

Effects of rheological behavior of slurries on the characteristics of multilayer LED packages

Gui Nam Sun and Eung Soo Kim*

Department of Materials Engineering, Kyonggi University, Suwon 443-760, Korea

The rheological behaviours of $\text{CaMgSi}_2\text{O}_6$ with Al_2O_3 slurries prepared by a tape casting process were investigated as a function of the amount and composition of organic additives. The slurry formulations were optimised with the solvent type, dispersant content, total binder and plasticiser content and the ratio of binder to plasticiser. The tape casting slurries exhibited a typical shear-thinning behaviour. The density and tensile strength of the green tapes were affected by the rheological properties of the tape casting slurries. The thermal conductivity of the sintered sheets was dependent on the sintering temperature. This result is thought to be attributed to the increase of crystallite size of sintered sheets. Additionally, the thermal diffusivity and specific heat capacity of the sintered sheets were discussed with the relation to the sintering temperature.

Key words: Rheological behaviour, $\text{CaMgSi}_2\text{O}_6$, Tape casting method.

Introduction

Tape casting is a well-known process extensively used in manufacturing thin sheets of ceramic materials for various applications such as multilayer capacitors, ceramic substrates and packages [1]. The rheological behaviour of slurries is an important characteristic of a powder suspension for the tape casting process. To prepare uniform dense green tapes, the slurry should be a well-dispersed, homogeneous, stable system with low viscosity, good shear-thinning behaviour and high solid loading [2]. The properties of the green tape are reflected in the quality of the final product of the sintered sheet [3]. Therefore, the conditions of organic additives such as the solvent type, dispersant content and binder/plasticiser system should be optimised for practical application of multilayer packages.

For the packages applicable to high-power light emitting diodes (LEDs), the materials with high thermal conductivity should be investigated to dissipate heat effectively, because the heat generated by LED chips with high power tends to reduce light efficiency, durability and reliability of LEDs. However, most ceramics with high thermal conductivity required a sintering temperature above 1600 °C. Therefore, it is necessary to reduce the sintering temperature of materials which can be co-fired with metallic electrodes such as silver (960 °C) and copper (1050 °C) [4] for the application of LED multilayer devices. Diopside ($\text{CaMgSi}_2\text{O}_6$) shows high mechanical properties and

good chemical resistivity. The diopside glass from the processes of melting and quenching can be sintered at low temperatures, up to the temperature of co-fired with metallic electrode mentioned above.

Based on the preliminary works for the thermal conductivity of $\text{CaMgSi}_2\text{O}_6$ with Al_2O_3 content, the rheological behaviours of slurries for the $\text{CaMgSi}_2\text{O}_6$ with 4 vol.% Al_2O_3 glass powder are investigated in this study, as a function of amount and composition of organic additives. The tensile stress and strain of green tapes are also discussed with the rheological behaviours of slurries. The thermal properties of sintered sheets with optimal slurry condition are studied.

Experimental

Starting materials

The oxide powders of CaCO_3 (99%), MgCO_3 (99.9%) and SiO_2 (99.9%) were used as starting materials. The powders were prepared according to the desired composition $\text{CaMgSi}_2\text{O}_6$ and ground with ZrO_2 balls for 24 hrs in ethanol. The mixed powders were melted in a platinum crucible at 1500 °C for 5 hrs and quenched into the distilled water. The pure diopside glass frits were prepared via grinding and re-milled with $\alpha\text{-Al}_2\text{O}_3$ (4 vol.%) for 24 hrs.

For the mixture of $\text{CaMgSi}_2\text{O}_6$ with Al_2O_3 , solvent, dispersant, binder and plasticiser were used as the material system of slurry for the tape casting process. Several solvent systems, such as toluene/ethanol (Tol/EtOH), methylethylketone/ethanol (MEK/EtOH) and ethanol (EtOH) were tested. The azeotropic mixture was adapted to avoid the differential evaporation. The dispersant commonly used in tape casting such as

*Corresponding author:
Tel : +82-31-249-9764
Fax: +82-31-244-6300
E-mail: eskim@kyonggi.ac.kr

sorbitan monooleate span 80 was chosen in this study. For the preparation of tape casting slurry, poly vinyl butyral (PVB, BM-SZ, Sekisui, Japan) and butyl benzyl phthalate (BBP, santicizer 160, Ferro, USA) were used as binder and plasticiser, respectively.

Preparation of slurries and tape casting of green tapes

The preparation of the slurry was performed by considering the effect of the addition order of the slurry additives [5]. In order to avoid the competitive adsorption, the slurry was prepared by a two-step mixing procedure. In the first step, the powder, the solvent and the dispersant were mixed together by ball milling for 4 hrs. In the second step, the binder and plasticiser were added to the mixture by ball milling at a very low speed of 40 rpm for 24 hrs. After the mixing and the homogenisation of the slurry was completed, the slurry in the nylon jar was de-aired using a vacuum pump (pressure: 0.1 Mpa). Then the slurry is cast by the doctor blade method. The cast tape is dried at room temperature for 24 hrs to evaporated residual solvent.

Characterisations

The rheological behaviours of the slurries were determined using a rheometer (DV-III, Brookfield, LORCH, Germany). The tensile stress and strain of green tapes were tested by universal testing machine (UTM, Model 5543, Instron Co., USA) and the density of green and sintered sheet was measured by the Archimedes method. Powder X-ray diffraction analysis (XRD, D/Max-2500V/PC, Rigaku, Japan) was used to determine the crystallite size of specimens. The thermal properties of the sintered specimens are obtained by a laser flash apparatus (LFA 457, Netzsch, Germany).

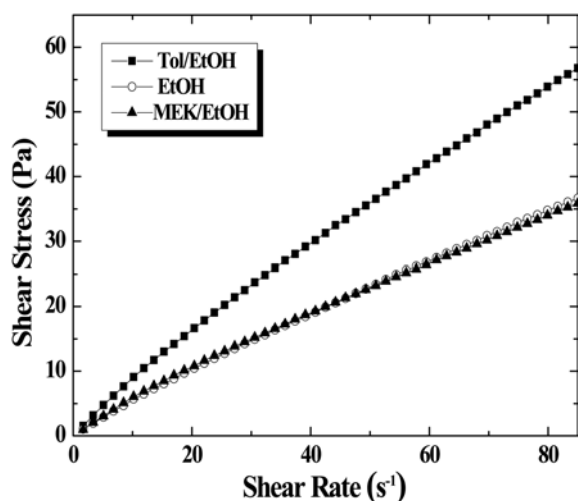


Fig. 1. Effect of solvent system content on the rheological behaviour of $\text{CaMgSi}_2\text{O}_6$ with Al_2O_3 (4 vol.%) slurries (dispersant : 1.25 wt.%, PVB : 11.2 wt.%, BBP : 4.8 wt.%).

Results and Discussion

Optimal condition of slurries

Viscosity control is well-known as an important factor in determining the optimal dispersion state of slurry. Fig. 1 shows the flow curves of $\text{CaMgSi}_2\text{O}_6$ with 4 vol.% Al_2O_3 (CMSA) slurry with different solvent system. Slopes of shear stress with shear rate are corresponded to the viscosity of slurries. All slurries display shear-thinning behaviour, which is described by Eq.(1) [6]:

$$\tau = k\gamma^n \quad (1)$$

where, τ is the shear stress, γ the shear rate, k a consistency factor and n the shear-thinning index. For shear-thinning suspensions, the value of n is less than 1. The shear-thinning behaviour is caused by the alignment of binder molecules at high shear rates. This behaviour is advantageous for the tape casting process, because the viscosity of slurry decreases with the slurry passes through the casting blade. After passing the blade, no shear force appears and the viscosity of the slurry increases again. The fast recovery to high viscosity preserves the homogeneous structure of the slurry by reducing the mobility of its constituents [3].

The maximum viscosity is shown in the slurry with Tol/EtOH solvent system. By contrast, the slurries prepared with MEK/EtOH and EtOH show lower viscosities. The component of the poly vinyl butyral (PVB) binder used in this study has the -OH group in its poly vinyl alcohol (PVA, 22%) part and -C=O group in its poly vinyl acetate (PVA, 4~6%) part. As known, the viscosity of the slurry is mainly affected by the solvent and binder used. If the solvent and the binder have similar functional groups, such as -OH, -C=O, in their molecules, they may exhibit similar polarity or have hydrogen bonds between their molecules,

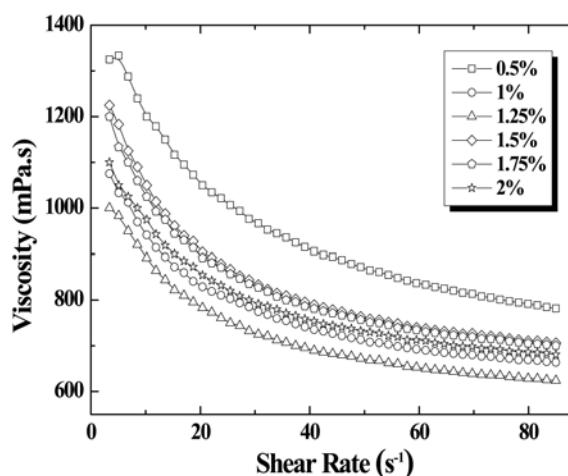


Fig. 2. Effect of dispersant content on the rheological behaviour of $\text{CaMgSi}_2\text{O}_6$ with Al_2O_3 (4 vol.%) slurries (solvent : 74 wt.%, PVB : 11.2 wt.%, BBP : 4.8 wt.%).

which promotes the dissolution of the binder in the solvent and decreases the viscosity of the slurry system. However, EtOH solvent system takes too long a time to dissolve the binder. According to these results, the MEK/EtOH is chosen as the best solvent for the CMSA slurries.

However, the further improvement can be achieved by changing the dispersant content to complete stabilisation. In order to determine the optimum dispersant content, viscosity values as a function of dispersant concentration from 0.5 wt.% to 2 wt.% of the CMSA powder are studied and shown in Fig. 2. With increasing dispersant content, viscosity of slurries is decreased up to 1.25 wt.% and then increased. This can prevent the agglomeration of the powder at a concentration of about 1.25 wt.%, at which the minimum viscosity is reached. As a result, a concentration of 1.25 wt.% referred to CMSA powder is selected as the optimum dispersant content for the preparation of stable slurries.

To investigate the effect of binder/plasticiser content on the stability of slurry systems, the rheological behaviours of the slurries are measured. Increasing the viscosity of a slurry with a binding system is the natural result. Therefore, the tensile stress and strain to failure of green tapes prepared from the above mentioned slurries are measured and shown in Fig. 3. The tensile stress and strain of green tape can be seen to increase up to 16 wt.% of the binding system and then decrease. The results of the tests at eight times exhibits the smallest value of errors at 16 wt.% of the binding system. This means that the tape state is better than other tapes. One of the most important roles of the polymer binder is to provide the tape with sufficient strength. As found, the small binder content with respect to the ceramic powder can not provide the green tape with sufficient strength to support the post handling, whereas the large binder content leads to high viscosity of the slurry and makes it much more difficult to obtain a homogeneous mixture. According to the above results, the optimum binder/plasticiser

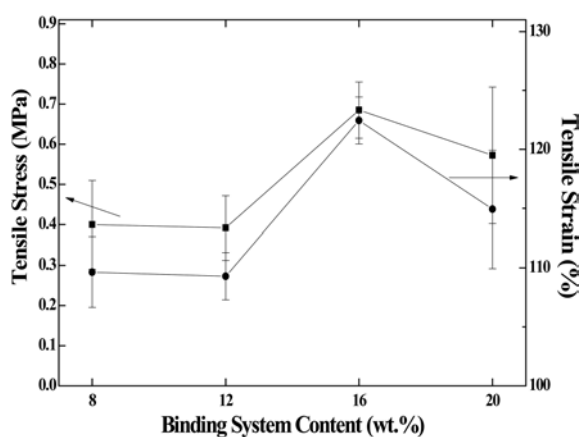


Fig. 3. Tensile stress and strain of $\text{CaMgSi}_2\text{O}_6$ with Al_2O_3 (4 vol.%) green tapes with binding system (PVB + BBP) content.

content is 16 wt.% of the CMSA powder for the preparation of stable slurries.

Fig. 4 shows the relative viscosity curves of the CMSA slurries with different ratios of binder to plasticiser by keeping the total content of binding system as constant. Different binding systems may exhibit different dispersive abilities in the slurries, which can be reflected by the relative viscosity of the slurry. The relative viscosity η_r [7] is measured by Eq.(2) :

$$\eta_r = \frac{\eta}{\eta_f} \quad (2)$$

where η_r is the relative viscosity, η is the viscosity of suspension and η_f is the viscosity of the fluid part only (not including CMSA powder). When the ratio of binder to plasticiser is 70 : 30 wt.%, the relative viscosity of the slurry is lowest and the optimum dispersion of the slurry is achieved. Compared with other slurries, the slurry containing this binding system shows the best rheological behaviour for the tape casting process.

Table 1 shows the bulk density of green sheet and sintered sheet with different ratios of binder to plasticiser. The green sheet with 70 PVB/30 BBP shows the higher value in comparison with other tapes, which indicates that a well-dispersed slurry produces a green sheet with higher density [8]. This is in line with the rheological behaviours (Fig. 4).

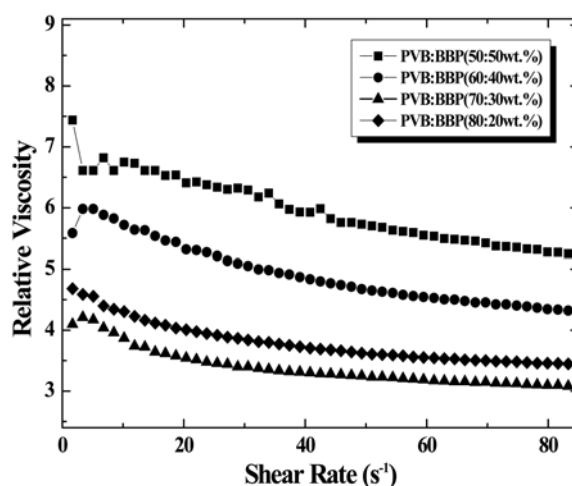


Fig. 4. Relative viscosity with the ratio of binder to plasticiser of $\text{CaMgSi}_2\text{O}_6$ with Al_2O_3 (4 vol.%) slurries.

Table 1. Bulk density of green and sintered sheets with different ratio of binder to plasticiser.

	Ratio of PVB to BBP (wt.%)	Green sheet	Sintered sheet		
			850 °C	900 °C	950 °C
Bulk density (g/cm ³)	50 : 50	1.756	2.969	2.972	2.976
	60 : 40	1.767	2.961	2.969	2.977
	70 : 30	1.807	2.973	2.976	2.981
	80 : 20	1.800	2.960	2.980	2.980

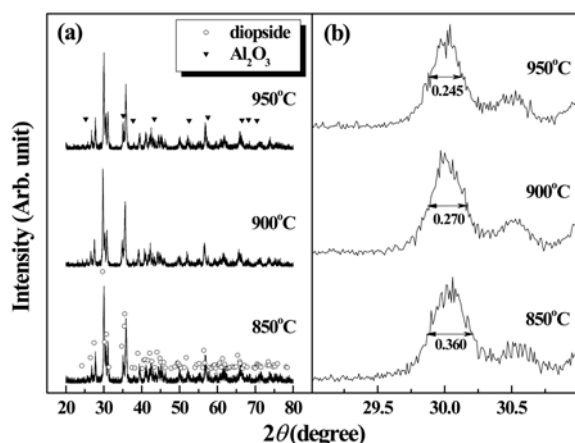


Fig. 5. XRD patterns of CaMgSi₂O₆ with Al₂O₃ (4 vol.%) sheets sintered from 850 °C to 950 °C for 3 hrs ((a) 2θ = 20–80°, (b) 2θ = 29.5–30.5°).

Table 2. Thermal properties of sintered sheet with different sintering temperature.

Sintering temperature (°C)	Cp (J/g/K)		Thermal diffusivity (mm ² /s)	
	Measurement temperature (°C)			
	25 °C	80 °C	25 °C	80 °C
850	0.772	0.851	1.371	1.190
900	0.774	0.851	1.446	1.260
950	0.753	0.831	1.541	1.347

Thermal properties of sintered sheet

Fig. 5 shows the XRD patterns of CaMgSi₂O₆ with 4 vol.% Al₂O₃ sheets sintered from 850 °C to 950 °C for 3 hrs. The monoclinic diopside (CaMgSi₂O₆) phase and rhombohedral α-Al₂O₃ phase are detected for the sheet with 4 vol.% Al₂O₃ through the entire range of sintering temperatures (Fig. 5(a)). The XRD patterns of sintered sheets are not changed remarkably with sintering temperature. Based on the XRD patterns of the sintered sheets, the reaction compounds between the CaMgSi₂O₆ and Al₂O₃ are not detected, which in turn means the chemical reactions between the CaMgSi₂O₆ and Al₂O₃ are not confirmed.

Thermal conductivity is dependent on crystallite size due to the amount of interface [9]. The crystallite size of sintered sheets can be estimated by the Scherrer equation [10]:

$$D = \frac{0.89\lambda}{\beta \cos \theta} \quad (3)$$

where D is crystallite size, λ is the wavelength of the CuK_α-radiation, β is the corrected full width at half-maximum and θ is the Bragg angle. The crystallite size of the sintered sheets is increased from 22.1 nm to 36.9 nm with increase of sintering temperature.

Table 2 shows the specific heat capacity and thermal diffusivity of CaMgSi₂O₆ with 4 vol.% Al₂O₃ sheets

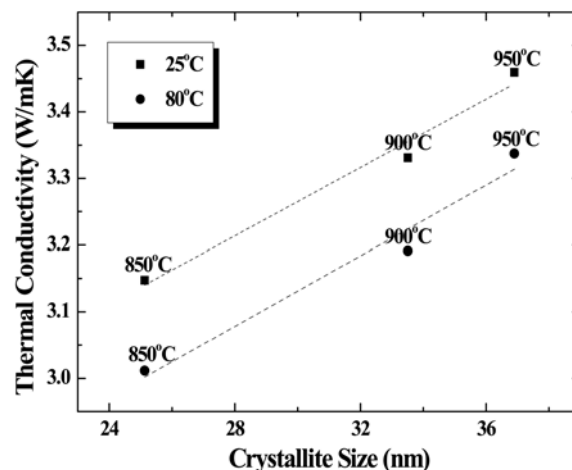


Fig. 6. Dependence of thermal conductivity on crystallite size of CaMgSi₂O₆ with Al₂O₃ (4 vol.%) sheets sintered from 850 °C to 950 °C for 3 hrs.

sintered from 850 °C to 950 °C for 3 hrs. The thermal diffusivity of the sheets is increased with the sintering temperature due to the above mentioned crystallite size of sintered sheets. However, the specific heat capacity of the sheets is nearly not changed. With an increase of measurement temperature, the specific heat capacity is increased, while the thermal diffusivity is decreased.

The dependences of the thermal conductivity on the crystallite size of CaMgSi₂O₆ with 4 vol.% Al₂O₃ sheets sinter from 850 °C to 950 °C for 3 hrs are shown in Fig. 6. With an increase of sintering temperature, the thermal conductivity of the sintered sheets is increased due to the increasing crystallite size of sintered sheets. This could be attributed to the decreased of interface area resulted from the increase of crystallite size. With an increase of measurement temperature, the thermal conductivity is decreased. Therefore, the heat dissipation efficiency is decreased when the environment temperature gets high.

Conclusions

In this study, the non-aqueous CaMgSi₂O₆ with 4 vol.% Al₂O₃ slurries for tape casting are optimised by their rheological behaviours and the thermal properties of the sintered sheets. Regarding the slurries, the best dispersion is achieved using an azeotropic mixture of MEK and EtOH as solvent, content of sorbitan monooleate span 80 as dispersant 1.25 wt.%, content of binding system 16 wt.% and binder/plasticiser ratio of 70 : 30 wt.%.

Thermal diffusivity and density of the sintered sheets prepared by the optimal slurry formulation is increased with sintering temperature from 850 °C to 950 °C. However, the specific heat capacity of the sheets is nearly not changed. As a result, the thermal conductivity of the sintered sheets is increased with sintering temperature due to the increase crystallite size of the sheets.

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