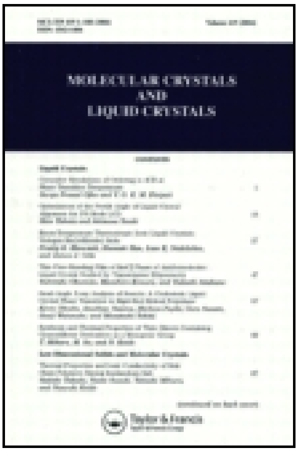

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Influence of Oil Absorption on Lead-Free Transparent Dielectric Frit for Green Sheets

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During the grinding of frit powder for the storage of raw materials, foreign substances such as oil can become attached to the surface of frit powder, adversely affecting the dispersion behavior and final properties of fired dielectric thin layers. This study reports the effect of the dispersion of artificially crushed frit powder containing oil. Green sheets of lead-free Bi_2O_3*-ZnO-BaO-*Al_2O_3 *dielectric frit containing oil of* $0 \sim 0.1$ *wt% were prepared by a tape casting method, which is an alternative to screen printing method. The frit powder was easily aggregated by contamination of oil, affecting its dispersion stability. However, the dispersion stability of the suspension liquid could be controlled by adjusting the amount of oil, and polymeric dispersant steric stabilization was effective to optimize the dispersion, resulting in enhanced physical properties. As the amount of oil contamination was increased, the number of pores and defects in the fired thin layer also increased. However, the optimized condition of the transparent dielectric thin layer at 500°C at a low firing temperature was obtained through the use of polyethylene glycol (PEG).*

Keywords Lead-free dielectrics; frit; oil contamination; green sheet; dispersion; tape-casting

Introduction

Screen-printing method is commonly used in the manufacture of transparent dielectric layers for PDPs; however, this method is likely to cause defects in the final characteristics of the dielectric layer as the layer is not uniform due to air bubbles that are generated by the repeating of the screen-printing process to make the desired thickness. To offset this shortcoming, a method of preparing green sheets via tape-casting has been adapted for the formation of a transparent dielectric layer. The tape-casting method simplifies the adjustment of the thickness, making it possible to manufacture high-quality and large-area green sheets. The method has the advantage of making a thick green sheet with a thickness up to several hundred microns without a repeated process, as in the screen printing method. [1] The tape-casting method requires an adequate dispersion condition of the ceramic powders it uses in a liquid medium for to optimize the outcome. In general, ceramic processing results in defects in a green body due to Brownian motion and van der Waals attraction, which are associated with unintended aggregation of the particles in the slurry.

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This type of aggregation is generated by collisions between particles that are caused by the large specific surface area of the powder during the slurry preparation process.

The dispersion degree of the ceramic slurry is generally explained by the mechanism of electrostatic repulsion or steric stabilization. It can be controlled by adding a dispersant capable of changing the surface potential of the aggregated particles or by stabilizing the aggregated particles in the dispersion medium. [1–3] It is important to manufacture a green sheet without defects during the tape-casting process, even when aggregation in the starting material exists. In procedure of grinding frit, electrostatic attraction forming broken bond occurs instantly the fracture when grinding. At this time, conditions for surrounding materials to easily combine are met and have tendencies to maintain electrical neutrality through components that are in the air when dry grinding. For frit powder to have electrical neutrality, absorption of surrounding oil is easy. In this research, therefore, lead-free Bi_2O_3-ZnO-BaO-Al_2O_3 dielectric frits containing a small quantity of oil were assessed for their ability to estimate the effects of oil contamination. The dispersion behavior of the oil-containing dielectric slurry and the mechanical properties of the resulting green sheets were investigated as a function of the amount of oil.

Experimental Procedure

In this study, a tape-casting method was used to fabricate lead-free transparent dielectrics for the upper panel of a PDP instead of a conventional screen-printing method. When grinding it in a jet mill, oil used in the motor rotating the classifier of the jet mill is artificially added in the procedure of grinding frit. During mass production, oil that can be flowed in is estimated to be within 0.1 wt%. Under consideration of the content of oil inserted for grinding, the oil was added by 0.01 wt%, 0.05 wt%, and 0.1 wt%. Bi_2O_3-ZnO-BaO-Al_2O_3 frit was used, with oil amounts of 0, 0.01, 0.05 and 0.1% (in weight ratio), as a raw material. The physical properties of the lead-free transparent dielectric frit are a density of 5.0g/cm^3, a dielectric constant of 12.7(1 MHz), a thermal expansion coefficient of 88.8×10^{-7}/K, a glass transition temperature of 460.2°C, a softening point of 488.6°C and an average particle size of 0.35 μm.

For the dispersion experiment on frit powder contaminated with oil, methyl alcohol (Daejung Chem., Korea), ethyl alcohol (Daejung Chem., Korea), acetone (Junsei, Japan), toluene (Junsei, Japan), methyl-ethyl-ketone (J. T. Baker, USA) and DI-water were used as a solvent. For a comparison of the dispersion ability, the ionic dispersants Nopcosperse-092 (Sannopco Korea, Ltd., Korea), SN-Dispersant 9228 (Sannopco Korea, Ltd., Korea) and Nopcoplus DS-106 (Sannopco Korea, Ltd., Korea) along with the polymeric dispersant polyethylene glycol (Mw 200, Aldrich, USA) were used. It was necessary for the dispersants to have a large surface adsorptive characteristic so that they would be easily adsorbed onto the surface of the particles and then segregate the aggregated particles by steric stabilization or other methods. [4]

The dispersion behavior of the frit powder according to the type of dispersant and solvent was analyzed in a precipitation experiment, while the viscosity and zeta potential were measured based on the fluidity of the suspension. [5] The precipitation experiment followed the method recommended by Mistler and Twiname. [6] The concentration of the frit powder and the solvent was fixed at 100 wt%. Several dispersants were added at concentrations of 0, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 wt%. The resulting mixtures were ball-milled for 4 hours. The suspensions were poured into 25 ml cylinders, covered, and then left for 7 days before the height of the precipitate and the precipitation-velocity were measured. The viscosity was measured by a rotary viscometer (Viscometer DV-II+, Brookfield Co., USA).

PEG (polyethylene glycol Mw 200, Aldrich, USA) and DBP (dibutyl phthalate, Aldrich, USA) were used as a plasticizer to make the sheet flexible, while PVB (polyvinyl butyral Mw 90,000∼120,000, Aldrich, USA) was used as a binder. The oil-containing frit powder was ball-milled for 24 hours together with a solvent, dispersants and Zirconia balls. The binder and plasticizers were then added to the mixed slurry and this was mixed again for 24 hours. Numerous bubbles were generated due to the vapor pressure of the air and the solvent during the ball-milling process. Therefore, a rotary pump was operated at 50 rpm under stirring while the pressure was reduced. After the removal of the bubbles, the slurry was cast onto a green sheet using an automatic doctor blade (STC-14A, Hansung System Inc, Korea). The average thickness of the green sheet was 50 μm. After drying for 24 hours at room temperature, the green sheets were attached onto soda-lime glass substrates and were fired at 500°C. [7–8]

The particle size was measured by a particle size analyzer (LS230, Coulter Electronics Ltd., USA) after dispersal in ethanol. The morphology was observed by ESEM (XL-30 FEG, Philips, Netherlands). The tensile strength of the green sheets was measured using a universal testing machine (Instron 4465, UK). The optical transmittance of the dielectrics layer plasticized on the soda-lime glass substrate was measured by an UV/Visible spectrometer (Lambda19 UV/VIS/NIR, Bodenseewerk Perkin-Elmer Co., Germany). The surface roughness was observed by AFM (DI-3000, Veeco, USA). To confirm the dielectric breakdown of the transparent dielectric layer, a voltage-withstand tester (Digital W/I Tester 8502) was used.

Results and Discussion

SEM micrographs and the particle size distribution of the raw material as a function of the oil content are shown in Fig. 1. The particle size of the raw material was 348 nm, but it changed to 869 nm upon oil contamination at 0.1 wt%. The average particle size was increased approximately three-fold as the oil content increased due to the aggregation of the particles. Inhomogeneity of the particle size was observed upon contamination with oil. Therefore, homogeneously dispersed slurry is necessary to sustain the physical properties for use with a PDP because the particles of the raw material were aggregated by contamination with oil.

The dispersion stability of the slurry can be analyzed by observing the changes in the precipitation height and the precipitation viscosity. [5] Figure 2 shows the dispersion stability results of the transparent dielectric frit powders without a dispersant when the oil content was 0.1 wt%. When a dispersant was not used, the sedimentation rate was clearly dependent on the type of solvent. Particularly, in methanol, transparent dielectric frit powder with and without oil had the highest precipitation density, indicating the best dispersion ability among the solvents tested. In the order of water, acetone and ethanol, it showed faster sedimentation and a faster layer precipitation velocity. Therefore, ethanol, acetone and water are not suitable solvents in this system. It was concluded that the dispersion capability of the frit powder was the best in methanol, which exhibited the lowest precipitation height over a long period.

The polarizing phenomenon in the solid-liquid interface required dispersion stability of the powder, and a solvent having a lower dielectric constant than water suppresses the dissociation of the ionization material.

Figure 3 shows a comparison of the sedimentation height according to the type of dispersant in the methanol system. The dispersion stability of the frit powder with an oil content of 0.1 wt% was significantly changed according to the type of ionic dispersant or

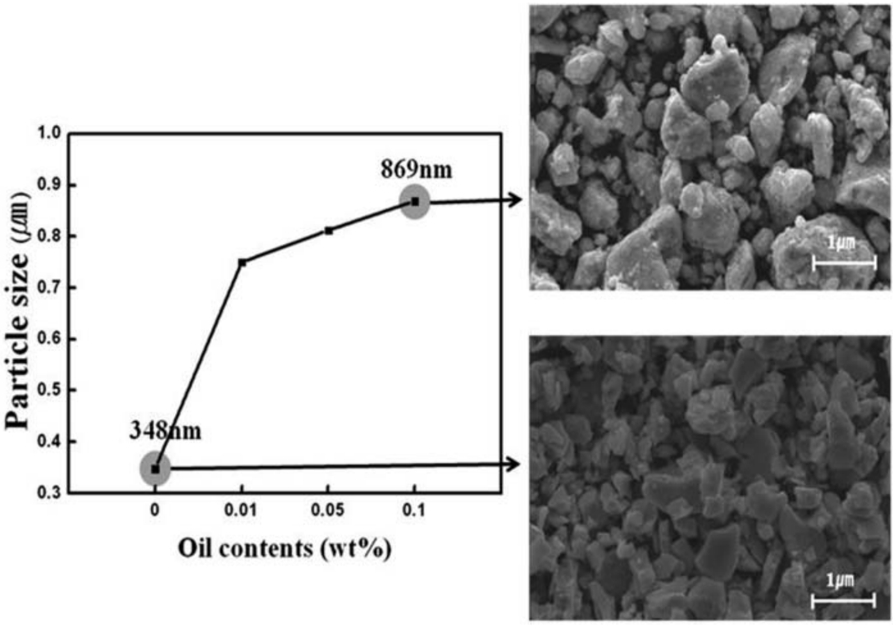

Figure 1. Average particle size and SEM images of the raw material as a function of oil contents.

polymeric dispersant used. When the frit powder was contaminated with oil, the dispersion stability was greatly reduced for the samples with ionic dispersants (Fig. 3(a)–(c)); however, there was less of an effect for the sample using a polymeric dispersant (Fig. 3(d)). The dispersion status was stabilized by the adsorption of the polymer on the surface of the particles. Therefore, the dispersants should be properly adsorbed for better dispersion. While the dispersion status is stably maintained, the precipitation speed of the frit particles slows, the precipitation density increases, and the precipitation height shrinks. Therefore,

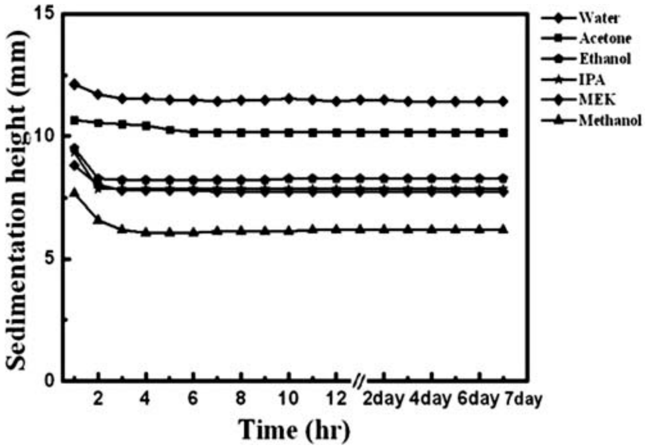

Figure 2. Sedimentation rate of the transparent frit powder containing oil of 0.1 wt% according to various solvents.

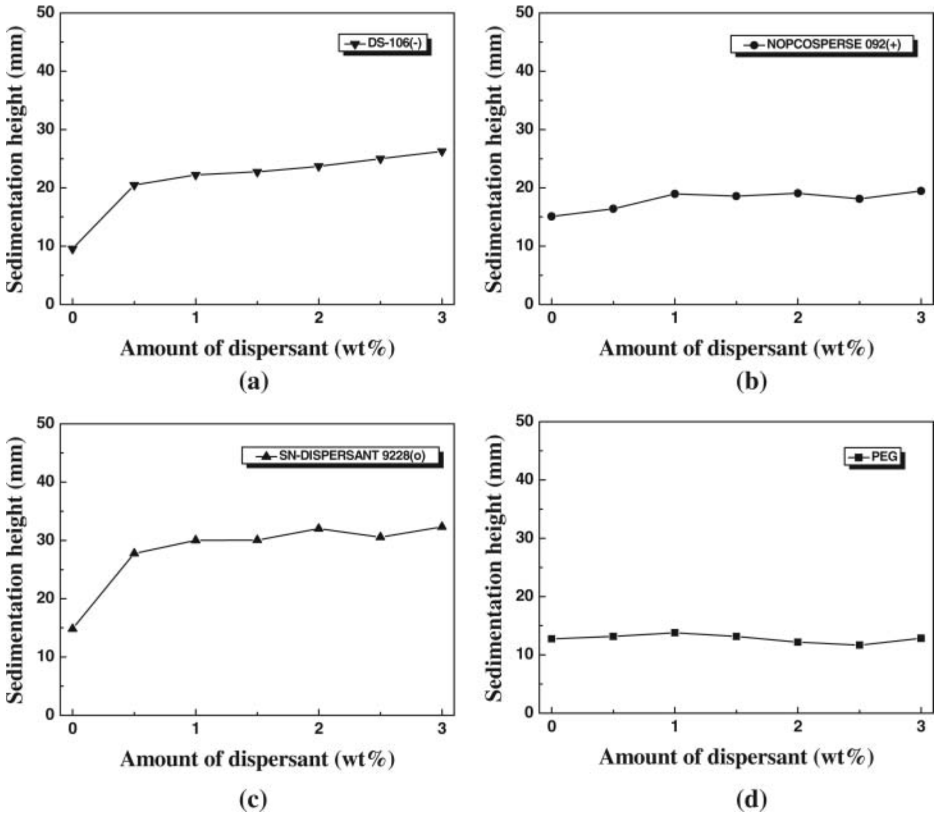

Figure 3. Sedimentation height of the frit powder containing oil of 0.1 wt% as a function of the amount of various dispersants.(solid loading: 33%): (a) NOPCOPLUS DS-106, (b) NOPCOSPERSE-092, (c) SN-DISPERSANT 9228 and (d) Polyethylene glycol.

the dispersion effect is greater with less dispersant and when the precipitation height is lower. The best dispersion result was noted when PEG was used as a polymeric dispersant in this system. There were no great differences, but an addition of PEG at 2.5 wt% showed a somewhat slow precipitation speed and the lowest precipitation height in both cases of oil contamination. In this case, the attractive force between the particles is decreased and the particles are easily stabilized when a polymeric dispersant is used. The minimum distance between the particles is increased by the physical force generated from the tangling of the polymer chains that form around the frit particles.

It was not sufficient to determine the dispersion efficiency by a precipitation test only. Therefore, a viscosity measurement according to the type of dispersant was conducted so that a more accurate dispersion effect could be identified.

Figure 4 shows the viscosity variation of the suspension liquid for the frit powder with 0.1 wt% oil as a function of the amount of dispersant. When an ionic dispersant was added, the viscosity of the suspension liquid increased considerably as the additive amount increased, which worsened the dispersion properties. When the polymeric dispersant PEG was added at amounts up to 3.0 wt%, however, the viscosity of the suspension liquid did not change, instead remaining nearly constant over the entire range. A dispersant that exists in macro-pores among the frit powder is typically not a homogeneous mixture. As the amount

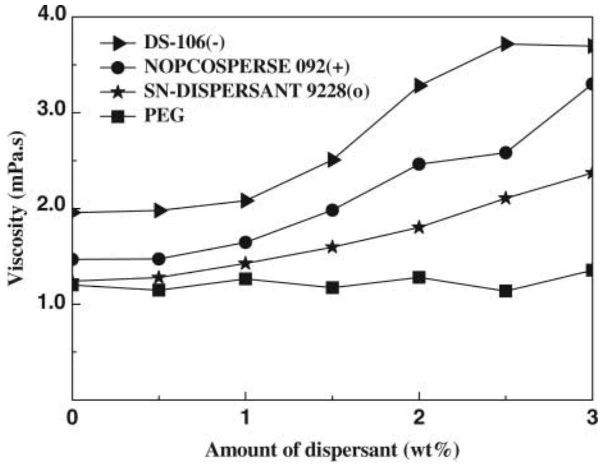

Figure 4. Viscosity of suspension liquid containing oil of 0.1 wt% as a function of the amount of various dispersants.

of dispersant is increased, the dispersant adsorbed on the surface of the frit powder easily aggregates. The agglomerated particles are separated by a repulsive steric stabilization mechanism.

SEM images of the surface and cross-sectional morphologies of the transparent dielectrics layer are shown in Fig. 5. A green sheet of transparent dielectrics with oil contamination manufactured by the doctor blade method was attached onto a soda-lime glass substrate and then heat-treated at 500°C. As the amount of oil was increased, the number of pores and defects also increased, even after firing. Although the pores completely disappeared via firing when the frit powder contained oil originally, this negatively affected the microstructure of the dielectric thin layer.

A partial list of the physical properties, including the transmittance, tensile strength and withstand voltage for the dielectric thin layers fired at 500°C as a function of the amount of oil contamination are shown in Table 1. At a standard wavelength of 550 nm, the transmittance was decreased from 81.4 to 70.2% as the oil content increased. In this case, the transmittance is degraded according to the small pores that form in the transparent dielectrics thick layer. Moreover, the frit powder contaminated with oil did not show greater dispersion when the slurry was created due to the aggregation of the frit particles. The tensile strength of the green sheet decreased as the oil quantity increased. The tensile strength was

Table 1. Some physical properties of the lead-free transparent dielectric layer as a function of oil contamination.

Oil contamination (wt%)	Transmittance (%)	Tensile strength (kg/cm^2)	Withstand voltage (kV)
0	81.4	6.54	1.6
0.01	76.9	6.47	1.57
0.05	71.7	6.27	1.56
0.1	70.2	6.01	1.53

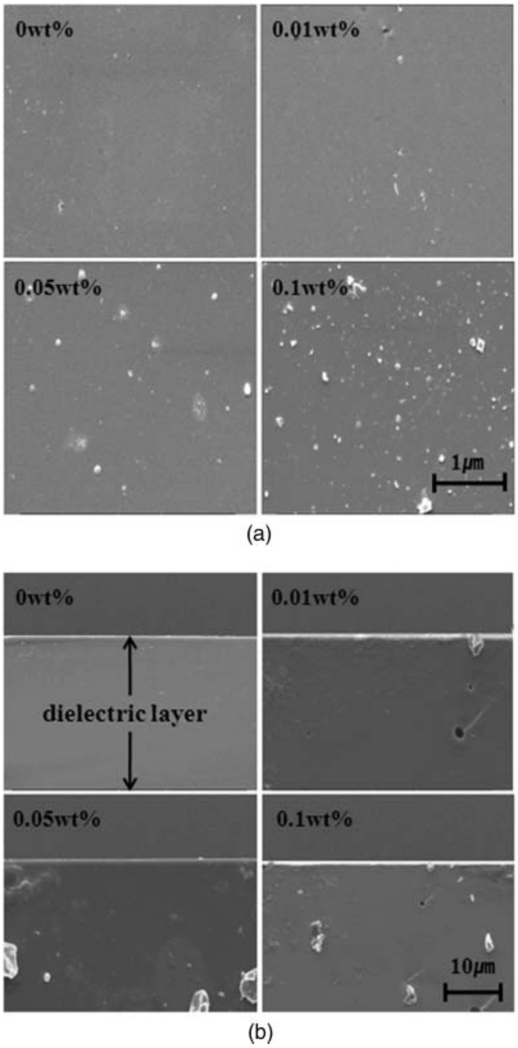

Figure 5. (a) Surface and (b) cross sectional SEM morphologies of the transparent dielectric layers fired at 500°C.

reduced due to microstructural inhomogeneity caused by the uneven precipitation between the dispersants and the frit powder. In this case, the slurry did not achieve a suitable dispersion in the beginning. The voltage-withstand characteristics were measured via DC voltage between upper and lower Ag electrodes. The thickness of the transparent dielectric layer was 30 μm. It was tested by increasing the voltage by 0.1 kV and holding at 60 sec for each voltage condition. Though the differences were small, the withstand voltage was also noted to decrease as the oil content increased. The pores formed from small particles can easily disappear during the firing process, even at the low temperature of 500°C, whereas the pores formed between large particles do not easily disappear upon the agglomeration of the particles. Therefore, more oil results in more pores in the layer, which reduces the strength and the withstand voltage.

Figure 6 shows an AFM photograph taken when the green sheet was adhered to the soda-lime glass substrate and plasticized at the low temperature of 500°C. The rms

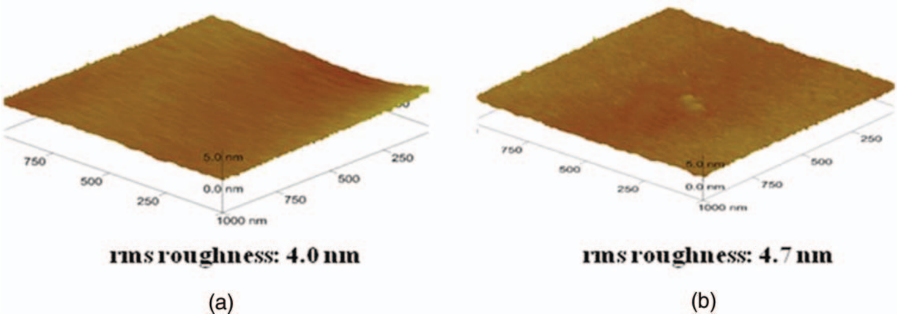

Figure 6. AFM images and rms roughness of the transparent dielectric layers fired at 500°C: (a) oil free (b) containing oil of 0.1 wt%.

roughness of the transparent dielectric layer without oil contamination was 4 nm, and it was a very flat surface. However, in contrast, the RMS roughness of the specimen with oil contamination of 0.1 wt% was 4.7 nm, which is slightly higher than that without oil. In addition, several open pores were clearly observed on the surface of the transparent lead-free dielectric thin layers.

Conclusions

Lead-free transparent dielectric frit easily became aggregated by contamination with oil, and this aggregation somewhat negatively affected the dispersion stability and physical properties. However, the optimization of the transparent dielectric thin layer at the low sintering temperature of 500°C was obtained through the use of PEG.

The dispersion stability and physical properties of the slurry can be controlled by adjusting the amounts of oil and the polymeric dispersant, PEG in this case. Methanol was a suitable solvent in the Bi_2O_3-ZnO-BaO-Al_2O_3 frit system with oil contamination. In this compositional system, the mechanism of steric stabilization was effective for optimum dispersion, which resulted in enhanced physical properties. As the oil contamination was increased, the pores and defects increased, even after firing.

The oil absorption into the frit powder affected several physical properties of the tensile strength of the green sheet, including the transmittance and withstand voltage of the fired dielectric thin layers, due to the pores that formed as a result of oil contamination.

To prevent oil pollution when grinding jet mill, only minimum amount of oil used in rotating the classifier wheel of the jet mill should be added. Also, blockage of air or other pollutant inflow is necessary when processing.

References

[1] K. Otsuka. Y. Ohsawa, K. Yamada, and K. Sekibat, *Yogyo-Kyokai-Shi*, **94**[3] 351–359 (1986)
[2] K. Otsuka. Y. Ohsawa, K. Yamada, and K. Sekibat, *Yogyo-Kyokai-Shi*, **94**[11] 1136–1141 (1986)
[3] K. Nagata, *J. Ceram. Soc. Jap.*, **100**[10] 1271–1175 (1992)
[4] A. Brewer, R. H. Moore, and J. S. Reed, *Am. Ceram. Soc. Bull.*, **60**[2], 212–6 (1931)
[5] D. J. Shanefield, pp. 211–254 in *Organic Additives and Ceramic Processing, Second edition with Applications in powder Metallurgy, Ink, and Paint, Ed. By* Kluwer Academic Publishers, (1999)
[6] R. E. Mistler, and E. R. Twiname, *Am. Ceram. Soc.* pp.24–36 Westerville, Ohio (2000)
[7] B-Y. Wang, D-S. Lim, and Y-J. Oh, *Mol. Cryst. Lig. Cryst.*, **514** 190/[518]–200/[528] (2009)
[8] Y-J. Oh, and J-W. Lee, *J. Ceram. Proce. Res.*, **10**[5] 657–663 (2009)