Mass-Spectrometric Study of Thermodynamic Properties in the $\text{RbBO}_2\text{-SiO}_2$ System

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Partial pressures of RbBO_2 (g) and $\text{Rb}_2(\text{BO}_2)_2$ (g) in the $\text{RbBO}_2\text{-SiO}_2$ system are measured by a mass-spectrometric Knudsen effusion method. On the basis of the partial pressures, chemical activities of the RbBO_2 and SiO_2 components and molar Gibbs energies of mixing are determined in the whole composition range. The chemical activities of both RbBO_2 and SiO_2 show negative deviation from Raoult's law at 1000 K. From low molar Gibbs energies of mixing, the melts in the $\text{RbBO}_2\text{-SiO}_2$ system are concluded to be very stable thermodynamically.

1. Introduction

The compositions of alkali borosilicate glasses are usually shown in terms of the oxide components such as $\text{R}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$, where R is an alkali metal. However, it is verified from a Raman spectrometry that, when the molar ratio of $\text{R}_2\text{O/B}_2\text{O}_3$ is equal to or less than unity, all the alkali ions are associated with borate units in the glasses.¹⁾ A similar conclusion has been reached from a nuclear magnetic resonance study.²⁾ Furthermore, the vapors of RBO_2 (g) and $\text{R}_2(\text{BO}_2)_2$ (g) are observed over alkali borosilicate melts.³⁾ Thus, according to Wenzel and Sanders,⁴⁾ the composition can be rewritten by using an alkali pseudo component, the chemical formula of which is the same as that of the vapor, to be $\text{RBO}_2\text{-SiO}_2$.

Recently, the present authors have studied the vaporization of alkali borosilicate melts in the $2\text{RBO}_2\cdot 3\text{SiO}_2$ system by a mass-spectrometric Knudsen effusion method and found that the chemical activities of the RBO_2 components in the melts decrease as going from lithium to cesium.^{5), 6)} A comparison between the vaporization of rubidium and strontium, which is one of main fission products and a neighbor of rubidium in the periodic table, from borosilicate melts has been made, and the RbBO_2 component has been found to have a smaller chemical activity than the SrBO_2 one.⁷⁾ For the solid solution in the $\text{RbBO}_2\text{-CsBO}_2$ system, the chemical activities and the molar Gibbs energies, enthalpies, and entropies of mixing have been determined from the ion-intensity ratios measured mass-spectrometrically.^{8), 9)}

Thermodynamic properties of the alkali borosilicate melts are very important, because high-level radioactive wastes will be stored after immobilization by incorporating into the melts at high temperatures. In the present work, to obtain more knowledge on the thermodynamic properties of the melts in the $\text{RbBO}_2\text{-SiO}_2$ system, partial pressures of RbBO_2 (g) and $\text{Rb}_2(\text{BO}_2)_2$ (g) are measured by the mass-spectrometric Knudsen effusion method. On the basis of the vaporization data, the chemical activities

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and the molar Gibbs energies of mixing in the whole composition range are determined at 1000 K.

In the $2\text{RbBO}_2 \cdot 3\text{SiO}_2$ and $\text{RbBO}_2 \cdot 4\text{SiO}_2$ systems, the glass transition temperatures have been reported to be 853 and 969 K, respectively.¹⁰⁾ Consequently, the formation of melts in the present system containing SiO_2 of less than 80 mol% is undoubted at 1000 K. However, there might be a possibility of glasses in the present system containing larger amount of SiO_2 .

2. Experimental

The samples were prepared from reagent grade rubidium carbonate, boric acid, and silicon oxide supplied from Morton Thiokole, Inc., Danvers, Massachusetts. About 10 g batches were well mixed by a pestle and melted in platinum crucibles in an electric furnace for 30 min–1.5 h at 1100–1500°C. In these preparations, an excess of 2 mol% of boric acid was used to compensate for the loss by the vaporization of HBO_2 (g) in the initial stage of heating.³⁾ The vaporization of a small amount of the rubidium component might occur. However, the effect of these losses on the sample compositions is considered to be ignored. The glass pellets were pulverized and then well mixed to obtain the powdered samples with homogeneous compositions. No X-ray diffraction lines of the samples are observed before and after the experiments. The compositions of oxides and their rewritten pseudo components of the samples are shown in Table 1.

A 0.2 m radius and 90° sector magnet single focusing Hitachi RM-6K mass spectrometer was used in combination with a platinum Knudsen cell. The cell has an inside diameter of 7 mm and an inside height of 9 mm. The diameter of the effusion orifice is 0.5 mm. The temperature of the cell was measured with a well calibrated W-5%Re/W-26%Re thermocouple inserted into the hole of the bottom of the cell.

Each powdered sample of about 50 mg was loaded into the cell and heated under a background pressure of less than 2×10^{-5} Pa. Vapors effusing from the orifice were ionized by electron impact and ion intensities were measured by raising and lowering the sample temperature step by step.

The partial pressure $p(i)$ of the vapor species i was calculated from the relation¹¹⁾:

$$p(i) = k \frac{I(i)T}{\sigma(i)g(i)n(i)}, \quad (1)$$

Table 1. Compositions of Glass Samples

Glass	Composition				
	Oxide			Pseudo	
	Rb_2O	B_2O_3	SiO_2	RbBO_2	SiO_2
31	10	10	3	20	3
30	1	1	1	2	1
29	1	1	2	1	1
12	1	1	3	2	3
32	1	1	6	1	3
33	1	1	14	1	7
34	1	1	24	1	12

where k is the pressure calibration constant, $I(i)$ the measured intensity of the ion formed from the i vapor, T the sample temperature, $\sigma(i)$ the relative ionization cross section, $g(i)$ the gain of the electron multiplier, and $n(i)$ the isotopic abundance ratio. The value of k was obtained by the silver reference method.¹²⁾ Molecular ionization cross sections were estimated by the method described by Kordis and Gingerich¹³⁾ from atom ionization cross sections¹⁴⁾ under the assumption that the cross sections for simple ionization and dissociative ionization of the molecules are equal. Multiplier gains for the ions were measured by the pulse counting method.¹⁵⁾ Isotopic abundance ratios for ⁸⁵Rb, ¹¹B, and ¹⁶O were taken from the literature.¹⁶⁾

3. Results and Discussion

3.1 Vapor species and their partial pressures

Ion species identified for the rubidium borosilicate melts in Table 1 are Rb⁺, RbBO₂⁺, and Rb₂BO₂⁺ in the temperature range from 796 to 1175 K. However, for glass samples 33 and 34 the intensities of the Rb₂BO₂⁺ ion could not be measured accurately as a function of the reciprocal temperature because of very weak intensities. The present authors have already studied in detail the ionization behavior of the vapor species for alkali borosilicate melts; that is, for the melts, in which the molar ratio of Rb₂O/B₂O₃ is equal to unity, the Rb⁺ ion is formed by both the dissociative ionization and the positive-negative ion pair process from RbBO₂ (g), the RbBO₂⁺ ion by the simple ionization from RbBO₂ (g), and the Rb₂BO₂⁺ ion by the dissociative ionization from Rb₂(BO₂)₂ (g).³⁾ No vaporization of the atomic vapor of Rb (g) may take place in the initial stage of heating.³⁾ From these results it is concluded that the observed vapor species is RbBO₂ (g) for glass samples 33 and 34, and are RbBO₂ (g) and Rb₂(BO₂)₂ (g) for

Fig. 1. Partial pressures of RbBO₂ (g) and Rb₂(BO₂)₂ (g) for glass samples in Table 1 and RbBO₂ (s).

other samples in Table 1.

On the basis of the assignment of the ion species, the partial pressures of RbBO_2 (g) were calculated from the measured intensities of the Rb^+ and RbBO_2^+ ions and those of $\text{Rb}_2(\text{BO}_2)_2$ (g) from the Rb_2BO_2^+ ion in the above temperature range. Logarithms of these partial pressures are plotted against reciprocal temperatures in Fig. 1. The partial pressures of RbBO_2 (g) and $\text{Rb}_2(\text{BO}_2)_2$ (g) for RbBO_2 (s)¹⁷⁾ are also shown in Fig. 1 as a reference. All the values lie on the respective straight lines drawn by the least squares method.

The partial pressures of $\text{Rb}_2(\text{BO}_2)_2$ (g) for glass samples 33 and 34 can be estimated from the measured partial pressures of RbBO_2 (g) by combining with the thermodynamic properties of $\text{Rb}_2(\text{BO}_2)_2$ (g).¹⁸⁾ At 1000 K, the estimated partial pressures of $\text{Rb}_2(\text{BO}_2)_2$ (g) for glass samples 33 and 34 are 5.2×10^{-7} Pa and 1.3×10^{-7} Pa, respectively. These values are below the sensitivity limit of the mass spectrometer.

3.2 Thermodynamic properties

Information on the chemical activities and activity coefficients of the RbBO_2 and SiO_2 components in rubidium borosilicate melts is very useful for the evaluation of the degree of the interaction between both components. The chemical activity and activity coefficient of the RbBO_2 component can be calculated from the partial pressures of monomer RbBO_2 (g) and dimer $\text{Rb}_2(\text{BO}_2)_2$ (g) for the melts and pure RbBO_2 (s)¹⁷⁾ by using the following equations:

$$a(\text{RbBO}_2) = \frac{p(\text{RbBO}_2)}{p^0(\text{RbBO}_2)}, \quad (2)$$

$$a(\text{RbBO}_2) = \left\{ \frac{p(\text{Rb}_2(\text{BO}_2)_2)}{p^0(\text{Rb}_2(\text{BO}_2)_2)} \right\}^{0.5}, \quad (3)$$

$$\gamma(\text{RbBO}_2) = \frac{a(\text{RbBO}_2)}{N(\text{RbBO}_2)}. \quad (4)$$

Here, a is the chemical activity, p the partial pressure for melt, p^0 the partial pressure for RbBO_2 (s) as a standard substance, γ the activity coefficient, and N the molar fraction. Table 2 shows the chemical activities obtained by the monomer and dimer methods, their average values, and the activity coefficients at 1000 K. The chemical activity is also obtained by the monomer-dimer method by the use of the equation:

Table 2. Chemical Activities and Activity Coefficients of RbBO_2 in the RbBO_2 - SiO_2 System at 1000 K

Glass	$N(\text{RbBO}_2)$	$a(\text{RbBO}_2)$				$\gamma(\text{RbBO}_2)$
		Monomer method	Dimer method	Average	Monomer-dimer method	
31	0.87	0.66	0.72	0.69	0.65	0.79
30	0.67	0.26	0.28	0.27	0.31	0.40
29	0.50	7.4×10^{-2}	8.5×10^{-2}	8.0×10^{-2}	9.0×10^{-2}	0.16
12	0.40	1.7×10^{-2}	3.0×10^{-2}	2.4×10^{-2}	2.8×10^{-2}	6.0×10^{-2}
32	0.25	1.3×10^{-2}	1.4×10^{-2}	1.4×10^{-2}	1.3×10^{-2}	5.6×10^{-2}
33	0.13	2.3×10^{-3}	—	—	—	1.8×10^{-2}
34	0.077	9.9×10^{-4}	—	—	—	1.3×10^{-2}

$$a(\text{RbBO}_2) = \left\{ \frac{I(\text{RbBO}_2^+)}{I(\text{Rb}_2\text{BO}_2^+)} \right\} \left\{ \frac{I^0(\text{RbBO}_2^+)}{I^0(\text{Rb}_2\text{BO}_2^+)} \right\}^{-1}, \quad (5)$$

where I^0 is the measured intensity of the ion formed from the vapor for RbBO₂ (s). These values are listed in Table 2 for comparison.

As can be seen in Table 2, the agreement of the average chemical activities with those by the monomer-dimer method is good for glass samples 31, 30, 29, 12, and 32. These results show that the values calculated from the partial pressures are valid. Thus, by adding the values evaluated by only the monomer method for glass samples 33 and 34 to the average ones for glass samples 31, 30, 29, 12, and 32, the chemical activities of the RbBO₂ component are determined in the whole composition range of the melts in the RbBO₂-SiO₂ system.

The activity coefficient of the SiO₂ component is obtained by the graphical integration of the following Gibbs-Duhem equation:

$$\ln \gamma(\text{SiO}_2) = -\alpha(\text{RbBO}_2)N(\text{RbBO}_2)N(\text{SiO}_2) - \int_{N(\text{SiO}_2)=1}^{N(\text{SiO}_2)=N(\text{SiO}_2)} \alpha(\text{RbBO}_2) dN(\text{SiO}_2), \quad (6)$$

$$\alpha(\text{RbBO}_2) = \frac{\ln \gamma(\text{RbBO}_2)}{N^2(\text{SiO}_2)}. \quad (7)$$

Figure 2 shows the chemical activities of the RbBO₂ and SiO₂ components in the whole composition range at 1000 K. Both values exhibit negative deviations from Raoult's law.

The equation to calculate the partial molar Gibbs energies $\bar{\Delta G}$ of the RbBO₂ and SiO₂ components and the molar Gibbs energies of mixing ΔG_m from the chemical activities is:

Fig. 2. Chemical activities in the RbBO₂-SiO₂ system at 1000 K.

Table 3. Chemical Activities, Partial Molar Gibbs Energies and Molar Gibbs Energies of Mixing in the RbBO₂-SiO₂ System at 1000 K

Glass	$N(\text{SiO}_2)$	$a(\text{RbBO}_2)$	$\Delta\bar{G}(\text{RbBO}_2)$ (KJ mol ⁻¹)	$a(\text{SiO}_2)$	$\Delta\bar{G}(\text{SiO}_2)$ (KJ mol ⁻¹)	ΔG_m (KJ mol ⁻¹)
31	0.13	0.69	-3.1	9.9×10^{-4}	-57.5	-10.2
30	0.33	0.27	-10.9	2.9×10^{-2}	-29.4	-17.0
29	0.50	8.0×10^{-2}	-21.0	0.16	-15.2	-18.1
12	0.60	2.4×10^{-2}	-31.0	0.33	-9.2	-17.9
32	0.75	1.4×10^{-2}	-35.5	0.56	-4.8	-12.5
33	0.87	2.3×10^{-3}	-50.5	0.85	-1.4	-7.8
34	0.92	9.9×10^{-4}	-57.5	0.92	-0.7	-5.1

Fig. 3. Molar Gibbs energies and ideal molar Gibbs energies of mixing in the RbBO₂-SiO₂ system at 1000 K.

$$\begin{aligned}\Delta G_m &= N(\text{RbBO}_2)\Delta\bar{G}(\text{RbBO}_2) + N(\text{SiO}_2)\Delta\bar{G}(\text{SiO}_2) \\ &= N(\text{RbBO}_2)RT \ln \{a(\text{RbBO}_2)\} + N(\text{SiO}_2)RT \ln \{a(\text{SiO}_2)\} .\end{aligned}\quad (8)$$

These calculated values at 1000 K are listed in Table 3. The molar Gibbs energies of mixing are shown as a function of the molar fraction of SiO₂ in Fig. 3 together with the ideal molar Gibbs energies of mixing:

$$\Delta G_m(\text{ideal}) = -RT \{N(\text{RbBO}_2) \ln N(\text{RbBO}_2) + N(\text{SiO}_2) \ln N(\text{SiO}_2)\} .\quad (9)$$

The molar Gibbs energies of mixing show a minimum at the equal molar composition and are considerably lower than the ideal values, indicating that the melts in the RbBO₂-SiO₂ system are stable thermodynamically.

4. Conclusions

Since high level radioactive wastes are immobilized in the matrixes of borosilicate glasses, the suppression of the vaporization of their melts is very important during the vitrification process at high temperatures. In order to suppress the vaporization, the

chemical activities and the activity coefficients of the vaporizing components are required to be as low as possible. The results obtained in the present work are useful to know the degree of the suppression of the vaporization of the rubidium component from the borosilicate melts.

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Keywords

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