Evaluation of Critical Cooling Rate for $30\text{Na}_2\text{O} \cdot 10\text{MgO} \cdot 60\text{SiO}_2$ Glass Based on Viscosity

Shigeki SAKAGUCHI and Shin-ichi TODOROKI

NTT Opto-Electronics Laboratories, 162, Shirakata-Shirane, Tokai-mura, Naka-gun, Ibaraki 319-11

$30\text{Na}_2\text{O} \cdot 10\text{MgO} \cdot 60\text{SiO}_2$ ガラスの粘性による臨界冷却速度の評価

坂口茂樹・轟 眞市

NTT 光エレクトロニクス研究所, 319-11 茨城県那珂郡東海村白方白根 162

The critical cooling rate for $30\text{Na}_2\text{O} \cdot 10\text{MgO} \cdot 60\text{SiO}_2$ glass, which exhibits low Rayleigh scattering, was evaluated based on viscosity. To this end, the viscosity and thermal expansion coefficient of this glass were measured using a thermomechanical analyzer. The beam bending and parallel plate methods were effective in measuring the viscosities in the range of interest of higher than 10^4 dPa·s. The critical cooling rate was determined as the cooling rate at which the density of the glass melt became identical to that of solid glass at the glass transition temperature when the melt was cooled from the liquidus to the glass transition temperature. The obtained value for this glass was $2.6^\circ\text{C}/\text{min}$.

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1. Introduction

Recent efforts to develop glass materials intended for optical fibers with lower transmission loss than current silica fibers seem to be directed to the development of oxide glasses with low light scattering (Rayleigh scattering) rather than non-oxide glasses with low infrared absorption. Several glass systems, such as $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (NAS) and $\text{BaO}-\text{Ga}_2\text{O}_3-\text{GeO}_2$ (BGG), have been recognized as potential materials.¹⁾⁻³⁾ The authors have recently revealed that $\text{Na}_2\text{O}-\text{MgO}-\text{SiO}_2$ (NMS) glass is also very attracting.⁴⁾ The NMS glass not only exhibits low Rayleigh scattering with a magnitude similar to that of NAS but also seems to be more thermally stable.⁴⁾ In order to realize optical fibers, these glasses must be thermally stable as regards crystallization during fiber fabrication process, since even a slight occurrence results in a fatal loss increase due to scattering.⁵⁾ Therefore, it is important to evaluate the thermal stability for the glass under consideration.

The critical cooling rate (R_c), which is the minimum cooling rate at which a glass melt is frozen into solid glass without crystallization when it is cooled from the liquidus temperature, is a useful measure to evaluate thermal stability. This is because the thermal stability is related to glass-forming ability which is often evaluated by R_c .⁶⁾ R_c is generally determined based on nucleation and growth properties which are reflected in the time-temperature-transformation (TTT) diagram.⁷⁾ Since it is time-consuming to obtain the nucleation and growth data and/or the TTT diagram, an evaluation method based on the glass melt viscosity has been proposed by Sakaguchi.⁸⁾

The viscosity model is based on the idea that crystallization in a glass melt is dominated by viscosity during undercooling. According to this model, R_c is given as the cooling rate at which the density of the melt at glass transition temperature (T_g) agrees with that of corresponding solid glass. The validity of this model is given by R_c evaluation for SiO_2 and GeO_2 , in which R_c values for these glasses close to those reported are obtained. In addition, it is rather easy to obtain viscosity and thermal expansion properties compared with measuring nucleation and growth rates.

The viscosity of an undercooled glass melt in the liquidus to glass transition temperature range is generally higher than 10^4 dPa·s up to 10^{13} dPa·s. Although there are many measurement methods, no single method can provide the viscosities of this wide range. The beam bending and parallel plate methods seem to be useful for measuring viscosities in this range, because both methods can be performed using a commercially available thermo-mechanical analyzer (TMA).^{9),10)} The former method allows the measurement of viscosities higher than 10^8 dPa·s, and the latter is effective for mid-range viscosities of around the softening temperature.

This report demonstrates the evaluation of R_c for $30\text{Na}_2\text{O} \cdot 10\text{MgO} \cdot 60\text{SiO}_2$ (NMS316) glass based on the viscosity model. To this end, the viscosity was measured by the beam bending and parallel plate methods and the thermal expansion coefficient was also measured using a TMA. In addition, we discuss the thermodynamic aspects of evaluating R_c based on viscosity.

2. Experimental

2.1 Measurements

The glass samples were prepared using reagent grade SiO₂, MgO and Na₂CO₃ powders. They were weighed and mixed to obtain 60 g batches with the desired composition. The mixtures were melted at 1400°C for 1h and cast into a cylindrical brass mold heated at 350°C to form rods with approximately 12 mm in diameter and 60 mm in length. They were annealed for 1h at 400°C, which was chosen based on glass transition temperature (T_g : 454±6°C).

The glass viscosity was measured by the beam bending and parallel plate methods, using a commercially available TMA. With the beam bending method, the viscosity is calculated by⁹⁾

$$\eta = \frac{gL^3}{I_{cv}} \left(M + \frac{\delta AL}{1.6} \right) \quad (1)$$

where η is the viscosity (Pa·s), g is the acceleration on gravity (m/s²), L is the span of the specimen (m), M is the applied load (kg), δ is the density of the glass (kg/m³), A is the cross-sectional area (m²), I_c is the moment of inertia (m⁴), and v is the deflection rate (m/s). Specimens with 13 mm in length, 5 mm in width and thickness varying from 0.6 to 2.6 mm were prepared from the rods.

With the parallel plate method, the viscosity is given by¹⁰⁾

$$\eta = \frac{2\pi MgH^3}{3Vv(2\pi H^3 + V)} \quad (2)$$

where H is the height of the cylindrical specimen and V is the specimen volume. Specimens with 6 mm in diameter and 15 mm in length were prepared from the rods.

The thermal expansion coefficient was also measured using a TMA. The specimens were the same as those used for the parallel plate method.

2.2 Evaluation of R_c

R_c is evaluated based on the viscosity model.⁸⁾ Under continuous cooling condition given by

$$T = T_m - Rt \quad (3)$$

where T is the temperature, T_m is the liquidus temperature, R is the cooling rate and t is the time, the density change in the glass melt of unit volume is represented by

$$\dot{\rho} = \frac{3\gamma}{2\eta} \left(\frac{3}{4\pi} \right)^{-1/3} \rho^{1/3} (1-\rho)^{2/3} \{1 + (1-\rho)^{1/3}\} \quad (4)$$

where ρ is the reduced density and γ is the surface tension. When the melt is cooled to T_g , the ρ value varies with R through η which is a function of T . R_c is given by the R value at which ρ agrees with ρ_g , which represents the density of corresponding solid glass at T_g , given by

$$\rho_g = 1/\exp\{3\alpha(T_g - T_1)\} \quad (5)$$

where α is the thermal expansion coefficient and T_1 is room temperature. The initial density of the melt

at T_m is given by

$$\rho_0 = 1/\exp\{3\alpha(T_g - T_1) + 3\alpha_1(T_m - T_g)\} \quad (6)$$

where α_1 is the thermal expansion coefficient of the melt. Since the ratio $\alpha_1 : \alpha$ is related to Poisson's ratio which varies little for silicate glasses,¹¹⁾ α_1 is assumed as $\alpha_1 = 3\alpha$.¹²⁾ The calculation is performed using a finite difference approximation.

3. Results

Figure 1 shows the plots of viscosity for NMS316 glass. A viscosity of 10⁷–10¹⁰ dPa·s is obtained by the beam bending method in the temperature range of 480–580°C. By the parallel plate method, a viscosity of 10⁴–10⁸ dPa·s is obtained in the temperature range of 550–730°C. In the figure, the published data¹³⁾ are also presented for comparison.

The viscosity data in the range higher than 10⁵ dPa·s agree well with the published data. However, the viscosity deviates slightly from the previous data in the 10⁴ dPa·s range. In the viscosity range measured in the present experiment, $\log \eta$ exhibits a linear relation to $1/T$, represented by

$$\log \eta = -15.724 + 19806/T.$$

Fig. 1. Plots of viscosity for 30Na₂O·10MgO·60SiO₂ glass obtained by the beam bending and parallel plate methods. The published data¹⁴⁾ are also shown.

Fig. 2. Plots of calculated density versus cooling rate during cooling from 730 to 460°C for 30Na₂O·10MgO·60SiO₂ melt. The curve is drawn to connect the calculated data smoothly.

The thermal expansion coefficient obtained in the temperature range of 40–450°C varies from 1.04 – $1.59 \times 10^{-5} \text{ K}^{-1}$. This value is in good agreement with published data.¹⁴⁾

Based on these measured properties, R_c is evaluated. Figure 2 shows the plot of the reduced density at T_g versus the cooling rate. Numericals used are 1.4×10^{-5} for α and 0.35 N/m for γ .¹⁵⁾ The liquidus temperature is assumed to be 730°C.¹⁶⁾ The R_c value of 2.6°C/min is obtained.

4. Discussion

The evaluation of R_c based on the viscosity of an undercooled glass melt is derived from the fact that crystallization during melt cooling is dominated by melt viscosity. This viscosity model is illustrated in Fig. 3. The model glass melt is composed of an incompressible viscous fluid and a cavity which is introduced to compensate thermal expansion. In this model, the glass melt is assumed to undergo viscous flow during cooling, since the melt must shrink due to thermal expansion with decreased temperature, as shown in Fig. 3. R_c is given as the cooling rate at which the density of the melt agrees with the density of the corresponding solid glass at T_g .

To consider this model from the viewpoint of thermodynamics, R_c is given as the cooling rate at which the energy dissipation due to viscous flow during melt cooling is maximized. The Gibbs function for the melt is given by¹⁷⁾

$$dG = dQ + dW + d(pV) - d(TS) \quad (7)$$

where Q is heat, W is non-expansion work, p is pressure and S is entropy. When the melt is cooled from the liquidus to the glass transition temperature, the melt is undercooled. In this cooling process, the melt is kept in an equilibrium condition,¹⁸⁾ i.e., $dQ = d(TS)$. When $dG = 0$, the maximum work is made. Then, the following equation is obtained from Eq. (7), for the melt cooling process;

$$-\int dW = \int p dV \quad (8)$$

assuming that the pressure is constant. The work,

Fig. 3. Schematic illustration of the viscosity model. The model glass melt is assumed to contain a cavity induced by thermal expansion in the center of incompressible viscous fluid. Since the cavity decreases in volume due to thermal expansion when it is cooled, the fluid undergoes viscous flow.

the left-hand term in Eq. (8), is made against the sur-

roundings as $-\int dW = p_{\text{ex}} \int dV$, where p_{ex} is the ex-

ternal pressure (see Fig. 3). Since $dV = -(V/\delta)d\delta$, the work is represented as $(-p_{\text{ex}})(V/\delta)d\delta$. On the other hand, the right-hand term in Eq. (8) is represented as $p\beta V dT$, using $\beta = (1/V)dV/dT$, where β is the volume expansion coefficient and is given by $\beta = 3\alpha$. If we assume that $p_{\text{ex}} = p$, when the melt is cooled from the liquidus temperature to T , Eq. (8) becomes

$$-\int_{\delta_0}^{\delta} \frac{d\delta}{\delta} = \int_{T_m}^T \beta dT \quad (9)$$

where δ_0 is the density at T_m . Finally,

$$\delta_0 = \delta / \exp\{\beta(T_m - T)\} \quad (10)$$

This density δ has a physical meaning when the melt is cooled at R_c . Since the reduced density ρ is represented by δ/δ_1 where δ_1 is the density of the

fluid (Fig. 3), ρ given by $\rho = \int_0^t \dot{\rho} dt$ under a continu-

ous cooling condition using Eq. (4), has a physical meaning when the melt is cooled at R_c .

As described above, physical meaning in terms of thermodynamics is given to the evaluation based on viscosity. In other words, R_c is given as a unique value as long as the thermal expansion coefficient and the viscosity on which this model is based are uniquely (in the sense of equilibrium condition) offered. In addition, the evaluation of R_c based on this viscosity model does not depend on nucleation and growth properties at all. In this respect, the viscosity model for evaluating R_c is quite unique.

The viscosity of NMS316 glass is represented by the Vogel-Fulcher form as $\log \eta = -0.48473 + 2547.5/(T - 528.8)$ with η in $\text{dPa}\cdot\text{s}$ and T in K based on the published data.¹³⁾ In the present study, the viscosity is measured in the range of 10^4 – $10^{10} \text{ dPa}\cdot\text{s}$. Although slight differences are recognized in the low viscosity range around $10^4 \text{ dPa}\cdot\text{s}$, the measured viscosity is in a good agreement with published data for the mid to high viscosity range. This result indicates that the measurement methods adopted in the present study can offer the valid values over a wide range from mid to high viscosity needed for evaluating R_c .

In the present measurement, a linear relation is obtained between $\log \eta$ and $1/T$ in the viscosity region above $10^5 \text{ dPa}\cdot\text{s}$. Since such an Arrhenius-type behavior in viscosity is an important property to represent that the glass is "strong",¹⁹⁾ this result seems to indicate that the thermal stability of the present glass is high. The obtained R_c value of 2.6°C/min is close to that of $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ glass.²⁰⁾

5. Conclusion

In order to evaluate the critical cooling rate of

30Na₂O·10MgO·60SiO₂ glass, its viscosity is measured by the beam bending and parallel plate methods. A linear relation to T^{-1} is obtained as $\log \eta = a + b/T$ for the temperature range of 480–730°C. The measured thermal expansion coefficient is $1.4 \times 10^{-5} T^{-1}$. Using these values, we evaluate the critical cooling rate of this glass to be 2.6°C/min.

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