

Effect of particle size in slurry manufacturing for green sheet of lead-free transparent dielectrics

Byung-Yong Wang^a and Young-Jei Oh^{b,c,*}

^aComponent Industry & Automotive Team, Samsung Electro-Mechanics, Pusan 46754, Korea

^bOpto-Electronics Materials & Devices Research Center, Seoul 02792, Korea Institute of Science and Technology, Korea

^cDepartment of Nano Material Science and Engineering, Korea University of Science and Technology, Daejeon 34113, Korea

The dispersion characteristics of the slurries according to the particle size (0.7 μm , 5 μm and 10 μm) of the lead(Pb)-free frit as a raw material were studied in order to aid in the manufacture of a green sheet for the transparent dielectric layers using the tape casting method. Effect of solvents and dispersants on the slurry formation was investigated by comparing the sedimentation height according to the particle size of the frit. Overall observations about precipitation and viscosity have been performed to establish the suitable manufacturing of slurry and the optimum working condition of the green sheet. When the powder of lead-free transparent dielectric frit was dispersed in methyl alcohol, it was found that polyethylene glycol was the most suitable among several dispersants. Higher dispersion stability was shown at 2.0 wt% addition for a particle size of 0.7 μm , 1.5 wt% for 5 μm , and 1 wt% for 10 μm , which can be explained by a steric stabilization mechanism. The smaller particle size is more recommendable for dispersion based on steric stabilization, and increases the effective solid contact rate per unit volume, leading to a higher transmittance and voltage withstand property.

Key words: Tape casting, Transparent dielectrics, Dispersion stability, Green sheet, Particle size, Lead-free frit.

Introduction

With the recent rise in environmental concerns, applications of transparent Pb-free materials in electronic devices have been receiving great attention. According to the EU's Restriction of Hazardous Substances Directive (RoHS), hazardous elements such as lead, mercury and heavy metals must be constantly replaced by environmentally friendly materials. In general, a screen printing process has been one of the main methods used for forming a transparent dielectric layer in electronic devices. This process, however, is prone to bubble formation and surface non-uniformity of dielectric thin film due to the fact that it involves applying two or three repetitive layer coatings, resulting in defects in transparent dielectrics. As an approach to solving this problem, a dry film method has been employed, which uses a green sheet manufactured via a tape casting method. Tape casting is a low-cost process that allows thin film adjustment and makes it easy to manufacture a high-quality ceramic sheet, having the advantage of allowing the fabrication of green sheets with a large area and a thickness ranging from several tens to several hundreds of microns. However, this process obtains a relatively low green density when

compared to conventional pressing processes because of difficulty in pressurization during molding.

Since the molding state of a normally prepared green sheet directly affects the structure of a sample, it is important to manufacture a uniform and packed green sheet in order to obtain a flawless and high-sintered density ceramics [2]. To this end, it is most crucial to produce uniform slurry with improved dispersion stability of powder in a solvent. In addition to such methods using dispersibility, methods for increasing solid fraction in slurry have been reported [1-4]. While the increase of solid content increases the viscosity of the slurry, the solid content cannot be indefinitely increased beyond the viscosity of slurry generally required for molding. Eventually, some difficulties accompany the increasing of the solid fraction, and the particle size and particle size distribution of powder have to be controlled so that powders after molding can be in a closest-packed state.

When a green sheet is manufactured through tape casting, the viscosity of slurry has to exhibit a pseudoplastic behavior, which decreases as the shear rate increases. In other words, low viscosity is shown due to a high shear rate during casting, whereas after casting, an aggregate holding a solvent is formed by the non-occurrence of shear deformation in the slurry and thus the viscosity is increased, thereby keeping the shape of a green sheet. Therefore, the packing density of a powder in a green sheet largely depends on the density and size distribution of the aggregates, as well

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

as the particle size of powder.

Studies which have been conducted so far on tape casting have focused on the change of the amount of dispersant according to particle size, the type of an organic material such as a binder or a plasticizer and determination of the amount thereof, and corresponding rheological property behavior; studies on the influences of the particle size distribution of the powder used have not been properly conducted. Accordingly, in this study, slurry conditions according to the change in particle size have been established to form a transparent dielectric with tape casting by using lead-free transparent frit powder. In addition, the rheological properties of the slurry have been studied by comparing the sedimentation phenomena, the physical, optical properties and microstructure of the green sheet after sintering.

Experimental Method

As the lead-free transparent dielectric composition used in this experiment, the $\text{Bi}_2\text{O}_3\text{-ZnO-BaO-Al}_2\text{O}_3$ frit group [8] is selected. The frit composition has a density of 5.0 g/cm^3 , thermal expansion coefficient of $88.8 \times 10^{-7}/\text{K}$, glass transition temperature of $460.2 \text{ }^\circ\text{C}$, and dielectric constant of 12.7 (at 1 MHz). Crystallization of the frit that occurs during sintering acted served to reduce the light transmittance. Fig. 1 shows the XRD pattern of the transparent dielectric frit as a raw

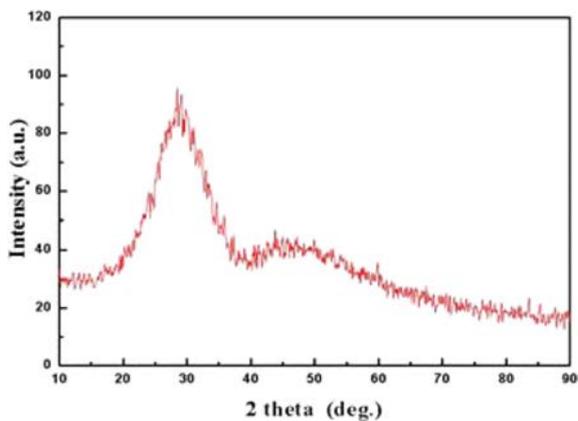


Fig. 1. XRD pattern of the powder of lead-free dielectric frit.

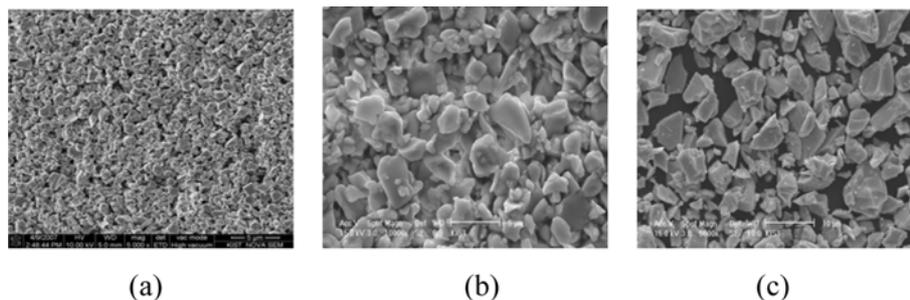


Fig. 2. SEM images of the raw materials: mean particle size of (a) $0.7 \text{ }\mu\text{m}$, (b) $5 \text{ }\mu\text{m}$, and (c) $10 \text{ }\mu\text{m}$, respectively.

material. The powder morphology of the frit samples, which had mean particle sizes of $0.7 \text{ }\mu\text{m}$, $5 \text{ }\mu\text{m}$, and $10 \text{ }\mu\text{m}$, respectively, is shown in Fig. 2. The particles are slightly irregular squares rather than being round in shape. Solvents such as ethyl alcohol (Daejung Chem., Korea), methyl alcohol (Daejung Chem., Korea), toluene (Junsei, Japan), acetone (Junsei, Japan), and MEK (J.T. Baker, USA) were used to compare the dispersion behavior of the frit powder. General-purpose dispersant fish oil (Aldrich, USA), polyvinyl butyral (Aldrich, USA), solspers 24000sc (ICI Co, UK), polyethylene glycol (Aldrich, USA), SN Dispersant-9228 (San Nopoco Ltd., Korea), and Nopcosperse-092 (San Nopoco Ltd., Korea) were used as a dispersant.

Rheological characteristics of the suspension slurry according to species of dispersant and solvent were analyzed through a precipitation experiment and viscosity measurement. The influences of particle size on dispersion stability were investigated. The precipitation experiment was carried out using the method developed by Mistler and Twiname [5]. Several dispersants of 0 - 3 wt% with 0.5 wt% intervals were added to raw frit powder of 100 wt% and mixed solvent of 200 wt%, respectively, after which ball milling was performed for 4 hrs. Next, the dispersed slurry was filled in a 25 ml sized cylinder and sealed tightly, and then was left for 7 days to measure and compare the change in the height of precipitate. The viscosity change according to the amount of dispersant was measured using a rotary viscometer (Viscometer DV-II+, Brookfield Co., USA).

For the optimal green sheet, PVB (Polyvinyl Butyral, Mw: 90,000~120,000), Aldrich, USA) was used as a binder and DBP (Dibutyl Phthalate, Aldrich, USA) and PEG (Polyethylene Glycol (Mw: 400), Aldrich, USA) were used as plasticizers, giving it plasticity by alleviating bonding to set up the optimal slurry condition for each particle size [6]. During slurry manufacturing, organic materials in which a dispersant, a plasticizer and a binder are simultaneously mixed are competitively adhered to the particle surface, thus hindering complete dispersion. For this reason, a solvent, a dispersant, and a frit were primarily mixed for 24 hours using Zirconia balls, and then a binder and a plasticizer were later added to the mixture. The

resultant mixture was subject to secondary ball milling for 24 hours, enabling the manufacture of uniform slurries.

Deaeration was carried out to maintain a viscosity suitable for tape casting by removing bubbles generated in the slurry during mixing and eliminating the excessive solvent added. Next, a green sheet was formed with a thickness of 50 μm on the Mylar film using the doctor blade (STC-14A, Hansung System Inc., Korea) machine, after which the dried green sheet was attached onto the PD-200 glass substrate having a low thermal shrinkage and finally was thermally processed at 500 $^{\circ}\text{C}$ for 320 minutes in the air.

Transmittance changes according to sintering temperature were measured using UV/Visible spectrometer (Lambda UV/VIS/NIR, Podenseewerk Perkin-Elmer Co., Germany), while voltage withstand properties were compared using a voltage withstand tester (Digital W/I Tester 8502). Microstructure of the cross-section of transparent dielectric thick film was observed using ESEM (XL-30 EDAX, PHILIPS, Netherlands).

Results and Discussion

The dispersion stability of the frit can be analyzed by observing changes in precipitation height, viscosity, and zeta potential [7-9]. Of these methods, the most generally used method is the measurement of precipitation height according to the amount of addition of dispersant. This method is based on the fact that as dispersion rate increases, the packing density of the precipitated particles increases, lowering the precipitation height [10]. Fig. 3 shows a comparison of dispersion stability of transparent dielectric frit among several organic solvents using this precipitation measurement when no dispersant is added. In other words, when no dispersant is added, the precipitation property varies according to the type of a pure organic solvent. When a solvent is water, the frit is precipitated rapidly and in a high amount, and thus fails to be sufficiently dispersed. The frit shows the best dispersion property in ethyl alcohol and methyl alcohol. A polarizing phenomenon in a solid-liquid interface is required in terms of dispersion stability of the frit material, and a solvent having a lower dielectric constant than that of water suppresses dissociation of an ionization material and reduces ion concentration and electric fields, eventually leading to improvement of the dispersion property of the frit.

Of the various solvents, methyl alcohol showed superior dispersibility over the entire particle size range. The dispersion property of methyl alcohol was investigated while changing the type of dispersant and the amount of the dispersant added according to particle size. Fig. 4 shows the dispersion property of the frit according to the addition of dispersant, and it

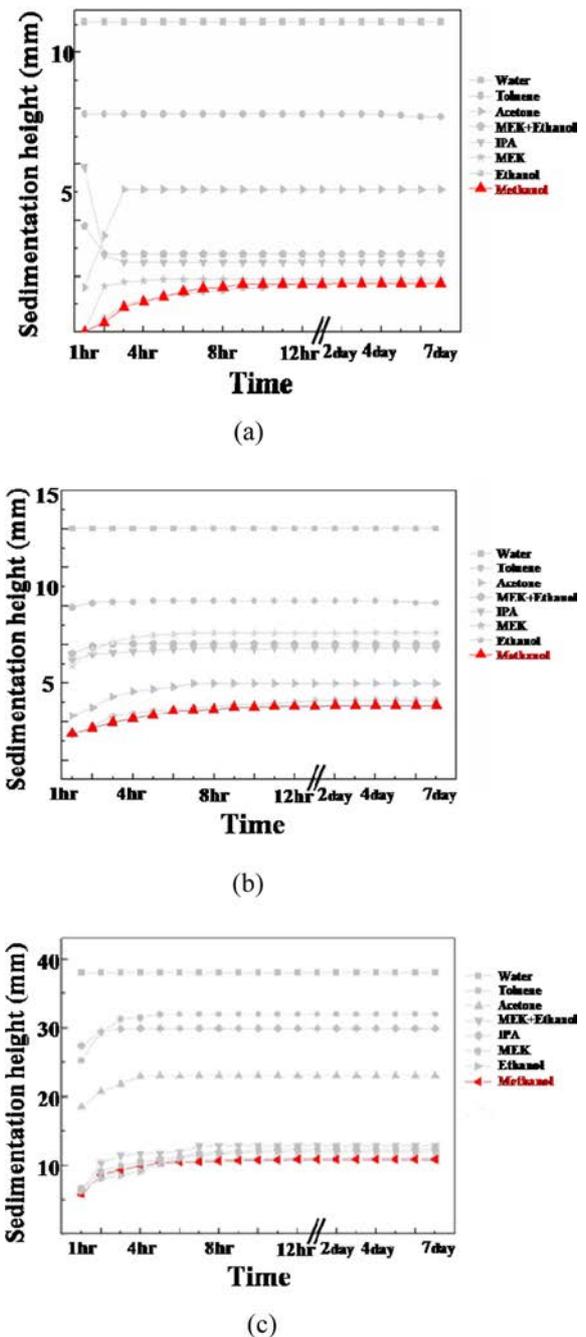
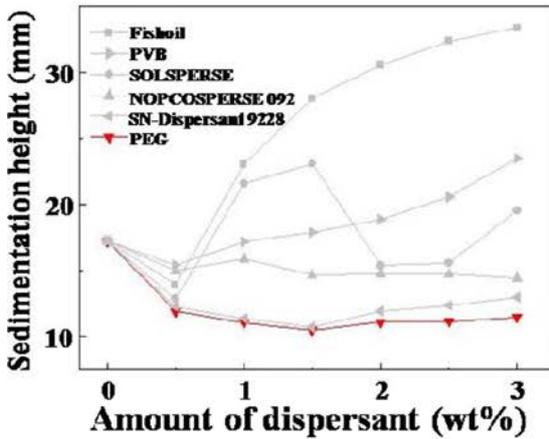


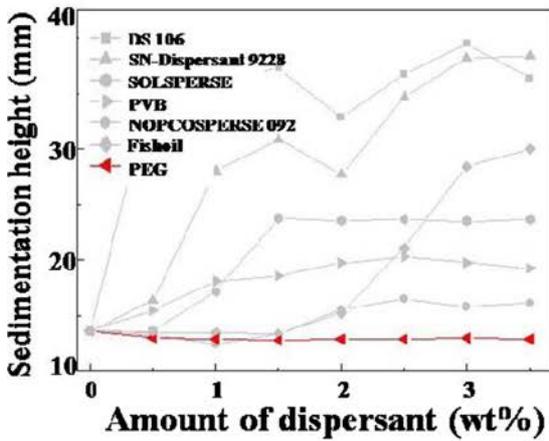
Fig. 3. Comparison of sedimentation rate of the frit in various solvents: mean particle size of (a) 0.7 μm , (b) 5 μm , and (c) 10 μm , respectively.

can be seen that polyethylene glycol exhibits the best dispersion ability in all particle sizes. This is because attraction between particles is reduced as the minimum distance between particles increases due to the physical force generated by mutual tangling of polymer chains surrounding the particles, leading to a steric stabilization.

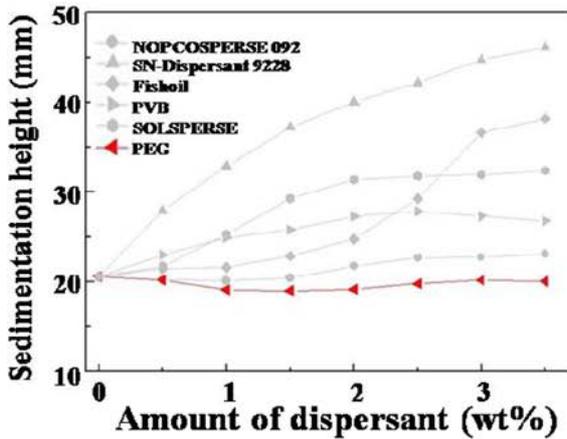
To identify the appropriate amount of dispersant corresponding to a suspension having the most superior



(a)



(b)



(c)

Fig. 4. Sedimentation rate of the frit as a function of the amount of dispersant: mean particle size of (a) 0.7 μm, (b) 5 μm, and (c) 10 μm, respectively.

dispersion stability according to particle size when the lead-free transparent dielectric frit is dispersed in methyl alcohol, precipitation velocity according to the

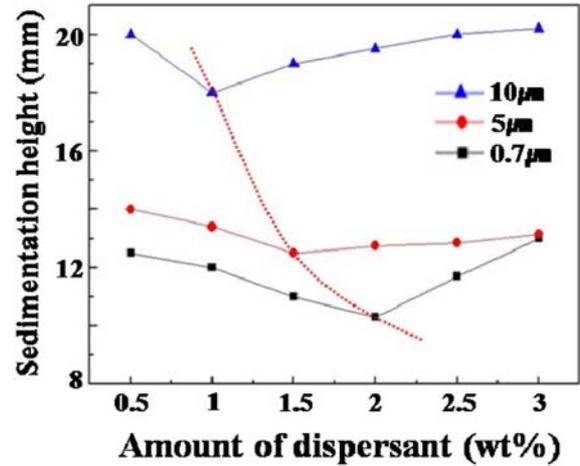


Fig. 5. Changes of sedimentation rate of the frit as a function of PEG.

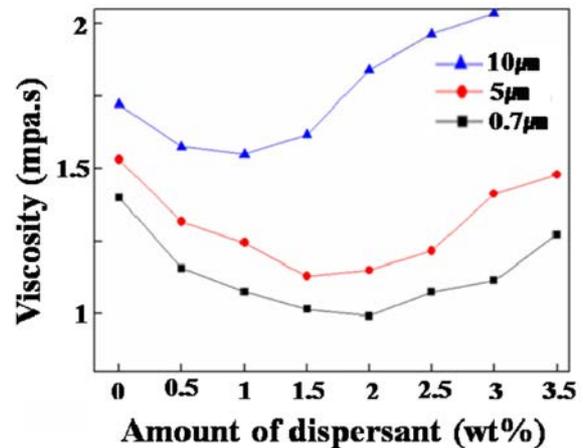


Fig. 6. Viscosity of the suspension as a function of the amount of dispersant.

amount of addition of polyethylene glycol is shown in Fig. 5. The most superior dispersion stability was shown with a dispersant of 2.0 wt% for a particle size of 0.7 μm, 1.5 wt% for 5 μm, and 1 wt% for 10 μm, indicating that more dispersant is required as the specific surface area increases.

Fig. 6 shows the viscosity change of a suspension according to the amount of dispersant for each particle size. For all suspensions, the viscosity is reduced and then increases again as the amount of the dispersant increases. When the amount of a dispersant is less than the appropriate amount, powder is maintained in the shape of secondary agglomerate. In this case, a solvent exists between macro pores of the secondary agglomerate, causing solvent insufficiency and thus hindering uniform mixing. However, as the amount of dispersant increases, the secondary agglomerate is dissociated by mutual repulsion between polymer functional groups adhered to the particle surface and dispersion is achieved through the steric stabilization scheme, reducing viscosity. As the amount of the

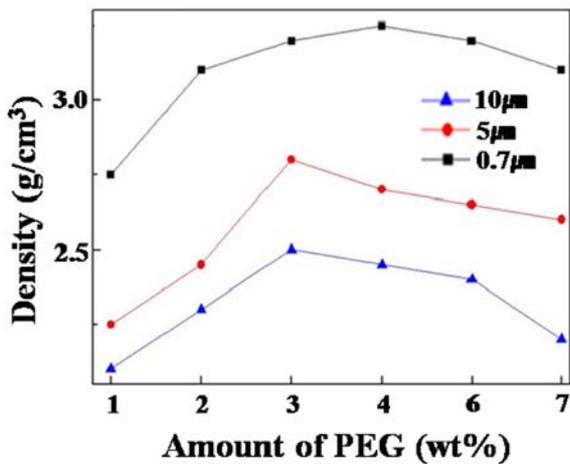


Fig. 7. Sintered density of the green sheet as a function of PEG.

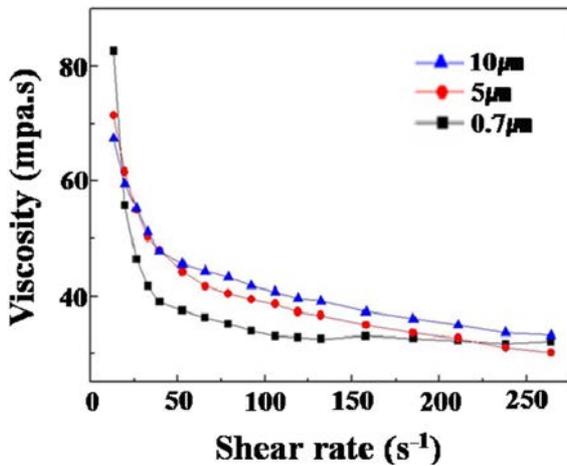


Fig. 8. Effect of particle size on the viscosity of slurry.

dispersant added increases beyond the appropriate amount, the viscosity of the suspension increases. This may be because excessive dispersant exists in the suspension and the flow of the suspension is interrupted by bridging or tangling of polymer chains. High viscosity is shown for large particle sizes of 5 μm and 10 μm . This is because influences between particles in the suspension increase. In other words, such attraction between particles forms agglomeration in the suspension, and in this case a portion of the solvents is captured by the agglomerate, increasing the effective solid contact rate.

Fig. 7 shows density change in lead-free transparent dielectric green sheet for PDP when a binder is changed between 2~6 wt% in a suspension manufactured using dispersion stability according to particle size. The binder bonds the powders of the frit during sheet manufacturing to prevent dry cracking, but when added excessively, it sharply reduces the density of the sheet and causes a pore or a defect in incineration. In other words, the optimal amount of the binder is an extent to which it can be uniformly adhered to the frit powder to improve

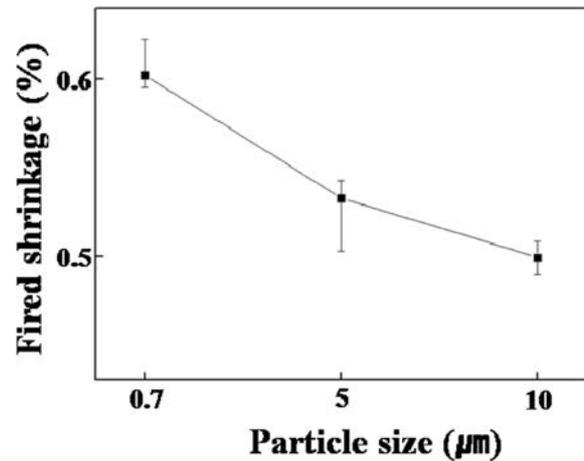


Fig. 9. Fired shrinkage according to the particle size.

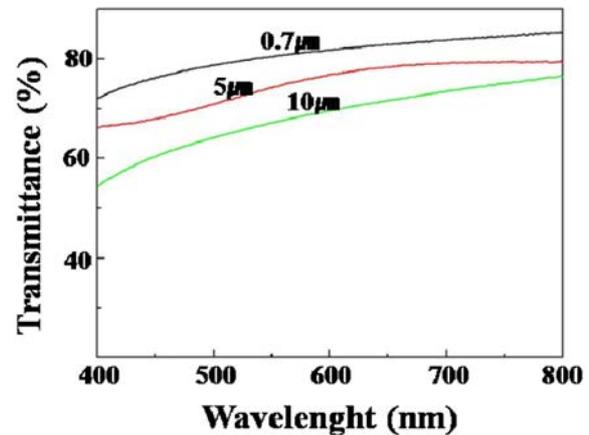


Fig. 10. Optical transmittance as a function of the particle size.

a bonding force, but if more than a specific amount of the binder is added, the adhered amount increases the distance between powders, reducing density. Therefore, the amount of the binder has to be fixed immediately before the occurrence of density reduction [11-13]. It can be seen that the density of the sheet is reduced when a binder of more than 4 wt% is added to a suspension having a particle size of 0.7 μm , and the density is reduced when a binder of more than 3 wt% is added to suspensions having particle sizes of 5 μm and 10 μm . However, fine powder having a particle size of 0.7 μm shows higher sintered density than coarse powder over the entire binder addition range. This result may also explain that fine particles are dispersed well by the steric stabilization scheme, leading to a high effective solid contact rate per unit volume and thus to more compactness than after plasticization [14].

Fig. 8 shows observations of the pseudo-plastic behavior of slurry manufactured in various experiments according to particle size. In the slurry showing the pseudoplastic behavior, the viscosity is low due to large shear deformation during tape-casting and increases due to the non-occurrence of shear deformation after

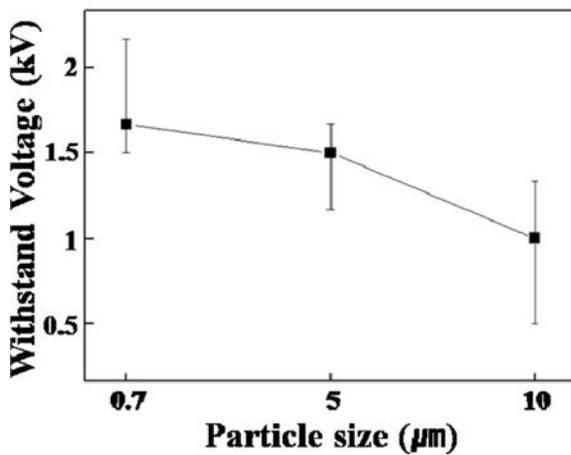
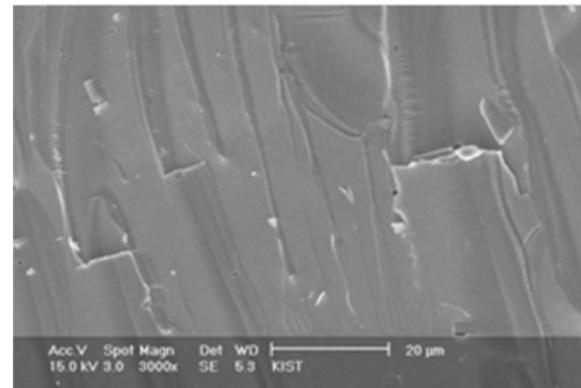


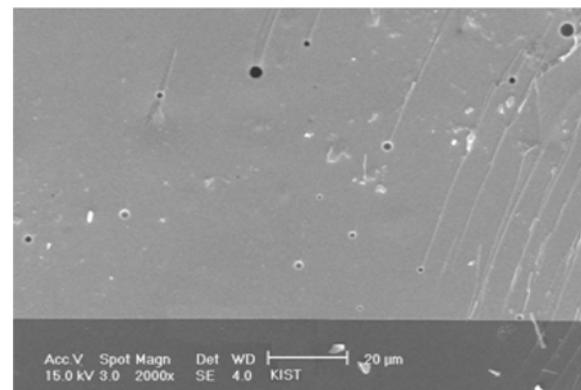
Fig. 11. Withstand voltage according to the particle size.

casting, thus providing an advantage in maintaining the shape of a compact [15-16]. This behavior is useful for tape casting, in which the slurry shows low viscosity under the Doctor Blade shear and shows high viscosity at a portion passing from the blade. The pseudoplastic slurry can be described as having a feature of “shear thinning.” As can be seen in Fig. 8, all slurries showed the shear thinning feature, in which apparent viscosity is reduced as shear rate increases. In addition, the pseudoplastic behavior was intensified as particle size decreases. Such intensification of the pseudoplastic behavior means that powders in slurry more easily form agglomerate, capturing a solvent in the case of low shear velocity, increasing the effective solid contact rate. Since the solvent included in the agglomerate is put into the slurry due to the destruction of the agglomerate when shear velocity is increased, the effective solid contact rate is increased and thus the slurry velocity is reduced again. This may be because the agglomerate is more easily formed due to the increase in the number of collisions between particles in the slurry as particle size decreases.

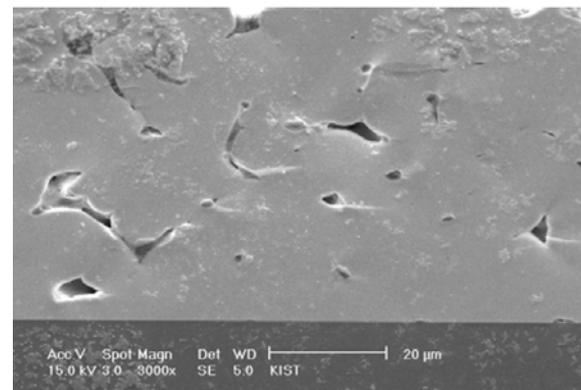
Fig. 9 shows measurements of shrinkage rate by attaching the green sheet on PD-200 glass substrate having low thermal shrinkage and then performing thermal treatment in the air. As particle size was reduced, firing shrinkage rate was increased. Specific surface area was increased as the size of the frit decreased, and thus the firing shrinkage rate was increased during sintering. Figs. 10 and 11 show a comparison of transmittance and voltage withstand properties of the transparent dielectric layer according to particle size when the film has a thickness of 30 μm . It can be seen that as particle size decreases, both the transmittance and voltage withstand properties increase. This may be because a pore formed by a small particle size disappears easily in terms of shape and size, whereas a pore formed by a large particle size



(a)



(b)



(c)

Fig. 12. SEM images showing pore changes inside lead-free transparent dielectric layer: (a) 0.7 μm , (b) 5 μm and (c) 10 μm mean particle size, respectively.

has a structure that does not easily disappear. This can be seen from SEM pictures of Fig. 12. A pore formed for a specimen formed with a particle size of 0.7 μm disappeared easily during sintering, whereas a pore formed for a specimen formed with a particle size of 10 μm is large in most cases, and thus did not easily disappear during sintering.

Conclusions

To manufacture lead-free transparent dielectric thick film, the dispersion stability of the slurry and physical property change of the green sheet according to particle size are as follows:

When a lead-free transparent dielectric frit is dispersed in methyl alcohol, polyethylene glycol was most suitable as a dispersant, and the most superior dispersion stability was shown with the addition of 2.0 wt% for a particle size of 0.7 μm , 1.5 wt% for 5 μm , and 1 wt% for 10 μm , a difference which can be explained by a steric stabilization mechanism.

As particle size decreases, sintered density and plasticization shrinkage rate of the sheet increase, which means that a smaller particle size is more suitable for dispersion based on the steric stabilization scheme and increases effective solid contact rate per unit volume, leading to more compactness.

Both transmittance and voltage withstand of lead-free transparent dielectric layer were higher for smaller particle sizes, since a pore formed by small particle size easily disappears in terms of shape and size whereas a pore formed by a large particle size has a structure that does not easily disappear in terms of shape.

Acknowledgments

The authors would like to acknowledge the financial support of the Korea Institute of Science and Technology research program, 2E28171.

References

1. K. Nagata, *J. Ceram. Soc. Jpn.* 100[10] (1992) 1271-1275.
2. D.C. Lam and M. Nakagawa, *J. Ceram. Soc. Jpn.* 102[2] (1994) 133-138.
3. R.J. Mackinnon and J.B. Blum, in *Advances in Ceramics Vol. 9* (Am. Ceram. Soc, Inc. Columbus, Ohio, 1984) p. 150-157.
4. S. Taruta, K. Kitajima, N. Takusagawa, K. Okada and N. Otsuka, *J. Ceram. Soc. Jpn.* 101[5] (1993) 583-588.
5. R.E. Mistler and E.R. Twiname, in *Tape Casting: Theory and Practice* (Am. Ceram. Soc. Inc., Westerville, Ohio, 2000) p. 24-36.
6. R. Moreno, *Am. Ceram. Soc. Bull.* 71[10] (1992) 1521-1531.
7. D.J. Shanefield, in *Organic Additives and Ceramic Processing*, Second edition, (Kluwer Academic Publishers, 1999) pp. 211-254.
8. Y.-J. Oh, J.-W. Lee, *J. Ceram. Process. Res.* 10 (2009) 657-663.
9. B.-Y. Wang, D.-S. Lim, Y.-J. Oh, *Mol. Cryst. Liq. Cryst.* 514 (2009) 190-200.
10. R.J. Hunter, "Effect of Polymer on Colloid Stability," in *Introduction to Modern Colloid Science* (Oxford New York, 1997) p. 54-56.
11. K.R. Mikeska, and W.R. Cannon, in *Advances in Ceramics*, Vol. 9. *Forming of Ceramics*, ed. by John A. Mangels (American Ceramic Society, Inc., Columbus, Ohio, 1984) p.164-83.
12. R. Moreno, and G. Cordoba, *Am. Ceram. Soc. Bull.* 74[7] (1995) 69-74.
13. P.A. Smith, *J. Am. Ceram. Soc.* 78[3] (1995) 809-812.
14. Y.-J. Oh, B.-K. Jang, H.-O. Kim, D.-S. Lim, *Mater. Chem. Phys.* 129 (2011) 134-137.
15. H.-O. Kim, B.-Y. Wang, Y.-J. Oh, *Mol. Cryst. Liq. Cryst.* 551 (2011) 198-205.
16. Y.-J. Oh, B.-K. Jang, H.-O. Kim, *Mater. Lett.* 65 (2011) 2357-2360.