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Authors(English)	Satoru Inoue, K. Wada, masayuki yamane, S. Shibata, Atsuo Yasumori, Tetsuji Yano, Akio Makishima, Hiroyki Inoue, M. Uo, Y. Fujimori
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Estimation of phase separation rates of PbO–B₂O₃ melts

S. Inoue, K. Wada, and A. Nukui

National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba 305, Japan

M. Yamane, S. Shibata, A. Yasumori, and T. Yano

Department of Inorganic Materials, Faculty of Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-Ku, Tokyo 152, Japan

A. Makishima, H. Inoue, and M. Uo

Department of Materials Science, Faculty of Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-Ku, Tokyo 113, Japan

Y. Fujimori

Tsukuba Space Center, National Space Development Agency of Japan, 2-1-1 Sengen, Tsukuba 305, Japan

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The rate of liquid-liquid phase separation was experimentally studied in the PbO–B₂O₃ system. The *in situ* measurements were made by observing the melts with a videocamera continuously as the melts were cooled down from homogenization temperatures at a rate of 2.5 °C/min. The time interval between the beginning and the completion of the darkening of the visual field was determined as a measure of the separation rate. The phase-separation rate was estimated to be at least 900 times larger than that of the metastable phase separation below the liquidus.

I. INTRODUCTION

The liquid-liquid phase separation in the PbO–B₂O₃ system has been studied by several researchers. Geller and Bunting¹ composed the phase diagram of the PbO–B₂O₃ system, including the miscibility gap. The structure of the phase-separated glasses was studied by Liedberg *et al.*² Zarzycki and Naudin³ applied the small-angle x-ray scattering technique to study the kinetics of the phase separation. A thermodynamic approach was made by Macedo and Simmons,⁴ and the miscibility gap boundary was analyzed from the regular solution concept. Podlesny *et al.*⁵ observed the phase separation under isothermal heating to determine the immiscibility temperatures accurately.

The phase separation is one of the phenomena applicable to prepare glasses with dispersed glassy or crystalline fine particles which give unique properties or functions. For example, the phase separation in the Na₂O–B₂O₃–SiO₂ system has been applied to prepare some unique glasses such as porous glasses,⁶ anisotropic glasses,⁷ etc. In applying the phase separation to the preparation of unique materials, it is very important to freeze the texture of the system when the separated particles grow to an appropriate size. For this purpose, it is necessary to know the phase separation rate or, if possible, the nucleation rate and the growth rate in the system of interest. However, our knowledge on the phase separation rate is rather scant, although the immiscibility temperatures were determined by several researchers as mentioned above.

In this study, the phase-separation rate was estimated from observation by using a videocamera within the miscibility gap of the PbO–B₂O₃ system.

II. EXPERIMENTAL

A. Preparation of the samples

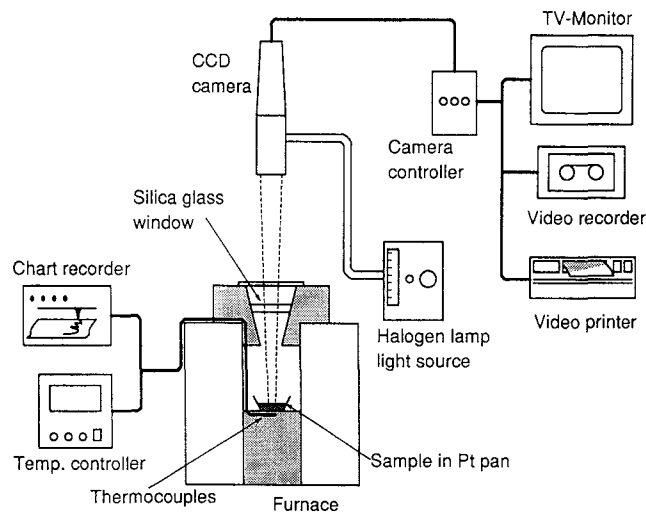
The batch compositions of the glasses studied are listed in Table I. The batches for 20 g glasses were heated up to 900 °C in a platinum crucible and held there for about 1 h. The melts were then quenched by squeezing between two carbon blocks.

B. Observation of the phase separation

The block diagram of the setup for the *in situ* observation of phase separation is shown in Fig. 1. A sample glass of 0.13–0.21 g was placed in a platinum pan (13 mm in diameter) and was remelted in an electric furnace at 820 °C to get a homogeneous melt. The weight of the sample glass was determined from the density of the glass so that the thickness of the melt in a pan would be around 0.5 mm. The phase separation was observed by a videocamera continuously as the melt was cooled down from the homogenization temperature at a rate of 2.5 °C/min. The pictures were recorded on a videotape. The size of the visual field was 590 × 801 μm, and the magnification on a TV monitor (14 in.) was 357 times. The picture observed became dark due to the light scattering when the droplets precipitated. The temperatures, *T*₁ and *T*₂, were read out from the

TABLE I. Batch composition of the glass samples.

Glass	PbO		B ₂ O ₃	
	Wt. %	Mol %	Wt. %	Mol %
A	3.14	1.0	96.86	99.0
B	5.43	1.76	94.57	98.24
C	9.02	3.0	90.98	97.0
D	11.78	4.0	88.22	96.0
E	14.93	5.19	85.07	94.81
F	19.44	7.0	80.56	93.0
G	23.08	8.56	76.92	91.44
H	26.27	10.0	73.73	90.0
I	30.42	11.0	69.58	89.0
J	34.29	14.0	65.71	86.0
K	36.13	15.0	63.87	85.0
L	38.78	16.5	61.22	83.5

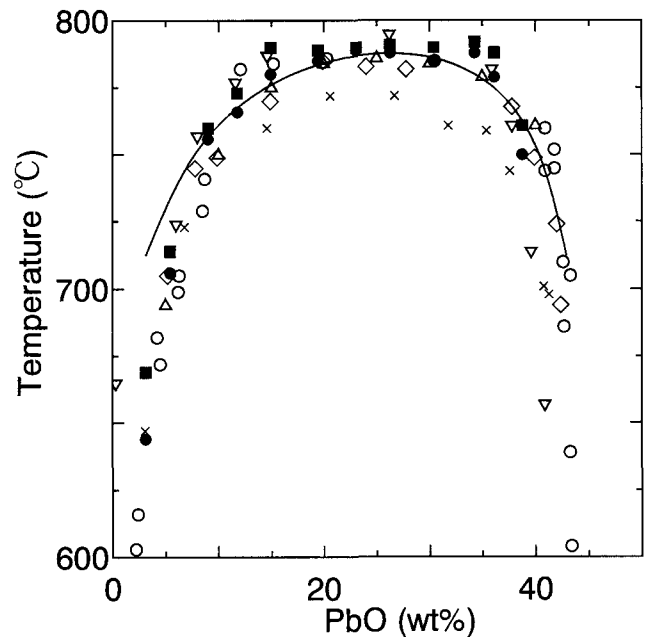
FIG. 1. Block diagram of the setup for the *in situ* observation of phase separation.

temperature-time charts at the times when the darkening of the visual field began and completed, respectively. The time interval, t , between the beginning and the completion of the darkening of the central $500 \times 700 \mu\text{m}$ area within the visual field was determined as the measure of the phase-separation rate. The observations were made several times and each of the values of T_1 , T_2 , and t was averaged.

III. RESULTS AND DISCUSSION

A. Immiscibility temperature

The temperatures, T_1 and T_2 , corresponding to the beginning and completion of the darkening of the visual field were plotted against PbO content in Fig. 2 along with the immiscibility temperatures obtained by other researchers. The immiscibility temperatures reported by previous researchers were in between T_1 and T_2 . The

FIG. 2. Immiscibility temperature curve of the PbO–B₂O₃ system. (■, ●) Present study, (○) Zarzycki and Naudin,³ (△) Geller and Bunting,¹ (▽) Liedberg *et al.*,² (◇) Podlesny *et al.*,⁵ and (×) Simmons.⁸

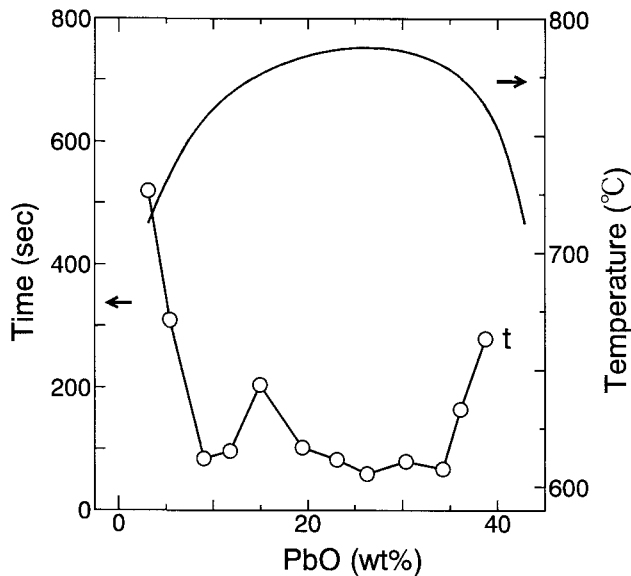
solid line in the figure was the binodal immiscibility curve calculated by the procedures described in the literature,⁸ where the critical temperature was taken as T_2 of the glass H. The calculated curve reproduced well the measured immiscibility temperatures.

B. Phase-separation rate

The time intervals, t , corresponding to the temperature drop from T_1 to T_2 were shown as a function of the PbO content in Fig. 3 along with the calculated immiscibility curve. The t increased in the composition range in both ends of the immiscibility dome, indicating that the phase separation was quick in the middle of the dome and slow near both ends of the dome. In the middle of the dome, the time t was less than 200 s, suggesting that it would be difficult to freeze the texture including particles of an appropriate size. The compositions near the B₂O₃-rich end of the dome were favored for the application of the phase separation to the preparation of glasses dispersed with fine particles.

The phase separation around the immiscibility temperatures in this system is driven by the binodal decomposition⁴ in which the nucleation and the growth of nuclei are taking place. Then the time t was considered to represent the apparent separation rate, including the effects of both nucleation and growth.

The measurements of t were made near the immiscibility temperatures, and the values of the normalized undercooling factors of $(T_m - T)/T_m$ were considered

FIG. 3. Dependence of darkening time t on the PbO content.

to be similar, irrespective of composition. The nucleation rate is dependent mainly on the interfacial energy and the activation energy of the diffusion process.⁹ The growth rate is governed by the transport process of diffusion.¹⁰ In a viscous liquid such as glass melt, the diffusion coefficient is strongly dependent on the viscosity of the melt. The decrease of melt viscosity, as well as the decrease of the interfacial energy, leads to the increase of the nucleation rate and the growth rate.

Figure 4 showed the relation between t and the viscosity of the melt of the compositions from A to L. The viscosity of the melt at the immiscibility temperature was calculated from the Fulcher equation fitted to the viscosity data in the report of Zarzycki and Naudin.³ The black dots correspond to glasses A and B in the B₂O₃-rich side of the dome and the open circles to glasses C, D, E, F, G, H, I, J, K, and L. The time t increased with the increase of the melt viscosity as predicted from the theory of the binodal decomposition. The dependence of t on the viscosity for glasses A and B (black dots) was different from that for the other glasses (open circles). The phase separation took place below the liquidus and in the phase of "PbO · 2B₂O₃ + Liquid" on glasses A and B. Thus, the difference of the dependence was considered to arise from the fact that the end member of the PbO-rich side changed from PbO · 4B₂O₃ to PbO · 2B₂O₃ on glasses A and B.

Figure 5 showed the time change of the normalized darkened area of the visual field for glasses A, C, F, and L. The normalized darkened areas reached 0.5 within about 50 s on the glasses C, F, and L.

In the literature,³ Zarzycki and Naudin presented transmission electron micrographs of the lead borate glass thin films containing 2 wt. % of PbO, which were

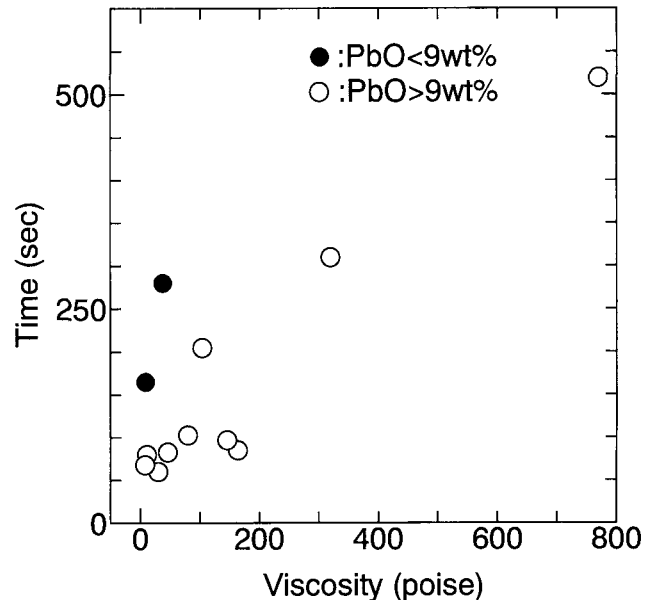
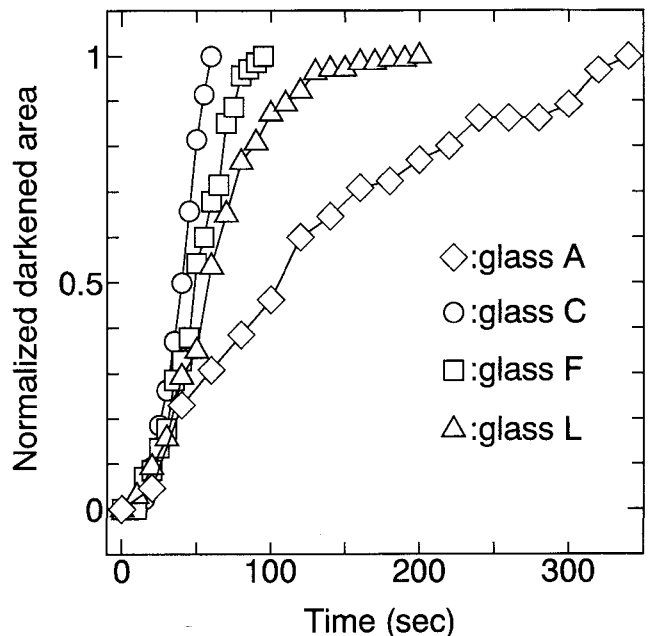
FIG. 4. Correlation between darkening time t and melt viscosity at immiscibility temperature [(○) PbO > 9 wt. %; (●) PbO < 9 wt. %].

FIG. 5. Change of the normalized darkened area of the visual field for glasses A, C, F, and L as a function of cooling time.

heat-treated at 415 °C below the liquidus for 1/4, 1/2, 1, 3, and 6 h. The photographs showed that the precipitated particles coalesced into large particles as the heating time increased. After a 6 h heat treatment, the sizes of the particles reached about 0.03–0.1 μm . The total volume fraction of the precipitated particles of the specimen heat-treated for 6 h was estimated to be about 20% from the photograph by measuring the fractional length intercepting each particle.¹¹

The fraction of the total growth of the droplets in binodal phase separation x can be expressed as a function of time like

$$x = 1 - \exp(-bt^m) \quad (1)$$

where t is time and b and m are the constants.¹⁰ The value of m (Avrami constant) is correlated with the mechanisms of growth. For the diffusion-controlled growth $m = 1.5$, and for the interface-controlled growth $m = 3$. In the B₂O₃-rich side of the dome, the growth was considered to be controlled by diffusion due to high melt viscosity. The constant b was determined by applying the values of $x = 0.2$, $t = 6$, and $M = 3/2$ to Eq. (1), and the time necessary for the growth fraction of 50% was calculated to be 12.8 h.

In this study, the phase separation was observed while the melt was cooled continuously, but the temperature difference in the observation ($T_1 - T_2$) was less than 10 °C on the glasses from C to L . The process could be regarded nearly as isothermal process. Moreover, the normalized darkened area was considered to be proportional to x in Eq. (1). Therefore, from the difference between the times elapsed at 50% of conversion, the separation rate in the two-liquid region was estimated to be at least 900 times larger than that of the metastable phase separation below the liquidus.

IV. SUMMARY

The liquid-liquid phase separation rates were experimentally studied in the PbO–B₂O₃ melt. The *in situ* measurements were made by observing the melts with

a videocamera as the melts were cooled down from the homogenization temperature at a rate of 2.5 °C/min. The elapsed time between the beginning and the completion of the darkening of the visual field was measured as an indicator of the phase-separation rate. The phase-separation rate was estimated to be at least 900 times larger than that of the metastable phase separation below the liquidus.

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