Combinatorial evaluation system for thermal properties of glass materials using a vertical furnace with temperature gradient

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Abstract

Critical cooling rate Q for zinc tellurite glass system is determined based on the time-temperature-transfer (T-T-T) diagrams, which are compiled by analyzing the crystallized area in the glass sample libraries annealed simultaneously by a furnace with temperature gradient. This method reduces the laborious routine work for preparation, which is needed in the conventional method. Since the surface/volume ratio of the present samples is large, their crystallization is mainly governed by heterogeneous nucleation. Thus, the Q values in this study can be used as a practical index for the glass products whose surface should be free of being ground and/or polished, such as fire-polished lenses, optical fibers and waveguides.

Key words: glass, crystallization tendency, critical cooling rate, time-temperature-transfer diagram
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1 Introduction

The methodology known as combinatorial chemistry has been widely used in the field of organic chemistry such as medicine to bring about fruitful results in its research and development. Recently, it is shown that this method is also applicable to the R & D of inorganic materials and devices whose form is thin film(See other articles in this volume). This paper reports about an expansion of this applicability into hot melt processes which are typical and important in glass industry.

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Evaluation of crystallization tendency of glass materials is important for manufacturing optical device such as optical fiber and waveguide, because the precipitates act as a origin of light scattering and fracture. The most quantitative information for this is obtained by T-T-T(time-temperature-transform) diagram, which shows the annealing temperature dependence of the time to precipitate(See the bottom of Fig. 1). This diagram shows how fast the melt should be quenched to avoid crystallization, but it needs laborious work to make a single diagram. The process is illustrated in the upper left of Fig. 1. In order to simplify the making process of T-T-T diagram, we propose an alternative method using a special furnace for making glass sample libraries and performing successive heat treatment under temperature gradient.

2 Experimental

Zinc tellurite glass melt (xTeO$_2$-(100$-x$)ZnO, x=90$\sim$65 mol%) in a Pt crucible is mounted at the bottom of the furnace where the temperature is kept at 800°C. A Pyrex glass capillary (75cm × 8mm OD × 1.5mm ID) is inserted into the furnace from the top so as to be heated under a temperature gradient of $800 \sim 300$°C in 50cm-span. The glass melt is sucked into the capillary by a vacuum pomp connected with the top of the capillary. The melt stops rising within 1 sec. because its temperature decreases and its viscosity increases along the pipe. After a heat treatment for the prescribed time (50 $\sim$ 4000 sec), the capillary is pulled out at a fixed speed and crystallization area is determined by eye.

The temperature profile inside the furnace is determined by using a thermo-couple mounted inside the glass capillary. The change of the temperature inside the pipe during pulling out is also recorded.

3 Results

The glass inside the capillary includes some bubbles and fractures due to a shrinkage during the quenching of the glass melt whose expansion coefficient is larger than that of outer Pyrex glass. No library is broken, however, because the pipe wall is thick enough. White crystallization area is clearly determined as a function of annealing temperature which is shown as closed rectangles in Fig. 2.

Sometimes it is observed that any devitrification does not occur even after the time when crystallized sample is once obtained. In such a case, re-examination is performed whether it crystallized accidentally or not. The accidental crystallization area is shown as open rectangles in Fig. 2.

Critical cooling rate, Q, is given as the slope of the line connecting between the point of melting state (t=0 sec, T=800 °C) and the nose of crystallization area, that is, the earliest point when crystallization is observed. Determined Q values are printed in Fig. 2 and plotted in the phase diagram of TeO_2-ZnO system[1] shown in Fig. 3 ($\triangle$, $\bullet$ and $\bigtriangledown$). The temperature variation at the bottom of the capillary during pulling out from the furnace is also shown as a curve in the Fig. 2. The quenching rate for this is about 2.0 K/s. Thus, the melt cannot be quenched at the rate faster than 2.0 K/s. For the samples of x=60, 85 and 90, Q is expected to be larger than 2.0 K/s ($\triangle$ in Fig. 3) because some crystallization is observed within 50s. For x=65 and 70, Q is to be smaller than 0.1 K/s (=400K/4000s) because precipitation does not occur even after 4000s annealing ($\bigtriangledown$ in Fig. 3).

4 Discussion

Crystalline phase appears via nucleation and growth processes. The temperature where the nucleation rate (between T_{g} and T_{x}) is maximized is, in general, lower than that where the growth rate is maximized ($\sim T_{\mathrm{x}}$). Thus, the quenched glass inside the capillary is exposed to the crystal growth temperature range before staying the nucleation temperature range. This means that the present method can exclude the chance to nucleate before annealing, which is inevitably included in the sample preparation of the conventional method. (Compare the thermal history in both methods as shown in the middle of Fig. 1).

Once crystallization occurs, the precipitated area seems to move as increasing the annealing time shown in Fig. 2. On the ground that the nucleation of super-cooled liquid is a phenomenon of non-equilibrium state, there is not enough time and volume to distribute nuclei uniformly in the glass, that is, the time for nucleation is eliminated to a short time during a quenching period to the the annealing temperature just after the suction, and the volume of the sample is also eliminated to 1.5 mmϕ. In addition, fractures and bubbles in the glass distribute randomly along the length, which are the main origin of heterogeneous nucleation. Thus, the determination of transfered area in T-T-T diagram needs to be cautious to reach statistically adequate. In this study, the nose of crystallization area is determined after examining several trials of same (or longer) annealing period in order to confirm it.

It is possible to examine the validity of Q of the present study by comparing the glass forming region determined before. A compositional dependence of critical cooling rate Q is roughly given as a cooling rate dependence of glass forming region, that is, a curve connecting the edges of the regions for different cooling rate. As shown in Fig. 3, Q values given by the present method($\triangle$, $\bullet$ and $\bigtriangledown$) is different from that estimated from their glass forming regions ($\ast$, $\times$ and $+$)[2]. This is because of the difference in mechanism of crystallization observed in these methods.

In Bürger's work, the glass forming region is determined by casting 100g batch of melt into copper or graphite moulds. Because of the large size of the samples, their surface is quenched faster than the inner, which bring about noticeable error in the corresponding cooling rates. At the same time, any surface crystallization is suppressed due to the faster quenching of the surface. On the other hand, the size of our samples is about 2 orders smaller than Bürger's, so the surface/volume ratio is also larger and the temperature difference between their surface and inside is small. This means the crystallization of our samples is governed mainly by heterogeneous nucleation compared with the Bürger's. In general, activation energy of heterogeneous nucleation is lower than that of homogeneous nucleation. Therefore it is reasonable that critical cooling rate of our samples is larger than that of Bürger's.

It is concluded that the Q values obtained by the present method is closely related with surface crystallization and, thus, provides useful information for the glass products fabricated without grinding and polishing, such as fire-polished lens, optical fibers and waveguides.

5 Conclusion

Parallel annealing of long glass samples performed by the vertical ring furnace with temperature gradient is useful for reducing the work required for making T-T-T diagrams. Since the crystallization occurred in the samples is governed by heterogeneous nucleation, this method provides unique and important information for the glass industry.

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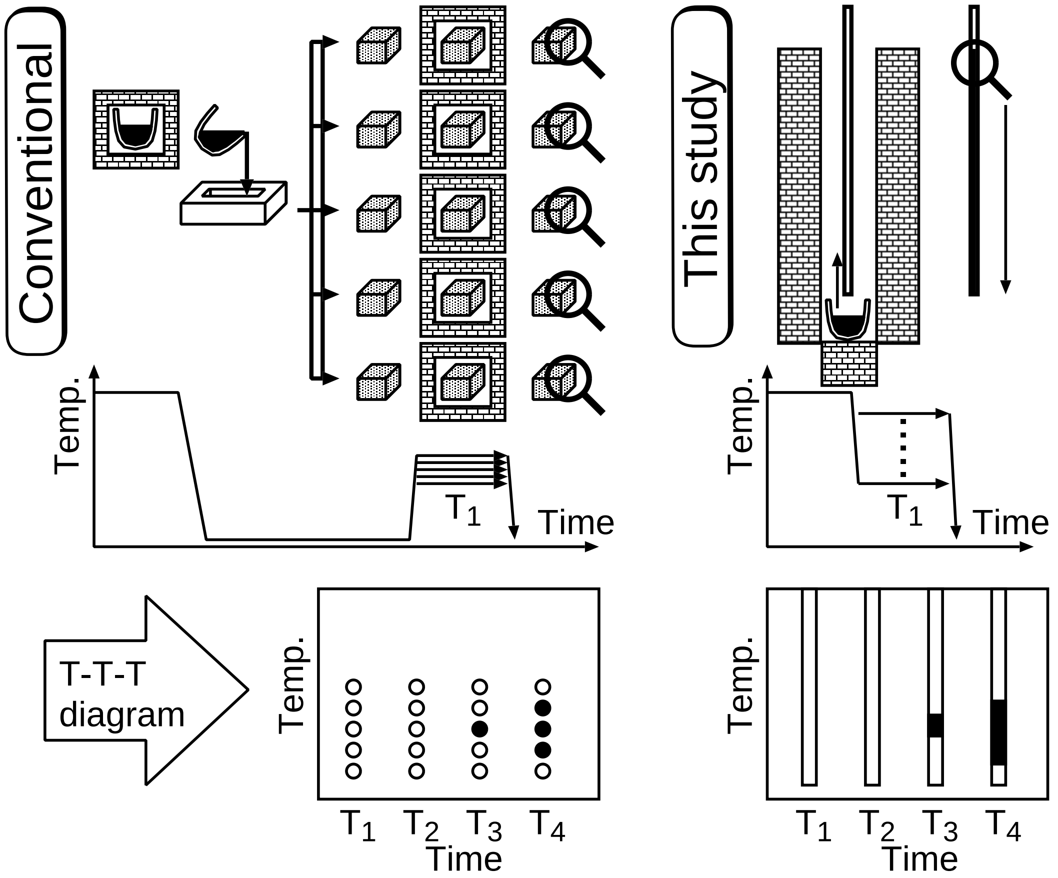
Figure Captions

Fig. 1 Two procedures to make T-T-T(time-temperature-transform) diagram, conventional and proposed. In the diagram shown in the bottom, crystallized point is shown by closed area. The former includes 3 steps; (1) making many glass samples(melting, casting and cutting), (2) annealing them at several temperatures for different periods, and (3) examining them. The latter includes 2 steps; (1) annealing a sample library in a temperature gradient furnace immediately after making it by sucking glass melt into a glass capillary, and (2) examining. Thermal history of glass samples are shown in the middle.

Fig. 2 T-T-T diagram of xTeO$_2$-$(100-x)$ZnO glasses prepared in this study. Each vertical line represents one glass sample library. Each closed rectangle is the temperature range where visible precipitation is observed. Open rectangle is accidentally precipitated area (see text). Curve represents the temperature change at the bottom of the capillary pulled at $t=0$ which is determined by a separate experiment. Arrows are the characteristic temperature for each glass composition, T_{m}: melting temp., T_{x}: crystallization temp., and T_{g}: glass transition temp., which are determined by DTA measurements.

Fig. 3 Critical cooling rate($\triangle$, $\bullet$ and $\bigtriangledown$), phase diagram[1] and glass forming region($\ast$, $\times$ and $+$)[2] of TeO$_2$-ZnO system. $\triangle$: $>$ 2 K/s, $\bigtriangledown$: $<$ 0.1 K/s, $\ast$: glasses were made by twin-roller technique ($>$ 10 K/s), $\times$: casted into copper mould ($\sim$ 10 K/s), and $+$: graphite mould(1K/min).



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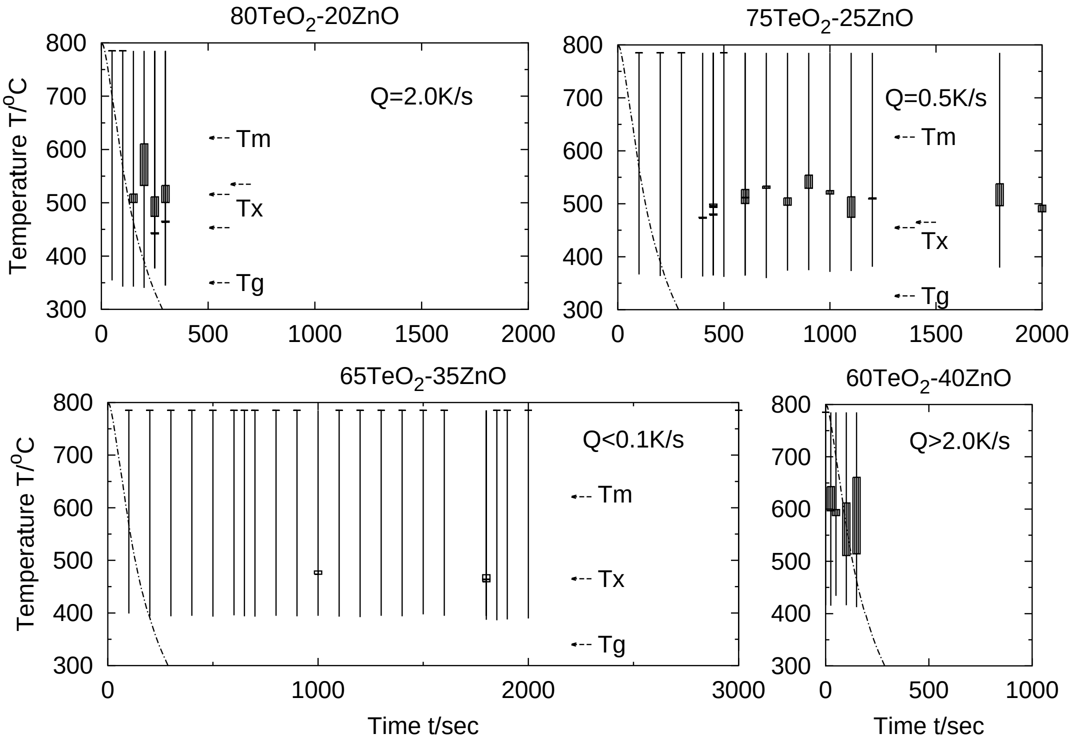

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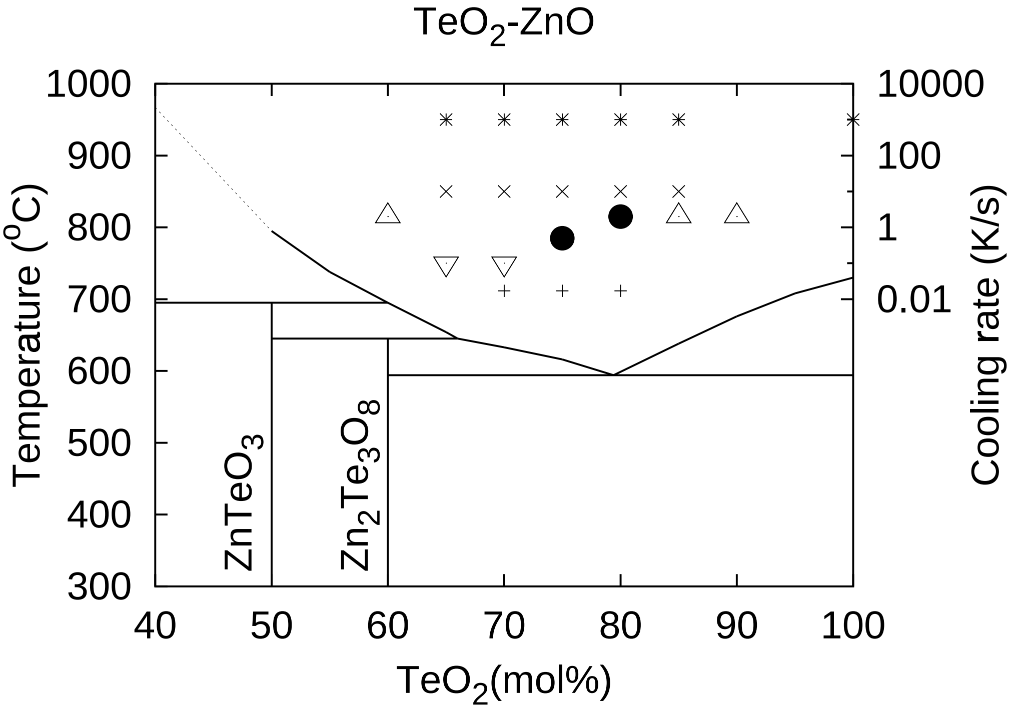

Fig. 3. Critical cooling rate(△, • and ▽), phase diagram[1] and glass forming region($\ast$, $\times$ and $+$)[2] of TeO_2-ZnO system. △: > 2 K/s, ▽: < 0.1 K/s, $\ast$: glasses were made by twin-roller technique (> 10 K/s), $\times$: casted into copper mould ($\sim$ 10 K/s), and $+$: graphite mould(1K/min).