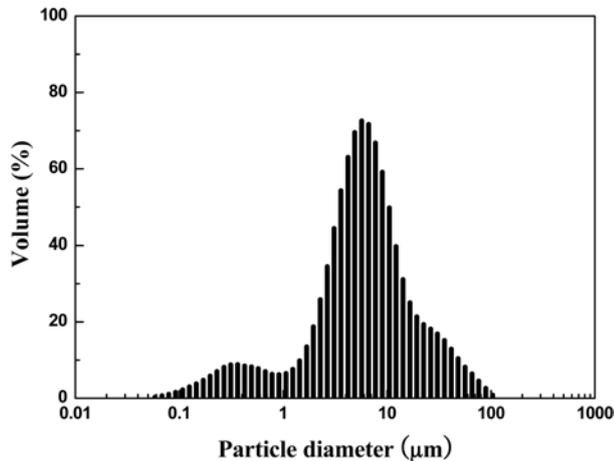
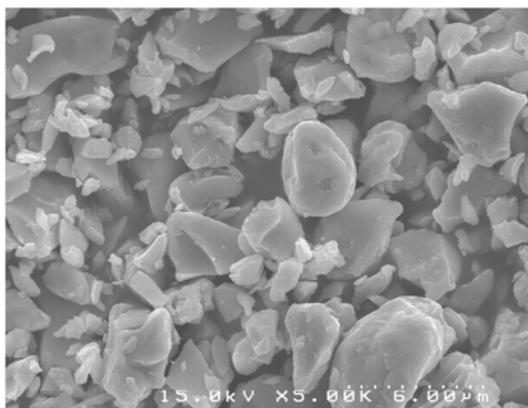
Experimental Method

For a lead-free transparent dielectric composition, a frit of the $\text{Bi}_2\text{O}_3\text{-ZnO-BaO-Al}_2\text{O}_3$ system was used as a starting material and the main properties are shown in Table 1. The particle size distribution of the starting material as prepared is shown in Figs. 1 and 2 in which each particle had a slightly angular shape rather than a round shape. To observe the dispersion behavior of the frit, ethyl alcohol (Daejung Chem., Korea), methyl alcohol (Daejung Chem., Korea), toluene (Junsei, Japan), acetone (Junsei,

*Corresponding author:
Tel : +82-2-958-5553
Fax : +82-2-958-5554
E-mail: youngjei@kist.re.kr

Table 1 Properties of the lead-free transparent dielectric as a raw material

Physical property	Value
Density(g/cm ³)	5.0
Dielectric constant(1 MHz)	12.7
Thermal expansion coefficient(10 ⁻⁷ /K)	88.8
Glass transition temperature(°C)	460.2
Softening point(°C)	488.6
Mean Particle size(μm)	5.69

**Fig. 1.** Particle size distribution of the raw material as prepared.**Fig. 2.** SEM image of the raw material as prepared.

Japan), and metylethylketon(J.T.Baker, USA) were used as solvents and general-purpose dispersing agents fish oil(Aldrich, USA), poly vinyl butyral(Aldrich, USA), solspere 24000sc(ICI Co, England), and polyethylene glycol(Aldrich, USA) were used as dispersing agents. The dispersion characteristics of the frit in each dispersing agent and solvent were observed by precipitation experiments, viscosity measurements, and particle size analyses and influences upon the dispersion stability were observed based on the fluidity of suspension.

The precipitation experiments followed a method recommended by Mistler and Twiname [4]. In other words, the concentrations of powder(frit) and solvent each were

fixed to 100 wt% and 200 wt%, respectively and each of the listed dispersing agents was added with each concentrations of 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, and 3.5 wt%. The resultants were ball-milled for 4 hours. After these dispersed suspensions were placed in 25 ml cylindrical containers, sealed, and then left for 7 days, the height and precipitation speed of a precipitate in each of the suspensions were measured. For the viscosity measurements, the viscosities of the suspensions and slurries were measured using a rotational viscometer (Viscometer DV-II+, Brookfield Co., USA).

To manufacture the optimal slurry, PVB (polyvinyl butyral (Mw : 90,000~120,000), Aldrich, USA) as a binder and DBP (dibutyl phthalate, Aldrich, USA) and PEG(polyethylene glycol(Mw : 400), Aldrich, USA) as plasticizers for a plasticity that alleviates bonding were added to the slurry [5]. To maintain a viscosity suitable for tape casting by removing bubbles in the prepared slurry and the excessive solvent added to the mixture, the slurry underwent a debubbling process and an aging process while being stirred at a constant speed of 50 rpm in a decompressed condition using a rotary vacuum pump.

The debubbled slurry was cast to a thickness of 50 μm on a Mylar film using a doctor blade(STC-14A, Hansung System Inc, Korea). The shear rate during casting was adjusted to 0.5 cms⁻¹ and the slurry was dried in a sealed space for 24 hours. The dried test piece was rapidly cooled in liquid nitrogen and then its cross-section was observed by SEM with an acceleration voltage of 15.0 kV.

After cutting the green sheet dried to a thickness of 50 μm to an appropriate size, the cut green sheet was placed on a soda-lime glass substrate, which was cut to a 5 cm × 5 cm size and was preheated to 60 °C and then thermally compressed by a pressure of 5 kg/cm²(4.9 MPa) at 60°C for 4 minutes using a laminator. The green sheet compressed on the soda-lime glass was thermally processed at 500-530 °C for 30 minutes, thereby forming a thick film of a lead-free transparent dielectric.

The tensile strength of the green sheet was measured using a universal testing machine(Instron 4465, U.K.) and the manufacturing and measurement of the test piece were performed according to ASTM D 638IV. For the optical characteristics of the thick film of the fired transparent dielectric, transmittance in the visible light band having a wavelength of 380-780 nm was measured using a UV/visible spectrometer(LAMBDA19 UV/VIS/NIR, Podenseewerk Perkin-elemer Co., Germany) and transmittance at a reference wavelength of 550 nm was compared with the optical characteristics of thick layers of transparent dielectric formed by several firing conditions. For the degree of bubble formation in the cross-section and surface of the thick layer of the transparent dielectric, observation was done using an optical microscope (NIKON OPTIPHOT, Nikon Co., Japan) and SEM(S-4100, Hitachi Ltd, Japan) and the reaction between the Ag electrode and transparent dielectric layer, i.e., the occurrence of a yellowing phenomenon, was determined by EDAX(XL-30 ESEM, PHILIPS, Netherlands).

Results and Discussion

Dispersion stability affects the precipitation and repletion behavior of the particles [6], such that unstably-dispersed particles are rapidly precipitated. The precipitates are slowly aggregated, and thus occupy a large volume and are easily dispersed again. On the other hand, stably-dispersed particles are slowly precipitated and a precipitate is densely aggregated and thus is difficult to disperse again. Fig. 3 shows differences between dispersion stabilities of transparent dielectric frits in various organic solvents and water using the precipitation comparison method. When a dispersant is not added, precipitation characteristics varied with the types of the pure organic solvents. As can be seen from Fig. 3, the dispersion characteristics of the frit was best in methanol and the frit was precipitated rapidly and to a high degree and thus was not well dispersed except for within ethanol and metylethylketon. Therefore, it can be seen that the dispersion characteristics of the frit is affected by the organic solvent.

For methanol which exhibited the best dispersion characteristics among the variety of organic solvents, the dispersion characteristics according to the type and the amount of addition of the dispersant were investigated. Fig. 4 shows the dispersion characteristics of the frit according

to amount of the dispersing agent. In Fig. 4, the height of precipitation in the suspension increased with the addition of fish oil, PVB, and solsperse, and thus it was confirmed that they are not suitable as dispersing agents. In contrast, the height of precipitation was very low when polyethylene glycol was added and the height was lowest when polyethylene glycol was added with a concentration of 1.5 wt%.

It is known that since the dispersant stabilizes the dispersed state by absorbing a polymer electrolyte on the particle surface, that adequate absorption of the dispersing agent leads to a stable dispersion and the stable dispersion leads to slow precipitation, resulting in a high charging density of a precipitate and thus a low precipitation height [4, 7]. Generally, it is important to absorb only the desired amount of dispersing agent in a monolayer on the particle surface by minimizing the amount of the addition of the dispersing agent. Thus, as the amount of the addition of the dispersant and the height of precipitation decrease for the same amount of slurry, a dispersion effect is improved. It could be seen that polyethylene glycol in which the height of precipitation was low and holding time, during which dispersion stabilization is maintained, is long worked effectively for dispersion of the lead-free transparent dielectric frit. However, it is difficult to determine a dispersion effect only with a precipitation experiment because this method is sensitive to fine vibrations in the peripheral environment. Thus, the change of viscosity according to the addition of a dispersant was observed to know degree of dispersion of the slurry more accurately than using precipitation comparison experiments. Fig. 5 shows viscosity measurements according to the addition of various dispersing agents to suspensions dispersed by methanol, in which the viscosity of the suspension increased with an increase in the amount of addition of fish oil, PVB, or solsperse. In contrast, when polyethylene glycol was added, the viscosity of the suspension hardly changed and the viscosity was smallest and thus showed the most stable dispersion characteristics, although it was a slight difference, when polyethylene glycol of 1.5 wt% was added.

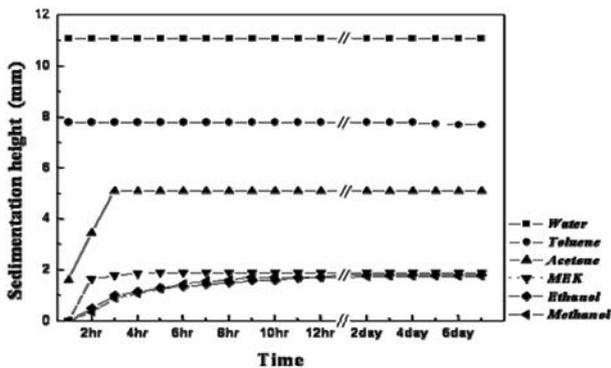


Fig. 3. Comparison of sedimentation rate of the frit in various solvents.

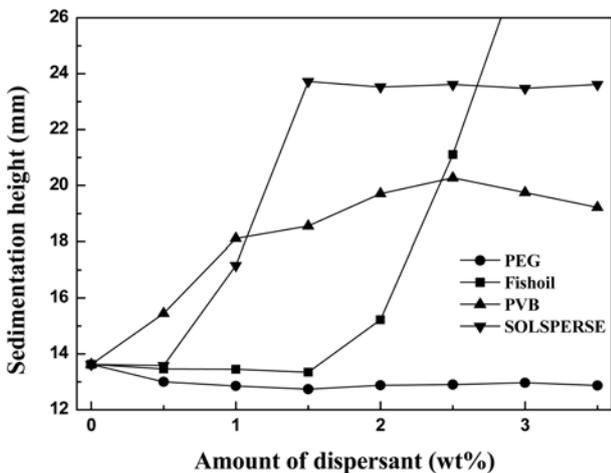


Fig. 4. Sedimentation height of the frit as a function of the amount of dispersant.

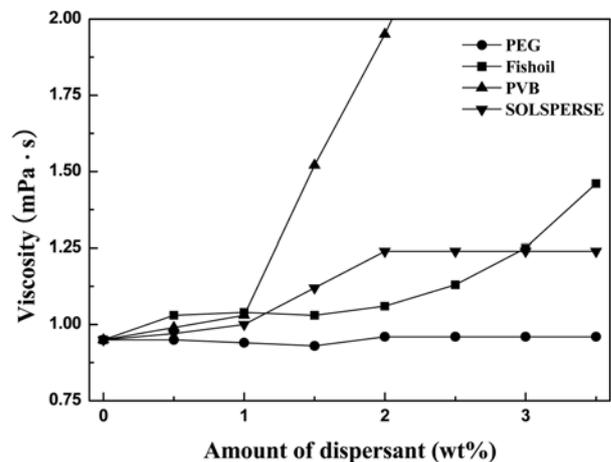


Fig. 5. Viscosity of suspensions as a function of dispersant.

Typically, when the amount of a dispersant is smaller than an adequate amount, the powder is maintained in the form of a secondary flocculant. In this case, a solvent exists between macropores of the secondary flocculant, resulting in a lack of the solvent which makes a uniform mixture difficult. However, as the amount of dispersant increases, the secondary flocculant is separated by mutual repulsion between the polymer functional groups absorbed onto the particle surfaces and is dispersed by a steric stabilization mechanism, leading to a decrease in the viscosity of the slurry [8, 9]. As the amount of addition of the dispersant increases over the adequate amount, the viscosity of the slurry increases because the excessive dispersing agent exists in the slurry and interrupts the flow of the slurry due to bridging or tangling of polymer chains. When the results in Figs. 4 and 5 are compared, precipitation comparison experiment and viscosity measurement showed the same tendency with respect to the amount of dispersing agent. Consequently, the optimal dispersing agent was regarded as polyethylene glycol.

Steric hinderance occurred between particles due to absorption of the polyethylene glycol layer onto the particle surfaces and the minimum distance between the particles increased due to the absorbed polyethylene glycol layer, reducing the attraction between the particles. In addition, repulsion between the lead-free transparent dielectric particles increased due to the interaction of the absorbed polyethylene glycol layer and the dispersion was sterically stabilized [10].

In order to determine the adequate amount of polyethylene glycol that showed the best dispersion stability when the lead-free transparent dielectric frit was dispersed in methanol, the precipitation speed of the frit and the particle size of the frit at the time of addition of polyethylene glycol are shown in Figs. 6 and 7. The precipitation of the frit occurred very slowly as polyethylene glycol was added, and the precipitation speed was lowest and the height of precipitation was also lowest when polyethylene glycol was added at a concentration of 1.5 wt%. The particle size of the frit was reduced from

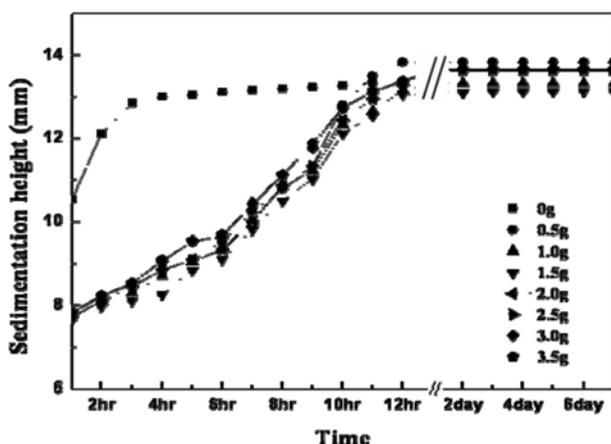


Fig. 6. Sedimentation rate of the frit as a function of the amount of PEG.

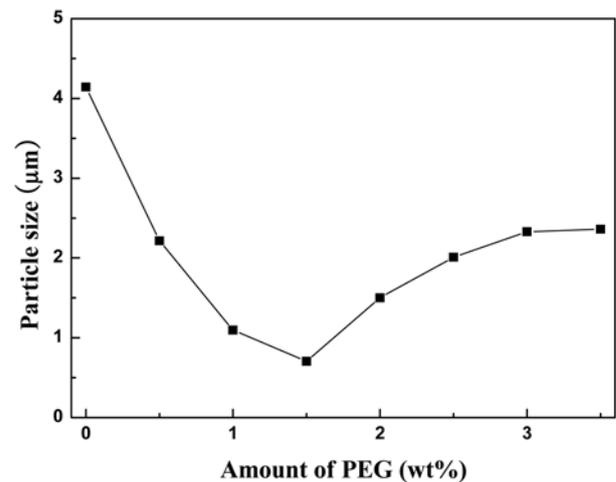


Fig. 7. Particle size of the frit as a function of the amount of PEG.

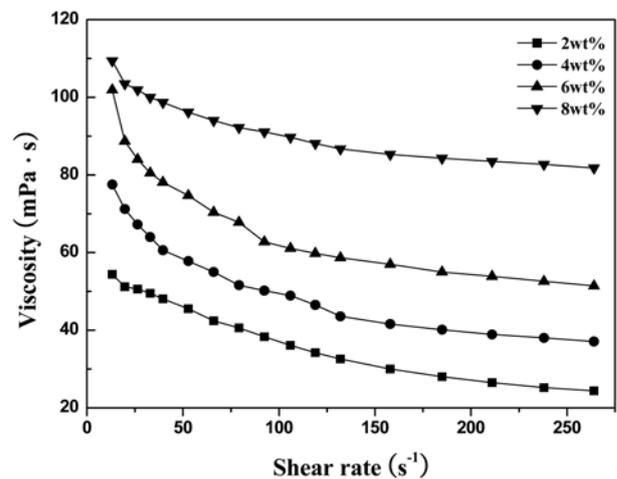


Fig. 8. Effect of the binder/plasticizer on the viscosity of the slurry.

an initial value of 5.69 μm to 4.14 μm by means of the dispersion capacity of methanol only, and then was reduced to 705 nm due to the dispersion stability with the addition of polyethylene glycol, and then increased again with an increase in the amount of polyethylene glycol added. Considering the foregoing results, the optimal amount of dispersant showing the best dispersion stability was within 1.5 wt% polyethylene glycol with respect to a solid content 33.3%.

As an experiment to determine the amount of binder/plasticizer contained, the change of viscosity of the binder/plasticizer is shown in Fig. 8. After fixing the ratio of binder to plasticizer to 3 : 1, the binder/plasticizer with respect to a solid loading of 60% was changed between 2-8 wt%. The viscosity of the slurry increased from 24 mPa.s to 109 mPa.s with the addition of the binder/plasticizer, and a shear thinning phenomenon occurred in which the apparent viscosity decreased with an increase in a shear rate. Fig. 9 shows the viscosity of the slurry to which 1.5 wt% polyethylene glycol was added shows the best dispersion and the viscosity of slurry to which 1.5 wt% polyethylene glycol was not added over time

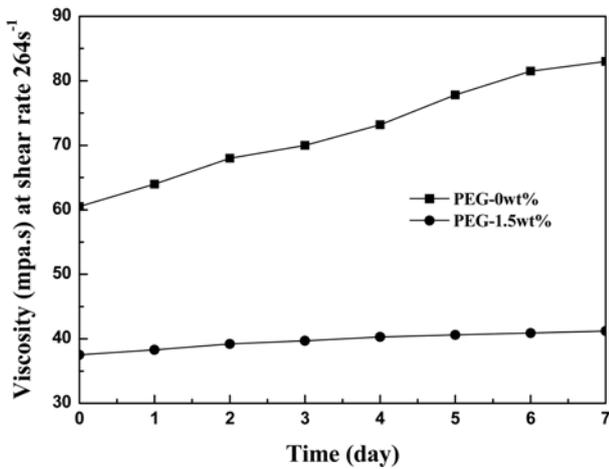


Fig. 9. Variation of the slurry viscosity as a function of aging time.

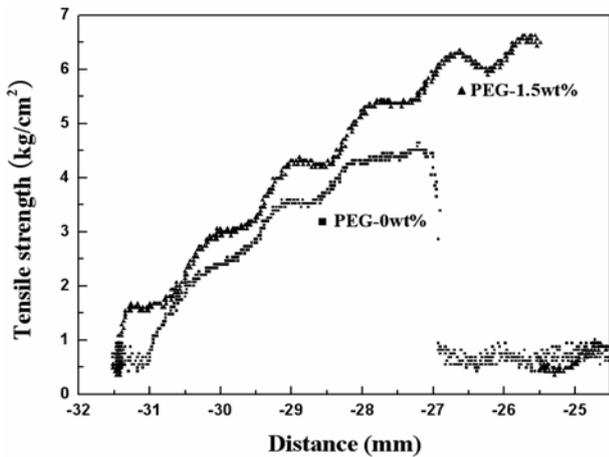


Fig. 10. Tensile strength of the green sheets as a function of PEG.

when the contained amount of the binder/plasticizer suitable for slurry manufacturing was fixed to 2 wt% based on Fig. 8. The slurry to which 1.5 wt% polyethylene glycol was added shows a much lower viscosity than that of the slurry to which polyethylene glycol was not added. With aid of the dispersion stability polyethylene glycol, the viscosity of the slurry exhibited stability without change over time.

Fig. 10 shows a comparison between the tensile strength of green sheets manufactured using the dispersion stability with the addition of 1.5 wt% polyethylene glycol and without. Referring to Fig. 10, the tensile strength of the green sheet manufactured using dispersion stability with the addition of 1.5 wt% polyethylene glycol was 6.6 kg/cm² (6.47 MPa), while one without the addition of polyethylene glycol was very low at 4.6 kg/cm² (4.51 MPa). It is thought that the low tensile strength results from non-uniform aggregation between particles and the organic additive due to the unstably dispersed slurry.

Fig. 11(b) shows an SEM micrograph of the cross-section of a green sheet manufactured using dispersion stability, in which the uniform distribution of transparent dielectric frit and the organic material that properly

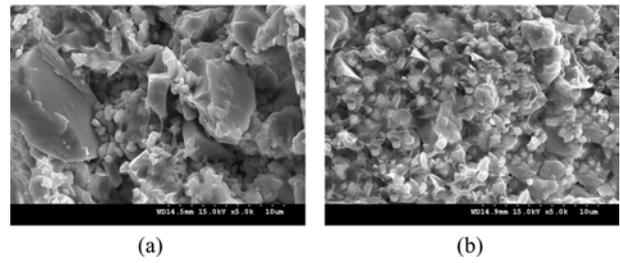


Fig. 11. Cross sectional SEM images of the green sheet prepared by (a) without and (b) with PEG.

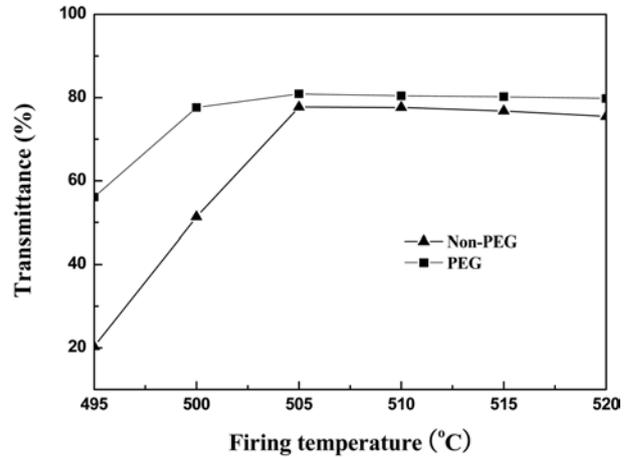


Fig. 12. Optical transmittance in the visible range as a function of firing temperature.

surrounds the fit can be seen. On the other hand, referring to Fig. 11(a), in the cross-section of a green sheet manufactured without using dispersion stability, air gaps and pores are observed and particles that are not covered with organic material uniformly and the organic material is sporadically aggregated. As can be seen from the foregoing results, a uniform and dense lead-free transparent dielectric green sheet can be manufactured using dispersion stability, which may affect the characteristics after a thermal process.

The lead-free transparent dielectric green sheets manufactured with and without the addition of polyethylene glycol were transferred onto soda-lime glass substrates and then thermally processed with the same condition at 495–520 °C for 30 minutes. A transmittance of 81% at 30 μm thickness can be obtained at a reference wavelength of 550 nm when fired at 505 °C for 30 minutes. Changes of transmittance of those green sheets in the visible light range of 380–780 nm with respect to a change in the firing temperature are shown in Fig. 12. The green sheet with the addition of polyethylene glycol using dispersion stability was not completely fired 495 °C and thus had low transmittance, and its transmittance increased with an increase in firing temperature and then was highest at 505 °C. As can be seen in Fig. 13, the lead-free transparent dielectric formed using dispersion stability had a small number of pores in the surface and layers, whereas the lead-free transparent dielectric formed without

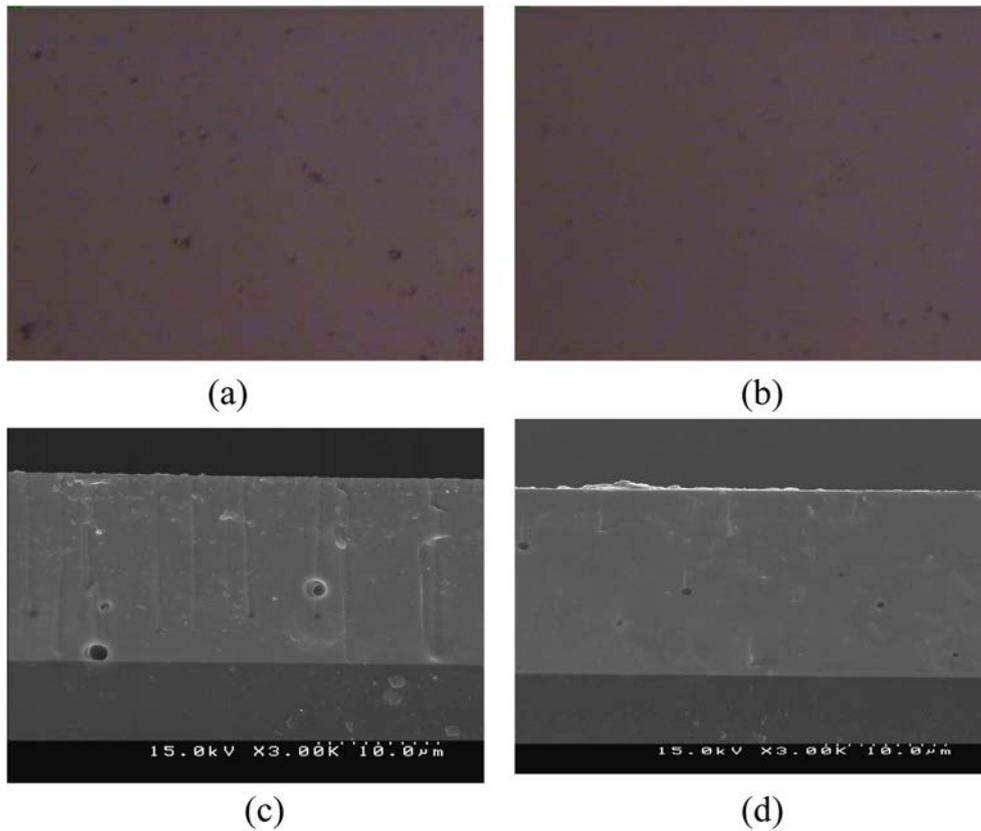


Fig. 13. Surface and Cross sectional SEM images of the transparent dielectric films fired at 505: (a) and (c) without PEG, (b) and (d) with PEG.

dispersion stability had a large number of pores, based on which the lead-free transparent dielectric formed using dispersion stability had a higher transmittance than that of the lead-free transparent dielectric formed without dispersion stability.

Fig. 14 shows results using EDAX line-scanning analysis in order to check the reaction between an electrode and a lead-free transparent dielectric layer, which may cause the yellowing phenomenon during the process of manufacturing PDP. As can be seen from Fig. 14, no ions of

Ag or Sn diffusing into the transparent dielectric layer during the thermal process were found and thus the yellowing phenomenon did not occur. Fig. 15 exhibits a lead-free transparent dielectric layer formed on a PDP front substrate where a bus electrode and an ITO transparent electrode are formed, which has a superior appearance of high transparency without the yellowing phenomenon.

Conclusions

The following conclusions were made after studying the dispersion stability of lead-free transparent dielectric

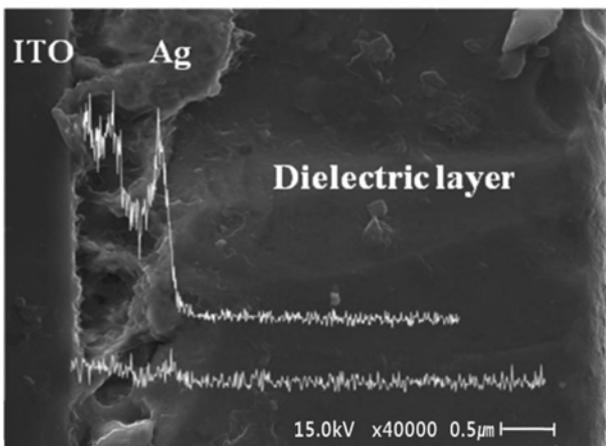


Fig. 14. EDAX line-scan profiles of the lead-free transparent dielectric layer on ITO/PD200 substrate: upper (Ag) and lower line(Sn), respectively.

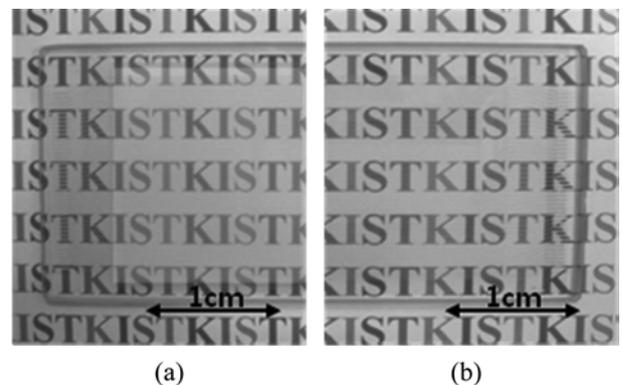


Fig. 15. Image of the lead-free transparent dielectric thick layer of 30 µm: (a) fired at 505 °C on mother substrate patterned with Ag/ITO/PD200 glass substrate (b).

slurries of the $\text{Bi}_2\text{O}_3\text{-ZnO-BaO-Al}_2\text{O}_3$ system to form a thick layer of the upper transparent dielectric used for a PDP by a tape casting method:

1) As to the dispersion stability effect of the slurry, for dispersion of the lead-free transparent dielectric frit of the $\text{Bi}_2\text{O}_3\text{-ZnO-BaO-Al}_2\text{O}_3$ system, the dispersion stability of methanol was best and a solid loading of 33.3% and 1.5 wt% polyethylene glycol were most effective as a dispersant.

2) A green sheet manufactured using dispersion stability exhibited superior properties in terms of tensile strength and a uniform distribution of the frit and organic material compared to a green sheet that was manufactured without using dispersion stability, which was due to steric stabilization.

3) As a result of forming a thick layer of lead-free transparent dielectric by firing the green sheet with dispersion stability on a soda-lime glass substrate, a transmittance of 81% at 30 μm thickness can be obtained at a reference wavelength of 550 nm (standard wavelength of visible range) when fired at 505 °C for 30 minutes, which sufficiently satisfies the required characteristics of a thick layer of lead-free transparent dielectric used for a PDP without yellowing phenomenon.

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