

Short communication

Enthalpy of mixing in $0.8[x\text{B}_2\text{O}_3-(1-x)\text{SiO}_2]-0.2\text{K}_2\text{O}$ melts at 973 K

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Abstract

$0.8[x\text{B}_2\text{O}_3-(1-x)\text{SiO}_2]-0.2\text{K}_2\text{O}$ (with $0 \leq x \leq 1$) glasses were synthesized by melt quenching techniques. DSC curves of the glasses exhibit only one glass transition. Calorimetric measurements of heats of dissolution in lead borate at 973 K indicated small negative enthalpies of mixing. Consequently phase separation was not observed over the whole composition range. The results are in good agreement with the structural data available in the literature.

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1. Introduction

Due to their good mechanical properties, borosilicate glasses are one of the most important types of technological glass-forming systems. Originally developed for railway applications and laboratory use, they now find a wide range of application in industrial and domestic applications such as confining high-level radioactive wastes and in ovenwares [1–4]. Most studies of borosilicate glasses were focused on structural analysis [5–15]. There is a surprising lack of calorimetric data since Charles and Wagstaff [16] and Navrotsky's [17] early pioneering work on binary $\text{B}_2\text{O}_3\text{--SiO}_2$ and ternary $\text{B}_2\text{O}_3\text{--SiO}_2\text{--Na}_2\text{O}$ borosilicate glasses. We did not find any literature data concerning calorimetric measurements on potassium borosilicate glasses. The aim of this work is to report calorimetric data on $0.8[\text{B}_2\text{O}_3-(1-x)\text{SiO}_2]-0.2\text{K}_2\text{O}$ glasses. The enthalpies of solution in lead borate ($2\text{PbO--B}_2\text{O}_3$) at 973 K were measured by high-temperature calorimetry.

2. Experimental

Potassium borosilicate glasses were prepared by melt quenching from high-purity reagent grade K_2CO_3 , B_2O_3 and

SiO_2 (all from Merck, the nominal purity was 0.99 mol fraction). The raw materials were thoroughly ground in an agate mortar. Then the mixture was slowly heated to 1450 °C in a platinum crucible in an electric muffle furnace. It was kept for 1 h at this temperature with frequent stirring to ensure a good homogeneity. The melt was rapidly quenched by dipping the bottom of the crucible into cold water. The samples were kept in vacuum desiccators just prior to calorimetric analysis to prevent possible moisture sorption. All glasses were optically transparent.

Samples were characterized by powder X-ray diffraction (XRD) and differential scanning calorimetry (DSC). All products investigated were X-ray amorphous. The glass transition measurements were performed in a SETARAM DSC 111. About 15 mg samples were encapsulated in platinum pans and scanned at 15 °C/min under argon. Typically, three or four independent measurements of T_g were made for each composition and an estimate of the experimental error is ± 2 K. The instrument was calibrated with Al standards [18].

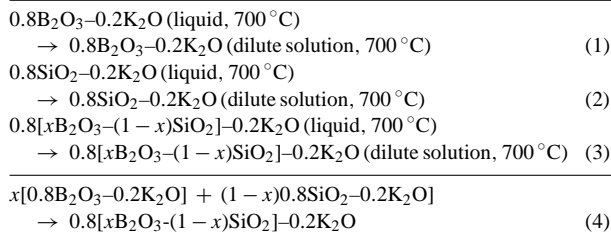
High-temperature solution calorimetry was performed in a Tian Calvet calorimeter at 973 K. A brief description of the calorimeter and the experimental procedure are outlined below. The calorimeter consists of two sample chambers, each separated from a metal block, which forms an isothermal heat sink, by a thermopile of Pt versus Pt–13% Rh thermocouples. The aim of solution calorimetric experiment is to convert reactants and products to the same final state, a dilute solution of the oxides dissolved in an oxide melt. Typically 7–20 mg of sam-

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ple are dissolved in 30 g of lead borate ($2\text{PbO}-\text{B}_2\text{O}_3$) melt. The sample in three platinum holders was slowly lowered into the calorimeter and was positioned just above the level of the melt. As the glass sample was metastable, it was equilibrated inside the calorimeter for a minimum time before dissolution. Careful sample loading can reduce the initial thermal imbalance and allow the equilibration time to be minimized to ~ 2 h. At the end of the equilibration period (indicated by steady baseline data) the glass sample was dissolved in the molten lead borate flux by dipping the sample holder into the flux and stirring. After stirring, the sample holder was returned to its initial position. This process of dipping and stirring was carried out to ensure that no sample remained undissolved in the cup. Completion of reaction was attained in 30–40 min in most cases. Before thermal equilibrium was achieved, the heat effect caused by stirring was measured. The stirring effect correction was then applied to the sample runs. For each composition five or six calorimetric measurements were realized. The concentrations of glass dissolved into the flux were always less than 0.1 wt%, so the conditions of infinite dilution were effectively satisfied.

The calorimeter is calibrated during the experiments by dropping weighed pieces of a platinum wire from room temperature to 973 K in the calorimeter. The enthalpy effects are calculated using well known enthalpy data of platinum [19]. The reproducibility of the calibration experiments is about $\pm 1\%$.

Under these experimental conditions, the enthalpy of mixing is calculated by the thermochemical cycle:



from which the enthalpies of mixing ΔH are computed according to the formula:

$$\begin{aligned} \Delta H = &x\Delta_{\text{sol}}H_1(0.8\text{B}_2\text{O}_3-0.2\text{K}_2\text{O}) + (1-x)\Delta_{\text{sol}}H_2 \\ &\times (0.8\text{SiO}_2-0.2\text{K}_2\text{O}) - \Delta_{\text{sol}}H_3 \\ &\times (0.8[x\text{B}_2\text{O}_3-(1-x)\text{SiO}_2]-0.2\text{K}_2\text{O}) \end{aligned}$$

3. Results and discussion

The glass transition data are summarized in Table 1. Only one T_g was observed for each composition, hence phase separation is not operating in this system. The highest T_g is obtained for about $x = 0.25$ i.e. the ratio $[\text{Na}_2\text{O}]/[\text{B}_2\text{O}_3] = 1$. At this composition, according to Yun and Bray [6], tetrahedral units, B_4 , enter the silicate network to form reedmergerite groups consisting of central B_4 units with all oxygen bridging to SiO_4 and consequently is fully connected.

Average values and the standard deviation of enthalpies of solution are listed in Table 1. The results of enthalpy of mixing are also given in Table 1. The uncertainties in the enthalpies

Table 1

Glass transition temperature (T_g), enthalpy of solution at infinite dilution ($\Delta_{\text{sol}}H^\infty$) in lead borate and enthalpy of mixing (ΔH) in $0.8[x\text{B}_2\text{O}_3-(1-x)\text{SiO}_2]-0.2\text{K}_2\text{O}$ glasses at 973 K

| x | T_g ($^\circ\text{C}$) | $\Delta_{\text{sol}}H^\infty$ (kJ/mol) | ΔH (kJ/mol) |
|------|----------------------------|--|---------------------|
| 0 | 502.2 ± 2.0 | -3.34 ± 0.79 | 0 ± 0.86 |
| 0.15 | 588.2 ± 2.0 | 0.25 ± 0.97 | -1.66 ± 1.21 |
| 0.25 | 624.9 ± 2.0 | 4.81 ± 0.66 | -4.30 ± 0.83 |
| 0.50 | 586.1 ± 2.0 | 10.51 ± 0.57 | -7.43 ± 0.83 |
| 0.75 | 483.2 ± 2.0 | 11.41 ± 0.99 | -5.11 ± 1.21 |
| 0.90 | 461.8 ± 2.0 | 9.70 ± 0.61 | -1.47 ± 0.97 |
| 1 | 453.7 ± 2.0 | 9.45 ± 0.35 | 0 ± 0.86 |

Errors on enthalpies of solution are standard deviations of the mean. The uncertainty (σ_t) of enthalpy of mixing given above is equal to the square root of the sum of the squares of the standard deviations of the means for individual reactions taking part in the thermochemical cycle considered: $\sigma_t = \sqrt{\sum (\sigma_{x_i})^2}$.

of mixing are extracted from the errors in the enthalpies of solution.

The enthalpies of mixing are negative over the whole composition range. Consequently, the free energy of mixing (ΔG) will always be negative, and the system will not exhibit phase separation. These results are consistent with the available structural data on the ternary alkali borosilicate glasses [20,21]. As mentioned by Galakhov et al. [22], the extent of immiscibility is inversely correlated with alkali cation size in the Li, Na, K, Rb and Cs borosilicate systems. Liquid immiscibility in many oxides systems is related to differences in ionic field strength z/a^2 , where z is the cation charge and a corresponding to the distance between the cation and the oxygen ion [23,24]. As confirmed by earlier NMR study of metastable immiscibility in alkali borosilicate glasses [25], potassium borosilicate glasses are much less likely to undergo macroscopic phase separation than sodium and lithium borosilicates which show considerable chemical heterogeneity due to extensive regions of immiscibility. In any case, the orders of magnitude of the enthalpies of mixing (from 0 to 8 kJ/mol) are the same order of magnitude as molten salt solutions of common cations and different anions [26].

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