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Experimental determination of the binodal temperature in the lead borate system

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An experimental determination of the phase boundary in the region of immiscibility of the $PbO-B_2O_3$ system is reported. Measurements were made by visual observations of both the clearing and clouding temperatures for a series of isothermal heatings. The results are compared with those obtained in previous studies.

1. Introduction

The lead borate system has a broad region of immiscibility in the composition region of approximately 0–45 wt % PbO, a large fraction of which occurs in the stable regime (i.e. above the liquidus). If this system exhibited normal behaviour, then one would anticipate a rather broad compositional regime where the phase-separation process should proceed via spinodal decomposition. However, experimental investigation has shown no evidence of an interconnected morphology and only droplet structures have been detected [1]. Furthermore, a study of physical properties of these phase-separated glasses [2] have been in accord with the conclusions given by Shaw and Uhlmann [1]. The latter have revealed a sharp transition from a morphology consisting of lead-rich drops in a nearly pure B_2O_3 matrix to lead-depleted drops in a matrix of about 45 wt % PbO.

The immiscibility boundary, too, is somewhat of an enigma, because the experimentally reported results of various investigators [3–8] for the phase equilibrium temperatures as a function of composition have differed. Particularly striking is the fact that the most recent study [8] exhibits a binodal temperature quite divergent from those previously reported, especially in the high PbO region [9]. These discrepancies provided the motivation for the present study.

2. Experimental procedure

Lead borate glasses were prepared in the following manner. Appropriate amounts of > 99.9% pure PbO and B_2O_3 were combined in order to produce approximately 30 g. glass. The powders were mixed in a bottle roller for 1h. Then the mixed powders were placed in a platinum crucible, covered with a platinum lid, and heated at 950 °C for 2 h. The melt was stirred twice during the heating period. The melt was cast on to a brass plate, and after reaching room temperature was crushed, mixed and remelted via the above procedure.

All glass compositions prepared were subjected to ICP analysis to determine the trace impurity content and to confirm the chemical composition of the glasses. In addition, density measurements were performed to provide a second experimental determination of glass composition. These measurements were made with the aid of a Troemner S-100 specific gravity chain balance, which is an Archimedean-type density-measuring device. The density–composition data of Shaw and Uhlmann [1] were used to establish the compositions from the measured values of densities.

Binodal temperatures were determined by both clearing and clouding point measurements. A box furnace, fitted with a type K chromel-alumel thermocouple, was used for executing the determinations. The thermocouple was calibrated by measuring the melting point of KCl. A platinum crucible containing 2–3 g glass was placed in the furnace and heated at various temperatures. The sample was monitored visually by placing a mirror near a hole at the top of the furnace. Clearing and clouding points were found employing two types of thermal histories. In the first procedure, the sample was heated for 20 min at 900 °C. The furnace temperature was then lowered to the vicinity of the reported binodal temperature for the given composition (but on the high-temperature side). Isothermal heating was executed for 20 min. If the melt remained clear, then the temperature was lowered by 2 °C, held for 20 min, and checked again for clouding. This process was repeated until cloudiness was observed. When clouding was in evidence, the temperature was raised by 1 °C, held at that temperature for 20 min, and then re-examined. The highest temperature at which cloudiness persisted was taken as the binodal temperature. Three measurements of

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this type were performed for each composition. In the second procedure a glass sample was phase separated at 600 °C. It was then heated to several degrees below the binodal temperature (determined by the first method), and held at this temperature for 20 min. If the melt was not clear, the temperature was raised by 2 °C and the process was repeated. The lowest temperature at which the sample cleared was taken as the binodal temperature.

3. Results and discussion

The target (theoretical) and experimentally determined glass compositions are shown in Table I. The last column of this table (headed difference) gives the absolute values between target densities and those obtained by density measurements. ICP and density values reported in Table I represent the averages of three measurements. ICP determinations were performed for both lead and boron and in many instances the total analysed compositions were less than 100% by 1%–2%. Thus, the ICP results are reliable only to this degree of accuracy. The density method of finding glass compositions should, in principle, yield very precise results because densities can be determined quite accurately. However, precise results require the availability of a nearly exact relationship between density and composition. One should note that the differences between target and measured compositions (density) are less than 1%, and for the highest PbO compositions are less than 0.5%.

Analyses were also performed to detect trace amounts of platinum, alumina, and zirconia because these components can dramatically alter the binodal temperature. It was found that less than 1 p.p.m. platinum, 0.2 p.p.m. alumina, and 0.1 p.p.m. zirconia were present in the glasses.

The results of the immiscibility boundary measurements are shown in Fig. 1a, where the average measured binodal temperature is plotted versus PbO composition. It is observed that the shape of the binodal envelope differs very little whether theoretical or measured compositions are employed. Furthermore, as will be shown, the differences in binodal temperatures exhibited in Fig. 1a are quite small compared to the differences between the data of various investigators.

TABLE I Theoretical and measured compositions (wt % PbO)

Target	ICP	Density	Difference
5.0	4.8	5.2	0.2
8.0	7.7	8.7	0.7
10.0	9.7	–	0.3 (ICP)
15.0	14.8	15.9	0.9
20.0	19.5	19.9	0.1
24.0	24.0	23.8	0.2
28.0	25.5	27.2	0.8
38.0	38.3	37.6	0.4
40.0	38.3	39.9	0.1
42.0	39.1	42.0	0.0
42.5	–	42.6	0.1

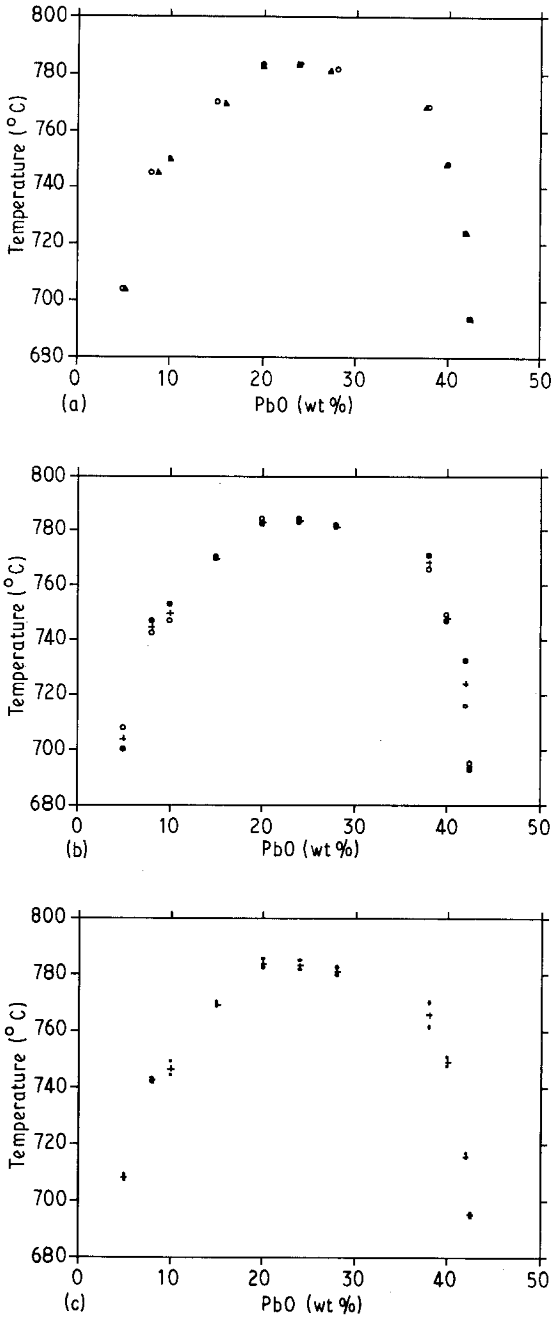

Figure 1 (a) Experimentally determined immiscibility temperatures versus (○) target composition and (△) composition determined by density measurements. (b) Experimentally determined immiscibility temperatures versus (+) target composition found by (●) heating and (○) cooling. (c) Standard deviations in immiscibility temperatures determined in cooling experiments. (+) Mean values, (·) separated by 2 S.D.

One measure of the accuracy of the present results is given by the difference in binodal temperatures determined by clearing and clouding measurements. This information is presented in Fig. 1b, where experimentally determined equilibrium temperatures are shown as a function of composition. It is observed that with the exception of the 42% PbO composition, the difference in results is within a few degrees. These differences are significantly smaller than those obtained by most previous investigators [3–8].

A second measure of the preciseness of the measurements is given by the standard deviation. It was found that the standard deviations of the binodal temperatures found in the cooling experiments were generally larger than those obtained in the heating experiments. The former are shown in Fig. 1c. It is observed that with the possible exception of the 38 wt % composition, the random errors in the measurements are quite small.

Errors in the experimental miscibility-gap boundary could arise from uncertainties in temperature measurements or glass composition, impurity cations, or uncertainties in equilibrium point determinations. In the discussion above we have illustrated that the latter three factors do not greatly influence our reported results. Perhaps, the largest potential source of error is connected with temperature measurements because the thermocouple was calibrated solely at one temperature (the melting point of KI). However, with the exception of Geller and Bunting [4] no other investigators reported any thermocouple calibration procedures. Hence, as will be discussed, we believe our results to be as, or more, reliable than those obtained previously.

Simmons [7] found that the experimentally determined coexistence temperatures which he obtained were described quite well by the modified regular solution model [10]. This model predicts the following expression for the reduced coexistence temperatures, $T_r = T/T_c$, where T_c is the critical temperature

$$T_r = [2 + \Delta S/R][1 - 2Y'] \times \{\ln[(1 - Y')/Y') + (1 - 2Y')\Delta S/R\}^{-1} \quad (1)$$

where $Y' = y/\{y + [1 - (n + 1)y]/m\}$, and y is the mole fraction of lead oxide. For the lead borate immiscibility dome, $n = 4$ and $m = 5$ [7]. The reduced entropy of mixing parameter, which accounts for changes in internal degrees of freedom, $\Delta S/R$, was taken as 10.0. We employed Equation 1 in conjunction with our experimentally determined value of the critical temperature (784.1 °C) to compute the coexistence curve. The results of this calculation are shown as the solid line in Fig. 2. The solid triangles in this figure represent our experimentally determined values. It is observed that the modified regular solution model provides a reasonably good fit to our data.

4. Comparison with previous investigations

Fig. 3 shows the currently determined immiscibility boundary as well as those obtained in four earlier studies [3–5, 7]. It may be observed that there is considerable variation in the reported critical temperatures (~ 20 °C), as well as in the shape and width of the curves. We note that our curve appears most similar to that of Zarzycki and Naudin [5], particularly at the higher PbO concentrations. We determined the critical temperature to be 784.1 °C at a composition of 26.3 wt % (10.0 mol %) PbO. Also, we found that the immiscibility gap extends at *least* from 5–42 wt % PbO. One notes that our reported critical temperature is approximately midway between the results of the other investigations, as shown in Fig. 3.

As indicated by Simmons [7], the low viscosity of these glasses over much of the immiscibility dome (100–1000 P), the rapidity of phase separation, and the extreme difference in density between the phases promote gravity-driven phase segregation which makes accurate determination of binodal temperatures very difficult. At high PbO concentrations, where the viscosity is much higher, the immiscibility curve is subliquidus and the metastable phase-separation process must compete with crystallization. This feature potentially complicates the immiscibility measurements in the high lead region. In fact, previous investigations have reported crystallization in the high lead portion of the immiscibility gap [3, 7]. Because crystallization would alter the residual glass composition, its occurrence would influence the measured binodal temperature. We believe that crystallization was absent during the course of our experiments involving compositions with PbO content no greater than 42.5 wt %. Our evidence for this presumption is twofold. First, when crystallization did occur in a composition with 43.8 wt % PbO, it was easily observable. Thus, because visual signs of crystallization were not present for the other compositions, this infers that it did not occur. Second, our experimentally determined immiscibility boundary is a smooth function of composition in the high lead regime. If crystallization occurred randomly in certain high lead samples, then one might expect discontinuities.

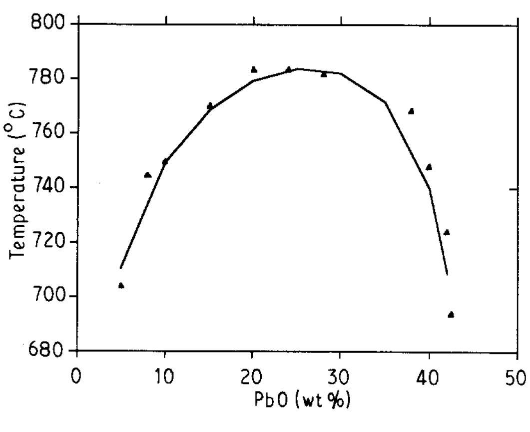

Figure 2 Comparison of (△) experimentally determined immiscibility curve and (—) calculated curve using the modified regular solution model.

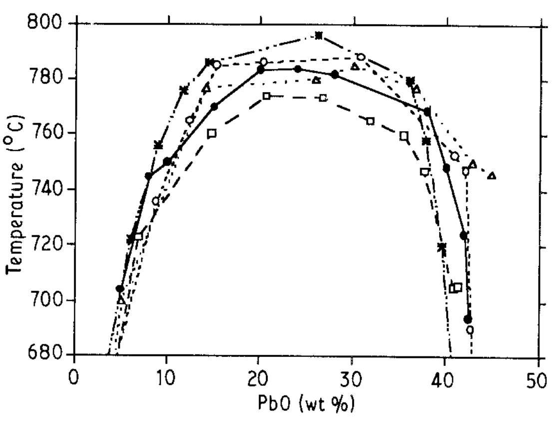

Figure 3 Comparison of experimentally determined binodal curves. (- - △ - -) [4], (— ● —) present results, (— □ —) [7], (- - ○ - -) [5], (— - - × —) [3].

All previous studies have used either cooling measurements to detect initial opalescence, heating measurements to detect final clearing, or a combination of both procedures. The time lag produced by using non-zero cooling/heating rates would tend to make the immiscibility temperature determined by cooling to be too low, and the binodal temperature determined via heating too high. These effects could be exacerbated in the former measurements by the incubation time needed for nucleation, and in the latter measurements by the excessive long clearing time required if massive phase separation occurred as a result of gravity-induced segregation of the phases. In any case, however, the true immiscibility temperature should lie between these two experimental immiscibility temperatures. Thus, the difference between the binodal temperatures determined by these two methods is a good indication of the maximum error. In only two of the previous studies [5, 7] were both heating and cooling measurements conducted. Simmons [7], by employing heating/cooling rates of 1 °C min^{-1}, or less, found that the difference in these two temperatures was less than or equal to 5 °C for most of the compositions studied.

In the present investigation, both the clearing and clouding experiments were performed under isothermal conditions. This procedure allowed us to reduce somewhat the temperature difference between the two types of immiscibility temperature measurements. Typically, we found differences of 3 °C, as illustrated in Fig. 1b.

Perhaps the greatest source of error in our measurements is the inability to determine precisely the temperatures at which the final clearing or initial clouding occur, using the visual procedure which we employed. This difficulty could have produced differences between clouding and clearing temperatures of 2–3 °C (as found). However, because our temperature measurement thermocouple was calibrated at 790 °C, we believe that the temperatures which we report for the upper dome region are quite accurate. We observe from Fig. 3 that a 10 °C upper shift of the immiscibility curve reported by Simmons would produce near coincidence with ours. We conjecture that the systematic 10 °C difference between these two curves may be due to the inability to calibrate a thermocouple after attaching a glass bead to it (as done in the study of Simmons).

The most recent determination of the lead oxide–boron oxide binodal curve was reported by Ohta *et al.* [8]. It is compared with the binodal determined in the present study in Fig. 4. Ohta *et al.* employed DTA analysis to determine the onset of phase separation. They claim that the DTA procedure significantly increases the precision of demixing temperature measurements, and provides accuracy to within 0.1 °C. However, it is seen that the shape of their binodal curve (and composition at the critical temperature) is considerably different from ours and those of previous investigators. In addition, their DTA results appear to be in disagreement with the DTA results reported by Zarzycki and Naudin [5].

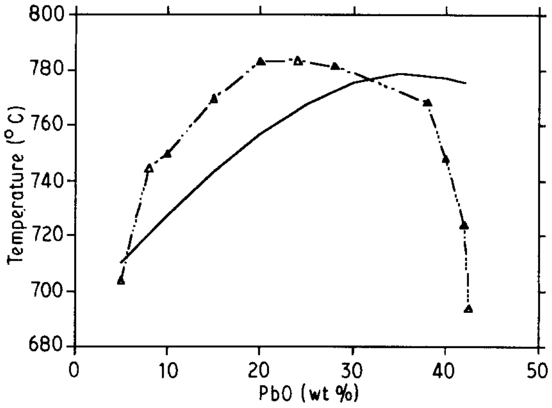

Figure 4 Binodal curves of (—) Ohta *et al.* [8] compared with (△) the present results.

5. Conclusions

The immiscibility curve for the lead borate system was determined and compared with the results of previous investigators. Close agreement was found between our binodal curve and that reported by Zarzycki and Naudin. The general shape of our curve and that of Simmons were similar, and both could be adequately described by a modified regular solution model. However, there was about a 10 °C displacement between these curves. All other previous determinations differed substantively from the present one, especially the most recent one reported by Ohta *et al.* We believe, however, that the immiscibility temperatures shown herein are quite precise for the reasons discussed in the previous sections.

Acknowledgements

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