Viscous Flow Behavior of $(90-x)\text{SiO}_2\text{-}x\text{Na}_2\text{O-}10\text{RO}$ ($x = 15\text{-}40$) Glasses with Low Sintering Temperature

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ABSTRACT

Silicate glasses with varying SiO_2 and Na_2O contents were prepared and their viscous flow property at the elevated temperature was studied. When the glass powders were packed and sintered at 550°C to examine their feasibility as a low sintering temperature glass frit, contrary to expectations, glasses with lower SiO_2 content than 60 mol% showed no vitrification after sintering. High temperature microscopy revealed the viscous flow change of the silicate glasses with varying temperature and duration time and also indicated that the viscous flow was limited at low SiO_2 content. X-ray diffraction (XRD) on the sintered samples and Raman spectroscopy were carried out to shed light on the compositional dependency of viscous flow of silicate glasses.

Key words : Silicate, Glass, Glass frit, Viscosity

1. Introduction

Glasses with low sintering temperature have been used for display and energy applications such as cathode ray tubes (CRTs), plasma display panels (PDPs), active matrix organic light emitting diodes (AMOLEDs), and dye-sensitized solar cells (DSSC) as a sealing material.^{1,2)} PbO-based glass frit materials have been widely used but recently have been replaced by Bi_2O_3 or V_2O_5 based glasses due to RoHS (restriction of hazardous substances) regulations. Recently, glass frit materials have been also used in white light emitting diode (wLED) applications as a host matrix to embed inorganic phosphors.^{3,4)} Color converting phosphors are mixed with glass frit and sintered to form a phosphor in a glass (PiG) plate that is mounted on top of an InGaN-based chip to compose a wLED. Due to the enhanced chemical and thermal stability of the inorganic glass matrix compared to the color converter using organic resins, long-term stability of the wLED could be achieved and high brightness and high power applications such as automobile headlamps and outdoor lightings are also enabled.⁵⁻⁷⁾ Glasses for wLED application also have been used even for the thick film matrix to embed phosphors.^{8,9)}

Glasses for PiG applications should be transparent to avoid possible color deterioration and non-reactant to the phosphors. Moreover, it is highly important to employ a

suitable sintering temperature at which the phosphor materials can be stable without thermal degradation. For example, commercial red phosphor, $\text{CaAlSiN}_3\text{:Eu}^{2+}$ (CASN:Eu²⁺), can start to degrade above 550°C and significantly loses its emission intensity above 600°C , thus requiring glass frits with sintering temperature lower than 550°C .³⁾ Although various glass frit materials used for display applications have a sintering temperature lower than 500°C , they are not suitable for PiG applications due to their visible absorptions induced by glass forming elements based on transition metal ions such as V^{5+} and Bi^{3+} .

In order to develop a transparent glass with low sintering temperature, various silicate glasses have been studied. Lee *et al.*³⁾ employed a $\text{SiO}_2\text{-Na}_2\text{O-RO}$ ($\text{R}=\text{Ba}$ and Zn) system to demonstrate a PiG that can be sintered at 550°C for the first time. The feasibility of the $\text{SiO}_2\text{-B}_2\text{O}_3\text{-ZnO-Na}_2\text{O}$ as a PiG glass matrix to give a high color rendering index (CRI) and improved stability with sintering temperature lower than 550°C was also demonstrated.⁷⁾ Phospho-silicate glass based on $\text{SiO}_2\text{-P}_2\text{O}_5\text{-ZnO-B}_2\text{O}_3\text{-R}_2\text{O}$ ($\text{R}=\text{Na}$ and K) further lowered the sintering temperature to 500°C for PiG fabrication, allowing a high CRI and thermal stability.¹⁰⁾ Lower the sintering temperature to 400°C for PiG fabrication has been achieved with glasses containing heavy-metal oxides such as TeO_2 and Bi_2O_3 ¹¹⁻¹⁶⁾ but they suffered from visible absorption of the heavy metal ions, thereby deteriorating the PiG color converting properties. Recently, a $\text{SnF}_2\text{-SnO-P}_2\text{O}_5\text{-KF}$ glass with sintering temperature below 400°C was reported¹⁷⁾ but the glass has very weak chemical stability and cannot be utilized in practical applications.

Considering practical feasibility including chemical stability, visible transparency, and sintering temperature, silicate

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glasses are a reasonable candidate for PiG applications. Among them, the $\text{SiO}_2\text{-Na}_2\text{O-RO}$ ($\text{R}=\text{Ba}$ and Zn) glass system is a strong candidate due to its simple composition and relatively high stability against humidity while not containing B_2O_3 or P_2O_5 . Although it is crucial to understand the viscous flow properties upon temperature and compositional change to find a proper glass and sintering conditions for PiG applications, a systematic study on silicate glasses has not yet been reported. Thus, in this study, we varied SiO_2 and Na_2O contents and monitored the viscous flow change with temperature and duration time. Possible phase change upon heat treatment and structural variation with composition were investigated with X-ray diffraction (XRD) and Raman spectroscopy, respectively, and discussed in relation to the viscous flow of the glasses.

2. Experimental Procedure

The nominal composition of the glass was $(90-x)\text{SiO}_2 - x\text{Na}_2\text{O} - 10\text{RO}$ ($\text{R}=\text{Ba}$, Zn) (in mol%), where x was varied from 15 to 40. Glasses were labeled according to their SiO_2 content as SNR75 ($x=15$ mol%) to SNR50 ($x=40$ mol%). High purity ($> 3\text{N}$) raw materials of SiO_2 , Na_2CO_3 , BaCO_3 , and ZnO were weighed and mixed thoroughly by ball-milling for 1 h. The mixed powders were then melted in an alumina crucible at 1400°C for 1 h and the melt was quenched on a brass mold to obtain a glass that was annealed at 350°C for 1 h to remove thermal stresses. The as-prepared glasses were grounded into powders for further examinations. Thermal properties including glass transition temperature were measured via differential thermal analysis (DTA; SDT Q600, TA Instrument, United States). Viscous flow change of the glasses with temperature and time was monitored by a high temperature microscope (Misura(R) 3 HSM, TA Instruments, United States). An X-ray diffractometer (XRD; D/MAX-2500U, Rigaku, Tokyo, Japan) was used to monitor the phase change while Raman spectroscopy (SPEX 1403, HORIBA, Jobin-Yvon Ltd, Germany) using an Ar laser with a center wavelength of 514 nm for excitation was applied for structural investigation.

3. Results and Discussion

When glasses were synthesized, all compositions formed clear glasses, as shown in Fig. 1. In order to examine their possible sintering ability at 550°C , after being pulverized below 20 μm size, 4 g of glass powders was packed into a disk shape with 12 mm diameter and then heat treated at 550°C for 30 min. The heating rate was $3.3^\circ\text{C}/\text{min}$. As summarized in Fig. 1, glass with high content of SiO_2 (SNR75) did not show any indication of sintering and started to densify with increased content of Na_2O (SNR70; $x=20$ mol%). Vitrification due to viscous flow of the glass was observed from SNR65 ($x=25$ mol%). Considering the structural role of Na_2O within the glass network breaking Si-O-Si bonds, lower viscosity is expected along with decreased glass transition temperature, which is responsible for the sintering behavior change with Na_2O . However, it should be noted that further increase of the disk size was not observed even with an increase of Na_2O content above $x=25$ mol%. The glass powders with SiO_2 content lower than 65 mol% were densified but hardly vitrified. This sintering behavior of the glasses is not consistent with the conventional viscosity change with alkali oxides, thus implying that another mechanism may contribute to hindering the viscous flow of the glasses with higher content of Na_2O .

In order to clearly examine the viscous flow property of the glasses, the glasses were also inspected using a high temperature microscope. Fig. 2(a) shows the images of the glasses obtained with increasing temperature varying SiO_2 or Na_2O content. As shown in the figure, the temperature at which the glass started to show viscous flow decreases from 700°C to 600°C as the SiO_2 content decreases from 75 mol% ($x=15$) to 60 mol% ($x=30$) at a heating rate of $10^\circ\text{C}/\text{min}$. However, SNR55 ($x=35$ mol%) started to show viscous flow at 800°C and SNR50 did not show any viscous flow until it started to melt at 1000°C , further supporting the results obtained in Fig. 1. Dynamic viscous flow of the glasses with time were monitored at 650°C and the results are exhibited in Fig. 2. SNR75 showed no change while the glasses with lower SiO_2 showed a shape change with time. Structural modification and network breakages induced by the Na_2O

No.	SNR50	SNR55	SNR60	SNR65	SNR70	SNR75
Glass
Pellet
Notice	Densified	Densified	Densified	Vitrified	Densified	Densified

Fig. 1. Photos of alkali silicate glasses varying SiO_2 content as obtained and after sintering at 550°C for 30 min.

Fig. 2. High temperature microscope images of alkali silicate glasses varying (a) temperature with heating rate of 10°C/min and (b) time at fixed temperature of 650°C.

are mostly responsible for the change of the viscous flow property with compositional change. As observed in Fig. 2(a), a further decrease of SiO₂ content below 60 mol% did not show any shape change with time in spite of the increased non-bridging oxygens, thus implying the presence of other constraining factors for high alkali oxide containing glasses. However, it should be noted that SNR60 also hardly showed a change of its shape after the first viscous flow while SNR65 showed a shape change to a half sphere. This discrepancy between SNR65 and SNR60 can also be observed in Fig. 1. Thus, it seems reasonable that the viscous flow property of the present alkali-silicate glass started to be constrained from 60 mol% of SiO₂ in SNR glass.

Although the structural change of alkali-silicate glasses is well known, possible structural variation that can hinder the viscous flow at low SiO₂ in the present glass system was investigated with Raman spectroscopy. As displayed in Fig. 3, with increasing Na₂O content (decreasing SiO₂ content), Raman shifted peaks centered at ~554 and 944 cm⁻¹ increased and shifted to high frequency while peaks centered at ~775 and 1098 cm⁻¹ decreased and shifted to low frequency. As summarized in Table 1, peaks at ~554 and 944 cm⁻¹ are due to vibration modes of Si-O⁻ related to non-bridging oxygens while ~775 and 1098 cm⁻¹ can be attributed

Fig. 3. Raman spectra of alkali silicate glasses varying SiO₂ content.

to the vibration modes of Si-O-Si bonds. Thus, the characteristic structural change of alkali-silicate glass reducing network connectivity and viscosity was observed with increasing Na₂O content. However, noticeable structural variation in the glass network was not observed even in glasses with lower SiO₂ content than 60 mol% (x=30).

Table 1. Raman Peak Assignment of Alkali-silicate Glasses

Wavenumber (cm ⁻¹)	Raman assignment	Reference
580	Si-O ⁻ rocking motions in fully polymerized SiO ₂ (Q ⁴) units	18
600	Si-O-Si bending vibration in depolymerized structural units	18
700–850	Si-O-Si symmetric stretching of bridging oxygen between tetrahedra	18
970	Si-OH stretching mode	19
1083	SiO ₄ asymmetric stretching vibration	20, 21
1100	Si-O-Si asymmetric stretching	18

Fig. 4. DTA results of alkali silicate glasses varying SiO_2 content.

Thermal analysis has been employed to find a possible explanation for the viscous flow change. Fig. 4 shows DTA results obtained for alkali-silicate glasses between 200 to 800°C. As shown in the figure, the glass transition temperature (T_g) decreased with a decrease of SiO_2 content. The decrease of T_g with increasing Na_2O content (decreasing SiO_2 content) is due to the network breaking role of Na_2O , further supporting the Raman results. However, it should

be noted that a small crystallization peak evolves from 60 mol% of SiO_2 and the crystallization temperature (T_x) also decreases with SiO_2 content. This implies that the glass can be crystallized upon heat treatment above T_x and thus the viscous flow can be impeded by the crystals within the glass matrix.

Crystallization of the glass before and after the heat treatment was examined with XRD and the results are depicted in Fig. 5. As shown in Fig. 5(a), all glasses showed characteristic diffuse patterns and no crystalline peaks were observed before heat treatment. However, SNR60 showed evolution of the small crystalline peaks, which implied possible crystallization within the glass matrix. Crystallization of the glasses was clearly identified after they were heat treated at 550°C for 30 min. As found in Fig. 5(b), glasses with higher content of SiO_2 than 60 mol% showed no crystalline peaks, thus suggesting their glass stability. However, glasses with lower content of SiO_2 than 60 mol% presented crystalline peaks with intensity that increased with increasing Na_2O content. Crystalline peaks were matched to Na_2SiO_3 and $\text{Na}_2\text{Si}_2\text{O}_5$. As found in Fig. 4, the crystalline peak started to appear in the thermal analysis from SNR60.

Based on the DTA and XRD results, it is reasonable to assume that the viscous flow of the SNR glasses can be impeded by crystalline phases when the SiO_2 content is lower than 60 mol%. As exhibited in Fig. 2(a), SNR60 started to show viscous flow at lower temperature than SNR65, because it has weaker network connectivity and thus has lower viscosity, resulting in a lower starting temperature than SNR65. However, crystallization of Na_2SiO_3 and $\text{Na}_2\text{Si}_2\text{O}_5$ phases also started from SNR60 and hindered the viscous flow. This can be clearly observed in Fig. 2(b). Although edge rounding started earlier in SNR60 than in SNR65, further development of the shape due to viscous flow was limited while SNR65 showed continuous flow with time evolution. This can also explain the vitrification behavior observed in Fig. 1 for the sample sintered at 550°C.

Fig. 5. XRD result of alkali silicate glasses varying SiO_2 content (a) as obtained and (b) after heat treatment at 550°C for 30 min.

Glasses with higher SiO₂ content showed no sintering due to their high viscosity while glasses with lower SiO₂ showed no vitrification due to the crystallization during the heat treatment.

In order to be used for a transparent glass frits to embed phosphors, crystallization of glasses should be avoided to ensure viscous flow and reduce additional scattering centers within the PiG plate. Thus, although low content of SiO₂ or Na₂O is preferred to reduce the sintering temperature and viscosity of glasses, the glass composition should be carefully compromised to avoid possible crystalline phases during the sintering process.

4. Conclusions

Alkali-silicate glasses with a composition of (90-x) SiO₂ - x Na₂O - 10RO (R=Ba, Zn) (in mol%) were synthesized with varying x content from 15 to 40 mol% and their sintering behavior was examined for transparent glass frit application with low sintering temperature. When the glass powders were sintered at 550°C for 30 min., glasses with SiO₂ content lower than 60 mol% showed no viscous flow in spite of their weak glass connectivity. High temperature microscope images obtained under varying temperature and time also showed the limited viscous flow at lower SiO₂ content. Raman spectroscopy showed continuous structural modification with Na₂O content. However, thermal analysis revealed a crystallization peak evolving at lower SiO₂ content and Na₂SiO₃ and Na₂Si₂O₅ crystalline phases were identified with XRD after heat treatment. Crystallization within the glass matrix at lower SiO₂ content was considered to impede the viscous flow and to be responsible for the sintering property of the glasses. When seeking a proper glass composition with low sintering temperature for PiG application, careful design of the glass composition considering possible crystallization as well as the viscosity of the glass matrix is necessary.

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