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ScienceDirect
Chinese Chemical Letters 20 (2009) 245–249
CHINESE CHEMICAL LETTERS
www.elsevier.com/locate/cclet

Contribution to thermochemical studies of $0.8[xB_2O_3–(1-x)SiO_2]–0.2Na_2O$ glasses

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Received 1 July 2008

Abstract

Calorimetric measurements in $0.8[xB_2O_3–(1-x)SiO_2]–0.2Na_2O$ glasses and melts are performed in HF calorimetry at 298 K and lead borate calorimetry at 973 K, respectively. Mixing enthalpy is affected by both temperature and composition. At 298 K, the mixing enthalpies are slightly negative and components are miscible at that temperature in the whole composition range. At 973 K, the sign of the mixing enthalpies reflect the tendency to phase separation at silica-rich compositions, which is avoided for kinetic reasons as shown by SEM results. Therefore, one is tempted to consider the quenched $0.8[xB_2O_3–(1-x)SiO_2–0.20Na_2O]$ glasses and melts as single-phase materials.

Keywords: Borosilicate; HF calorimetry; Lead borate calorimetry; Mixing enthalpy

Borosilicate glasses are the main investigated oxide glasses due to their potential applications such as confining materials of high-level radioactive wastes, optical glasses, ovenwares and also in the electronic industries [1–3]. An analysis of data, available in the literature, reveals that the most studies were focused on broad structural analysis [4–9]. In a few studies realised by Hervig and Navrotsky [10], sodium borosilicate leads to a positive mixing enthalpy at 974 K, for low alkaline content, particularly for $SiO_2–B_2O_3$ and $SiO_2–(0.2NaO{\cdot}0.8B_2O_3)$. On contrary, negative mixing enthalpies along $SiO_2–(0.5NaO{\cdot}0.5B_2O_3)$ were observed. However, sodium borosilicate glasses have not investigated by HF calorimetry.

The importance of thermodynamic description, for both practical tasks and theoretical development a theory of the vitreous state, is obvious. Thermodynamic data can be used to estimate the degree of ordering of the glass structure and to determine the character of the ordering processes occurring in the course of the glass formation. The values of the Gibbs free energy of formation determine the extent of rearrangement which occurs during the fusion and interaction of oxides forming glass. Experimental thermodynamic data serve as a criterion for the reliability of statistical models and determine how to choose the best ones.

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1001-8417/$ – see front matter
doi:10.1016/j.cclet.2008.10.010

As a first step toward consistent investigation of thermodynamic miscibility on two glass-forming oxides, we report, in this present work, the calorimetric measurements on $0.8[xB_2O_3–(1-x)SiO_2]–0.2Na_2O$ glasses and melts, performed in HF calorimetry at 298 K and molten lead borate calorimetry at 973 K, respectively.

1. Experimental

Sodium borosilicate glasses were prepared by melt quenching from high-purity reagent grade Na_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. Glassy state of the samples was ascertained by X-ray powder diffraction (XRD) and differential scanning calorimetry (DSC) [11].

The surface morphology was analyzed by scanning electron microscopy equipped with energy-dispersive analysis by X-ray (SEM-EDAX, Model stereoscan 90). Specimens were leached for 100 min at 25 °C in HNO_3 (1 mol/L), coated with 20 nm of Au, and imaged on the same microscope at 25 kV.

HF calorimetry experiments were performed with a rotating calorimeter. Both the apparatus and the operating have been extensively described elsewhere [12,13] and so only a brief description will be given here. The stirring procedures were standardized and corrections were made for small effects associated with stirring. All measuring cells are in polytetrafluoroethylene (PTFE). Samples of about 5–20 mg were placed in the container, closed and stored in the calorimeter cell at 298 K to reach thermal equilibrium. During the dissolution, the sample was broken in the calorimeter cell which contained in a mixture of 25 mL of HF (6 mol/L) and 25 mL of HNO_3 (4 mol/L) solvent. The dissolution took 4 h and the heat effect was measured. The calorimeter was calibrated by using the heat effect of the well-known enthalpy of the protonation of THAM 0.37 mol/L in HCl 0.12 mol/L.

Molten lead borate calorimetry experiments were performed in a Tian Calvet calorimeter at 973 K described elsewhere [14]. 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. Prior to measurements, all the glasses were ground. Typically 7–20 mg of sample is dissolved in 30 g of lead borate ($2PbO–B_2O_3$) melt. The sample in three platinum holders was slowly lowered into the calorimeter and was positioned just above the level of the melt. Careful sample loading can reduce the initial thermal imbalance and allows 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. 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 run. The concentration of glass dissolved into the flux was always less than 1 wt%, so the condition of infinite dilution was effectively satisfied. The calorimeter was calibrated by dropping weighed pieces of small quantities platinum from room temperature to 973 K in the calorimeter. The reproducibility of the calibration experiments is about ±1–2%.

2. Results and discussion

According to the SEM micrograph, the specimen appeared topologically homogeneous (Fig. 1).

Table 1 showed the values of solution enthalpy at infinite dilution at 298 K. They were deduced by linear extrapolation to zero concentration of the solution enthalpy. The accuracy of determination was ±0.5 kJ mol^{-1}. The heat of solution was strongly negative and less exothermic than the mechanical mixture of the end-members. The values of the corresponding mixing enthalpies referring to the two composition limits were also listed in Table 1. These values were reproduced with an approximate accuracy of ±0.7 kJ mol^{-1}. Mixing enthalpy depends on the glass composition (Fig. 2). As shown in Fig. 2, there was a little variation of mixing enthalpy at 298 K of $B_2O_3–SiO_2$ compared to that of $B_2O_3–P_2O_5$. $B_2O_3–SiO_2$ interaction was less energetically favourable than that of $B_2O_3–P_2O_5$ interaction. The exothermic effect was less marked, about one order of magnitude, than for alkaline borophosphate glasses. At 298 K, mixing enthalpy in $0.8[xB_2O_3–(1-x)SiO_2]–0.2Na_2O$ appeared weakly negative and was close