

MASS SPECTROMETRIC STUDY OF THE VAPORIZATION OF SODIUM BOROSILICATE GLASSES

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A mass spectrometric Knudsen effusion method has been used to study the vaporization behaviors of three sodium borosilicate glasses with the compositions of $1\text{Na}_2\text{O}-1\text{B}_2\text{O}_3-3\text{SiO}_2$ (Glass-1), $1\text{Na}_2\text{O}-1.5\text{B}_2\text{O}_3-3\text{SiO}_2$ (Glass-2) and $1.5\text{Na}_2\text{O}-1\text{B}_2\text{O}_3-3\text{SiO}_2$ (Glass-3) in the temperature range 915–1172 K. Vapor species of $\text{NaBO}_2(\text{g})$ and $\text{Na}_2(\text{BO}_2)_2(\text{g})$ have been identified over Glass-1 and Glass-2, in which the mole ratio of Na_2O to B_2O_3 is equal to and less than unity, respectively. Over Glass-3, in which the ratio is larger than unity, vapor species of $\text{Na}(\text{g})$ has been observed in addition to $\text{NaBO}_2(\text{g})$ and $\text{Na}_2(\text{BO}_2)_2(\text{g})$, and the total vapor pressure over Glass-3 is much higher as compared with those over Glass-1 and Glass-2. From the measured partial pressures of $\text{Na}(\text{g})$, $\text{NaBO}_2(\text{g})$ and $\text{Na}_2(\text{BO}_2)_2(\text{g})$, the activity coefficient of NaBO_2 in Glass-1, enthalpies of vaporization, enthalpies of formation and dissociation energies for the vapors have been determined.

1. Introduction

High-level radioactive wastes are being considered to be incorporated into various stable host matrices, most likely into sodium borosilicate glasses, for technological storage and then disposal in the deep earth underground. Vaporization behaviors of both sodium borosilicate glasses and volatile fission products, which are incorporated into the glasses, are directly related to the safety requirements for the design of off-gas systems in the vitrification processes and the storage facilities. Consequently, it is very important to accumulate the knowledge of the chemical forms of vapors and the compositional dependence of their partial pressures over various sodium borosilicate glasses.

It has been known that the vaporization of sodium oxide and boron oxide constituents is most significant for sodium borosilicate glasses [1–7]. Chemical forms (or mole ratio of the constituents) of vapors containing sodium oxide and boron oxide have been determined to be $1\text{Na}_2\text{O} \cdot 1\text{B}_2\text{O}_3(\text{g})$ from the composition in the vapor condensates [2,3,5,6] and from the change of constituent concentrations in the glasses after the vaporization [7]. By the mass spectrometric analysis, small amounts of $\text{Na}_2\text{BO}_2(\text{g})$ [5] and $\text{B}_2\text{O}_3(\text{g})$ [5] have also been detected in addition to $\text{NaBO}_2(\text{g})$ [1].

Furthermore, Wenzel and Sanders [4] have studied the densities and atomic ratio of sodium and boron vapors over a $1\text{Na}_2\text{O}-1\text{B}_2\text{O}_3-4\text{SiO}_2$ glass by a transpiration method and the influence of water vapor content of the atmosphere on the vaporization. From their study, they have found that even at low water vapor concentrations the vapor is slightly boron-rich in the sodium to boron ratio, compared to the glass which is equimolar. Namely, they have emphasized that sodium and boron does not vaporize exactly congruently from the sodium borosilicate glass. Wilds [5] has reported that when the content of sodium oxide in the sodium borosilicate glasses is increased the amount of $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$ vaporized increases exponentially. However, the correlation of the vapor species with the mole ratio of Na_2O to B_2O_3 in the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ glasses is still obscure.

In the present work, chemical forms of vapors and their partial pressures over three $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ glasses have been studied by a mass spectrometric

Table 1
Compositions of glass samples

Glass	Composition
Glass-1	$1\text{Na}_2\text{O}-1\text{B}_2\text{O}_3-3\text{SiO}_2$
Glass-2	$1\text{Na}_2\text{O}-1.5\text{B}_2\text{O}_3-3\text{SiO}_2$
Glass-3	$1.5\text{Na}_2\text{O}-1\text{B}_2\text{O}_3-3\text{SiO}_2$

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Knudsen effusion method. To make clear the influence of the mole ratios of Na_2O to B_2O_3 in the glasses on their vaporization behaviors, mole ratios are selected as shown in table 1. For Glass-1 the mole ratio of Na_2O to B_2O_3 is just equal to unity, that is, the contents of Na_2O and B_2O_3 are just in the stoichiometry for forming imaginary compound NaBO_2 in the glass. On the other hand, for Glass-2 the ratio is less than unity and for Glass-3 the ratio is larger than unity, indicating that the contents of Na_2O are in shortage and in excess of forming NaBO_2 in these glasses, respectively. The content of SiO_2 in all of the glasses is chosen by referring the composition of borosilicate glasses which have been used for the incorporation of simulated high-level radioactive wastes.

2. Experimental

Experiments were carried out with a 0.2 m radius of curvature, 90° sector single focusing Hitachi RM-6K mass spectrometer equipped with a platinum Knudsen cell in a tungsten holder. The cell has an inside diameter of 7 mm and an inside height of 9 mm. The diameter of effusion orifice is 0.5 mm. The Na_2O - B_2O_3 - SiO_2 glass samples with the mole ratios as shown in table 1 were prepared by heating mixtures of sodium carbonate, boric acid and silicon dioxide in platinum crucibles at 1200°C for 1.5 h. The samples before and after the vaporization experiments indicated no X-ray diffraction lines.

A small portion of each sample, being about 50 mg, was loaded in the Knudsen cell and heated under a background pressure less than 2×10^{-5} Pa. The temperature of the sample was measured with a well calibrated W5Re/W26Re thermocouple inserted into a hole at the bottom of the cell holder.

Vapors effusing from the cell were ionized by elec-

tron impact. Ion species were identified from peak spacings between interested ions and background ones of known masses for all the ions and further from isotopic abundance ratio for boron-containing ions. Appearance energies for the identified ions were determined by the linear extrapolation method from the ionization efficiency curves. Ion intensities were measured by raising and lowering step by step the sample temperatures to obtain the temperature dependence of partial pressures of corresponding vapor species.

The resolution of the mass spectrometer was held at about 1200 based on the 50% valley definition, except for Na_2BO_2^+ and NaO^+ ions being about 2700, to measure the intensities of above ions without interference of background ions at respective same nominal mass numbers. A beam shutter was used to measure the portion of the vapor effusing from the cell.

3. Results and discussion

3.1. Determination of vapor species

In order to study the vaporization behavior by the mass spectrometric method, a search of ion species was made at 1100 K by impacting the vapors with 53 eV electrons. By impacting with electrons of such an energy, the maximum ion intensity was obtained for all of the ions. Ion species identified for each glass are shown in table 2 together with appearance energies and vapor species. Here, the results obtained for $\text{NaBO}_2(\text{s})$ [8] are also shown as a reference, because the vaporization behavior of sodium borosilicate glasses has been pointed out to be similar to that of $\text{NaBO}_2(\text{s})$ [7].

In fig. 1 are shown ionization efficiency curves of the Na^+ ion for Glass-1, Glass-2, Glass-3 and $\text{NaBO}_2(\text{s})$. The curves for Glass-1 and Glass-2, as can be seen in

Table 2
Appearance energies and vapor species for identified ions

Ion species	Appearance energy (eV) ^{a)}				Vapor species
	$\text{NaBO}_2(\text{s})$ ^{b)}	Glass-1	Glass-2	Glass-3	
Na^+	—	—	—	5.1	$\text{Na}(\text{g})$
Na^+	4.7 ; 10.1	5.0 ; 10.2	5.0 ; 10.4	—	$\text{NaBO}_2(\text{g})$
NaBO_2^+	9.2	9.2	9.6	9.4	$\text{NaBO}_2(\text{g})$
Na_2BO_2^+	9.6	10.2	10.1	9.8	$\text{Na}_2(\text{BO}_2)_2(\text{g})$
NaO^+	16.8	—	—	—	$\text{NaBO}_2(\text{g})$
B^+	21.2 ; 32.5	—	—	—	$\text{NaBO}_2(\text{g})$

^{a)} Estimated error is ± 0.5 eV.

^{b)} Identification of Na^{2+} , $\text{Na}_3(\text{BO}_2)_2^+$, Na_2^+ , Na_2O^+ , BO^+ , BO_2^+ and BO_2^- ions has been further made.

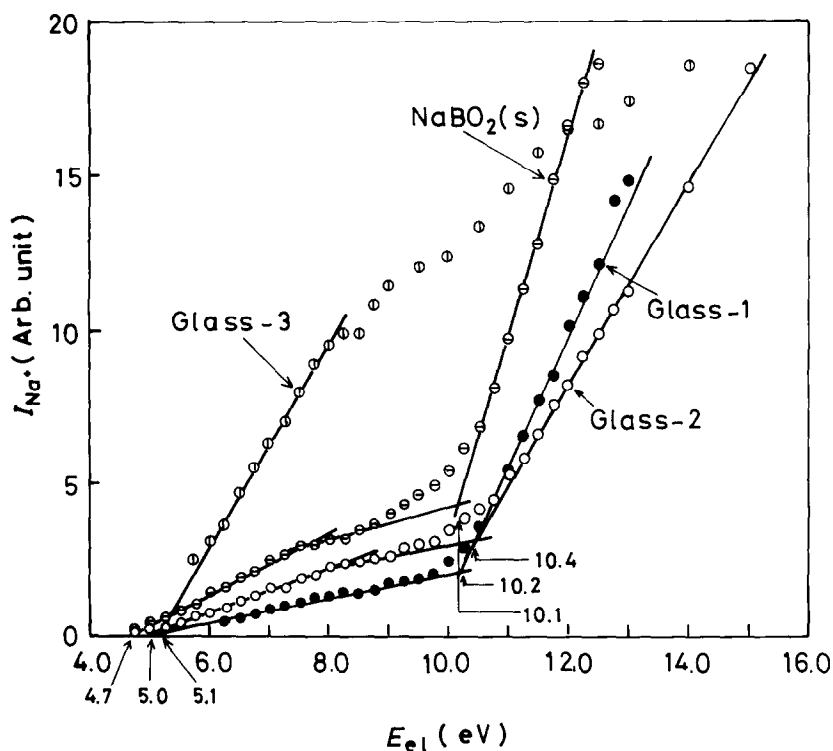


Fig. 1. Ionization efficiency curves of the Na^+ ion obtained from Glass-1, Glass-2, Glass-3 and $\text{NaBO}_2(\text{s})$.

fig. 1, show distinct breaks at about 10.5 eV electron energy, being similar to that for $\text{NaBO}_2(\text{s})$ [8]. It has been well established that the process for the formation of the Na^+ ion with $A(\text{Na}^+) = 10.1 \pm 0.5$ eV for $\text{NaBO}_2(\text{s})$ is the dissociative ionization from $\text{NaBO}_2(\text{g})$ and that with $A(\text{Na}^+) = 4.7 \pm 0.5$ eV is the positive-negative ion formation from $\text{NaBO}_2(\text{g})$ [9]. Consequently, the vapor species corresponding to the Na^+ ion for Glass-1 and Glass-2 is concluded to be $\text{NaBO}_2(\text{g})$. In contrast, the shape of the curve for Glass-3 differs from those for Glass-1, Glass-2 and $\text{NaBO}_2(\text{s})$, and only the value of $A(\text{Na}^+) = 5.1 \pm 0.5$ eV is obtained as an appearance energy for the Na^+ ion without a break in the curve at about 10.5 eV. This means that the origin of the Na^+ ion may not be considered to be only $\text{NaBO}_2(\text{g})$. Taking into account a value of the ionization energy of the $\text{Na}(\text{g})$ vapor $I(\text{Na}^+) = 5.139$ eV [10], one can emphasize that the vapor species corresponding to the Na^+ ion for Glass-3 is a mixture of large and small amounts of $\text{Na}(\text{g})$ and $\text{NaBO}_2(\text{g})$, respectively.

Appearance energies of the NaBO_2^+ and Na_2BO_2^+ ions for all of the glasses are in agreement with those for $\text{NaBO}_2(\text{s})$ within errors, respectively, leading to the

conclusion that the ionization process for the formation of the NaBO_2^+ ion is the simple ionization of $\text{NaBO}_2(\text{g})$ and that for the Na_2BO_2^+ ion is the dissociative ionization from $\text{Na}_2(\text{BO}_2)_2(\text{g})$. The vapor species corresponding to the Na_2BO_2^+ ion is not $\text{Na}_2\text{BO}_2(\text{g})$ reported by Wilds [5]. Intensities of the NaO^+ and B^+ ions for all the glasses were too weak to determine their appearance energies. However, it is clear from the ionization study of the vapors over $\text{NaBO}_2(\text{s})$ [9] that the processes for the formation of the NaO^+ and B^+ ions are also the dissociative ionization from $\text{NaBO}_2(\text{g})$.

In the study of the ionization process of the vapors over $\text{NaBO}_2(\text{s})$ [9], the following minor ions: Na^{2+} , $\text{Na}_3(\text{BO}_2)_2^+$, Na_2^+ , Na_2O^+ , BO^+ , BO_2^+ and BO_2^- have been further found in addition to the ions in table 2. However, no finding could be made for such ions in the mass spectra of vapors over the glasses.

Any ions, which are evidently corresponding to the vapors containing boron such as $\text{B}(\text{g})$, $\text{BO}(\text{g})$, $\text{BO}_2(\text{g})$ and $\text{B}_2\text{O}_3(\text{g})$ could not be identified for all the glasses. Furthermore, no identification could be made for the following vapor species: $\text{Si}(\text{g})$, $\text{SiO}(\text{g})$, $\text{SiO}_2(\text{g})$ and $\text{Na}_2\text{SiO}_3(\text{g})$.

Shultz et al. [11] have studied the vapor species over

Table 3
Summary of vapor species over sodium metaborate, sodium borosilicate glasses and sodium borogermanate glasses

Material	Temperature (K)	Vapor species	
Composition	Na ₂ O/B ₂ O ₃		
NaBO ₂ ^{a)}	= 1	1123	NaBO ₂ (g), Na ₂ (BO ₂) ₂ (g), Na ₃ (BO ₂) ₃ (g)
1Na ₂ O-1B ₂ O ₃ -3SiO ₂	= 1	1100	NaBO ₂ (g), Na ₂ (BO ₂) ₂ (g)
1Na ₂ O-1.5B ₂ O ₃ -3SiO ₂	< 1	1100	NaBO ₂ (g), Na ₂ (BO ₂) ₂ (g)
1.5Na ₂ O-1B ₂ O ₃ -3SiO ₂	> 1	1100	Na(g), NaBO ₂ (g), Na ₂ (BO ₂) ₂ (g)
1Na ₂ O-7.2B ₂ O ₃ -1.8GeO ₂ ^{b)}	< 1	1273	NaBO ₂ (g), Na ₂ (BO ₂) ₂ (g)
4Na ₂ O-3B ₂ O ₃ -3GeO ₂ ^{b)}	> 1	1273	Na(g), O ₂ (g), NaBO ₂ (g)
4Na ₂ O-1.2B ₂ O ₃ -4.8GeO ₂ ^{b)}	> 1	1273	Na(g), O ₂ (g), NaBO ₂ (g)

^{a)} Ref. [9].

^{b)} Ref. [11].

sodium borogermanate glasses with the compositions of 1Na₂O-7.2B₂O₃-1.8GeO₂, 4Na₂O-3B₂O₃-3GeO₂ and 4Na₂O-1.2B₂O₃-4.8GeO₂, in which germanium is used in stead of silicon in the IV-b group of the periodical table. From their mass spectrometric study, they have reported that NaBO₂(g) and Na₂(BO₂)₂(g) are found at 1273 K in vapors over the 1Na₂O-7.2B₂O₃-1.8GeO₂ glass, in which the mole ratio of Na₂O to B₂O₃ is less than unity and that the vapors over both 4Na₂O-3B₂O₃-3GeO₂ and 4Na₂O-1.2B₂O₃-4.8GeO₂ glasses, in which the ratio is larger than unity, contain Na(g), O₂(g) and NaBO₂(g). Namely, the vaporization of Na(g) can be observed over the sodium borogermanate glasses with the ratio of Na₂O to B₂O₃ being larger than unity. This vaporization trend is just similar to the case of the present sodium borosilicate glasses as shown in table 3, although oxygen has not been detected in the present glasses.

The knowledge about the influence of the mole ratio of the constituents in the Na₂O-B₂O₃-SiO₂ glasses on their vaporization behaviors offers very useful guide for the decision of the composition in sodium borosilicate glasses as a host matrix which will be used for the incorporation of actual high-level radioactive wastes in the near future. The sodium borosilicate glass such as Glass-3, from which Na(g) vaporizes, should be avoided its use as a matrix glass, because the condensation of atomic sodium vapor might lead to the appearance of many troublesome problems and further, as will be described in the following section, the total vapor pressure over Glass-3 becomes high.

3.2. Partial pressures of vapor species

The measured ion intensity I_i of the vapor species i was converted into corresponding partial pressure p_i at

the sample temperature T by the relation $p_i = kI_iT/\sigma_i g_i n_i$, where k the pressure calibration constant, σ_i the relative ionization cross-section, g_i the gain of the electron multiplier and n_i the isotopic abundance ratio.

In the case of the Glass-3, three ionization processes, that is, the simple ionization of Na(g), the dissociative ionization from NaBO₂(g) and the positive-negative ion formation from NaBO₂(g) are contributed to the formation of the Na⁺ ion. Among them the portion of the Na⁺ ion from Na(g) may be measured with ionizing electrons of 8.1 eV energy, which is 3 eV above the ionization energy of the sodium vapor. Under this electron impact, the Na⁺ ion by the dissociative ionization process from NaBO₂(g) does not form and that by the ion pair formation from NaBO₂(g) is negligible small. Furthermore, the intensity of the Na⁺ ion for Glass-3 decreased initially with the lapse of time and then reached plateau, although those of other ions were very stable for many hours. Consequently, the measured intensity of the Na⁺ ion under 8.1 eV electron impact within the plateau region was used for the evaluation of the partial pressure of Na(g) over Glass-3.

Since the contribution of the NaO⁺ and B⁺ ions to the partial pressures of NaBO₂(g) was negligibly small, the pressures were evaluated from both of the measured intensities of the NaBO₂⁺ and Na⁺ ions under 53 eV electron impact. Unfortunately, for Glass-3 another portion of the Na⁺ ion formed from only NaBO₂(g) could not be discriminated experimentally from Na(g). Therefore, the intensity of the NaBO₂⁺ ion and that of the Na⁺ ion, which was estimated by multiplying the intensity of the NaBO₂⁺ ion by a factor of $I_{\text{Na}^+}/I_{\text{NaBO}_2^+} = 7.0 \pm 4.0$, were used to obtain the partial pressure of NaBO₂(g) over Glass-3. The above intensity ratio of the Na⁺ ion to the NaBO₂⁺ ion formed from NaBO₂(g) under 53 eV electron impact was obtained by taking an

average of many measurements for Glass-1 and Glass-2.

Partial pressures of $\text{Na}_2(\text{BO}_2)_2(\text{g})$ over all the glasses were determined from the intensities of the Na_2BO_2^+ ion under 53 eV electron impact.

The silver reference method was used to obtain the values of k . In this method, the intensities of the Ag^+ ion were measured under 37 eV electron impact, where the maximum Ag^+ ion intensity was obtained, and under 10.6 eV, which was 3 eV above the ionization energy of the silver vapor $I(\text{Ag}^+) = 7.576$ eV [10]. Then, the values of k obtained from the Ag ion intensities under the former electron impact were used to convert the intensities of the Na^+ and NaBO_2^+ ions under 53 eV into the partial pressure of $\text{NaBO}_2(\text{g})$ and also to convert those of the Na_3BO_2^+ ion under 53 eV into $\text{Na}_2(\text{BO}_2)_2(\text{g})$ over all the glasses. The values obtained are $k = (2.70 \pm 0.54) \times 10^{13}$ Pa · at%/A · K for Glass-1, $(2.92 \pm 0.44) \times 10^{13}$ Pa · at%/A · K for Glass-2 and $(2.39 \pm 0.24) \times 10^{13}$ Pa · at%/A · K for Glass-3. A value of $k = (4.83 \pm 0.49) \times 10^{13}$ Pa · at%/A · K obtained under the latter electron impact was used to convert the intensity of the Na^+ ion under 8.1 eV into the partial pressure of $\text{Na}(\text{g})$ over Glass-3.

Ionization cross-section for $\text{Na}(\text{g})$ was taken from Mann [12] to be $\sigma_{\text{Na}} = 4.02$ and those for $\text{NaBO}_2(\text{g})$ and $\text{Na}_2(\text{BO}_2)_2(\text{g})$ were estimated by the same method as described by Kordis and Gingerich [13] to be $\sigma_{\text{NaBO}_2} = 5.15$ and $\sigma_{\text{Na}_2(\text{BO}_2)_2} = 7.73$ under the assumption that the cross sections for the simple ionization and dissociative ionization of molecules are equal. Multiplier gains were measured by the pulse counting method [14] to be $\sigma_{\text{Na}^+} = 1.5 \times 10^6$, $g_{\text{NaBO}_2^+} = 1.8 \times 10^6$ and $g_{\text{Na}_2\text{BO}_2^+} = 1.6 \times 10^6$. Isotopic abundance ratios for ^{11}B and ^{16}O were taken from ref. [15] to be $m_{11\text{B}} = 81.17\%$ and $m_{16\text{O}} = 99.76\%$.

The determined partial pressures of $\text{Na}(\text{g})$, $\text{NaBO}_2(\text{g})$ and $\text{Na}_2(\text{BO}_2)_2(\text{g})$ over the glasses are shown as a function of reciprocal temperature in fig. 2 along with the data over $\text{NaBO}_2(\text{s})$ [8] for comparison. As can be seen in fig. 2, the partial pressure of $\text{NaBO}_2(\text{g})$ and $\text{Na}_2(\text{BO}_2)_2(\text{g})$ over the glasses are lower than those over $\text{NaBO}_2(\text{s})$ [8], respectively, but they are almost the same order, respectively, for all the glasses, that is, they are not influenced markedly by the mole ratio of Na_2O to B_2O_3 in the glasses. In contrast, the partial pressure of $\text{Na}(\text{g})$ over Glass-3 is much higher, leading to the result that the total vapor pressure over Glass-3 is high as compared with Glass-1 and Glass-2. This means that the use of such a glass as Glass-3, in which the mole ratio of Na_2O to B_2O_3 is larger than unity, is unsuitable for a host matrix glass as has been pointed out already. The partial pressures of $\text{Na}_3(\text{BO}_2)_3(\text{g})$ could not be

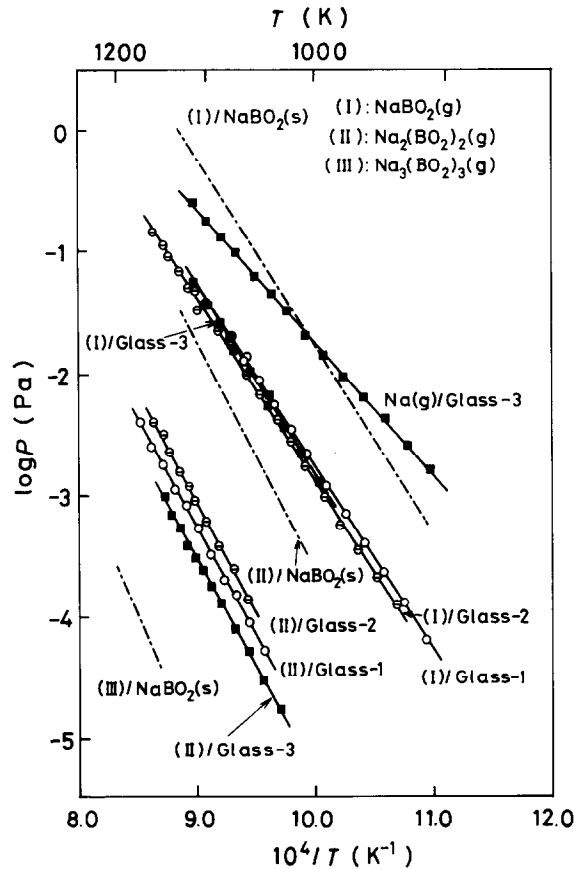


Fig. 2. Partial pressures of $\text{Na}(\text{g})$, $\text{NaBO}_2(\text{g})$, $\text{Na}_2(\text{BO}_2)_2(\text{g})$ and $\text{Na}_3(\text{BO}_2)_3(\text{g})$ over Glass-1, Glass-2, Glass-3 and $\text{NaBO}_2(\text{s})$.

obtained over the glasses.

The data for the partial pressures were fitted by the linear least squares method. The resulting equations are as follows:

for Glass-1,

$$\log p_{\text{NaBO}_2} = (12.28 \pm 0.08) - (15.06 \pm 0.08)10^3/T \quad (915-1100 \text{ K}),$$

$$\log p_{\text{Na}_2(\text{BO}_2)_2} = (12.83 \pm 0.15) - (17.88 \pm 0.16)10^3/T \quad (1045-1172 \text{ K}),$$

for Glass-2,

$$\log p_{\text{NaBO}_2} = (12.33 \pm 0.08) - (15.21 \pm 0.08)10^3/T \quad (936-1158 \text{ K}),$$

$$\log p_{\text{Na}_2(\text{BO}_2)_2} = (13.55 \pm 0.26) - (18.46 \pm 0.29)10^3/T \quad (1060-1158 \text{ K}),$$

for Glass-3,

$$\log p_{\text{Na}} = (9.22 \pm 0.08) - (10.94 \pm 0.08)10^3/T$$

(915–1115 K),

$$\log p_{\text{NaBO}_2} = (12.84 \pm 0.26) - (15.67 \pm 0.27)10^3/T$$

(996–1112 K),

$$\log p_{\text{Na}_2(\text{BO}_2)_2} = (12.49 \pm 0.10) - (17.79 \pm 0.11)10^3/T$$

(1030–1144 K),

where the unit of pressure is Pascal. The errors quoted in the above equations are the standard deviation of the slopes and intercepts, respectively. However, uncertainties in the partial pressures arise from errors in the measurements of ion intensities and also in factors used for the conversions of the intensities into the corresponding partial pressures. From these errors the uncertainties in the partial pressures are estimated to be $\Delta p_i/p_i = 0.6$, except for the partial pressure of $\text{NaBO}_2(\text{g})$ over Glass-3 being $\Delta p/p = 0.9$.

3.3. Activity coefficient of NaBO_2 in Glass-1

Under the assumption that Glass-1 consists of pseudo binary component system $1\text{NaBO}_2\text{--}1.5\text{SiO}_2$, the activity coefficient of NaBO_2 in Glass-1 can be calculated by the following equations:

$$\gamma_{\text{NaBO}_2} = \frac{p_{\text{NaBO}_2}}{p_{\text{NaBO}_2}^\circ} \times \frac{1}{0.4} \quad (1)$$

from the partial pressures of $\text{NaBO}_2(\text{g})$, and

$$\gamma_{\text{NaBO}_2} = \left(\frac{p_{\text{Na}_2(\text{BO}_2)_2}}{p_{\text{Na}_2(\text{BO}_2)_2}^\circ} \right)^{1/2} \times \frac{1}{0.4} \quad (2)$$

from those of $\text{Na}_2(\text{BO}_2)_2(\text{g})$ over Glass-1 and $\text{NaBO}_2(\text{s})$ [8]. Here, p is the partial pressure over Glass-1, p° is the partial pressure over $\text{NaBO}_2(\text{s})$ [8] and an amount of 0.4 is the mole fraction of NaBO_2 in Glass-1.

At 1100 K, the partial pressures are measured to be $p_{\text{NaBO}_2} = 0.039$ Pa, $p_{\text{NaBO}_2}^\circ = 0.44$ Pa [8], $p_{\text{Na}_2(\text{BO}_2)_2} = 3.8 \times 10^{-4}$ Pa and $p_{\text{Na}_2(\text{BO}_2)_2}^\circ = 0.013$ Pa [8] with the uncertainty of $\Delta p/p = \Delta p^\circ/p^\circ = 0.6$. Thus, one can obtain $\gamma_{\text{NaBO}_2} = 0.22 \pm 0.19$ from eq. (1) and $\gamma_{\text{NaBO}_2} = 0.43 \pm 0.18$ from eq. (2). The agreement of both values is good within errors.

Wenzel and Sanders [4] have obtained an activity coefficient of NaBO_2 in a $1\text{Na}_2\text{O--}1\text{B}_2\text{O}_3\text{--}4\text{SiO}_2$ glass to be $\gamma_{\text{NaBO}_2} = 0.18$ at 1583 K from the measurement of vapor densities of sodium and boron over their glass sample. The present values as well as the value by Wenzel and Sanders [4] indicate some negative deviation from ideal solution.

3.4. Thermochemical quantities for vaporization

The partial pressures of $\text{NaBO}_2(\text{g})$ have been determined from both intensities of the Na^+ and NaBO_2^+ ions formed from $\text{NaBO}_2(\text{g})$ under electron impact. However, as has been described in section 3.2, the intensity of the Na^+ ion is much higher as compared with that of the NaBO_2^+ ion. Consequently, the temper-

Table 4
Second-law enthalpies ($\text{kJ} \cdot \text{mol}^{-1}$) of vaporization and gaseous reaction

	$\text{NaBO}_2(\text{s})$	Glass-1	Glass-2	Glass-3
$\Delta H_v^\circ(\text{Na}, \text{g})$	–	–	–	210.2 ± 1.5 ^{g)}
$\Delta H_v^\circ(\text{NaBO}_2, \text{g})$	286.1 ± 4.8 ^{a)}	290.1 ± 3.6 ^{d)}	276.7 ± 3.3 ^{f)}	300.0 ± 5.2 ^{h)}
$\Delta H_v^\circ(\text{Na}_2(\text{BO}_2)_2, \text{g})$	360.2 ± 3.3 ^{b)}	342.3 ± 3.1 ^{e)}	353.2 ± 5.6 ^{e)}	340.6 ± 2.1 ⁱ⁾
$\Delta H_v^\circ(\text{Na}_3(\text{BO}_2)_3, \text{g})$	425.5 ± 19.0 ^{c)}	–	–	–
$\Delta H_r^\circ(2\text{NaBO}_2(\text{g}) \rightleftharpoons \text{Na}_2(\text{BO}_2)_2(\text{g}))$	-212.0 ± 10.2 ^{b)}	-237.9 ± 7.8 ^{e)}	-200.2 ± 8.7 ^{e)}	-259.4 ± 7.5 ⁱ⁾
$\Delta H_r^\circ(3\text{NaBO}_2(\text{g}) \rightleftharpoons \text{Na}_3(\text{BO}_2)_3(\text{g}))$	-423.5 ± 23.8 ^{c)}	–	–	–

a) 1071 K.

b) 1066 K.

c) 1175 K.

d) 1031 K.

e) 1109 K.

f) 1069 K.

g) 1015 K.

h) 1054 K.

i) 1087 K.

ature dependence of the determined partial pressures of $\text{NaBO}_2(\text{g})$ is extremely influenced by the dependence of the Na^+ ion. Since it has been pointed out that the Na^+ ion by the dissociative ionization process from $\text{NaBO}_2(\text{g})$ would probably be formed with kinetic energy and that such kinetic energy shows some spurious effect on the dependence of the Na^+ ion [16–18], one can not obtain second-law enthalpies of vaporization for $\text{NaBO}_2(\text{g})$ from the slopes of the partial pressure equations mainly from the Na^+ ion. For this reason, the second-law enthalpies of vaporization for $\text{NaBO}_2(\text{g})$ $\Delta H_v^\circ(\text{NaBO}_2, \text{g})$ were determined from the slopes of the relation of $\log IT = a - b/T$ by the use of the intensity of the NaBO_2^+ ion formed by the simple ionization process of $\text{NaBO}_2(\text{g})$. The product of the ion intensity and temperature has been known to be proportional to the partial pressure of the corresponding vapor species [19].

The second-law enthalpies of vaporization for $\text{Na}_2(\text{BO}_2)_2(\text{g})$ $\Delta H_v^\circ(\text{Na}_2(\text{BO}_2)_2, \text{g})$, however, were evaluated from the slopes in their partial pressure equations, because only Na_2BO_2^+ ion, which was formed by the dissociative ionization process, was identified for $\text{Na}_2(\text{BO}_2)_2(\text{g})$. In addition, the second-law enthalpy of vaporization for $\text{Na}(\text{g})$ from Glass-3 was also obtained from the slope in its partial pressure equation.

The second-law enthalpies of gaseous reaction for $2\text{NaBO}_2(\text{g}) \rightleftharpoons \text{Na}_2(\text{BO}_2)_2(\text{g})$ $\Delta H_r^\circ(2\text{NaBO}_2(\text{g}) \rightleftharpoons \text{Na}_2(\text{BO}_2)_2(\text{g}))$ were calculated by subtracting twice $\Delta H_v^\circ(\text{NaBO}_2, \text{g})$ from $\Delta H_v^\circ(\text{Na}_2(\text{BO}_2)_2, \text{g})$.

These values are listed in table 4, where those over $\text{NaBO}_2(\text{s})$, including the values for $\text{Na}_3(\text{BO}_2)_3(\text{g})$, are shown for comparison. Among the enthalpies of vaporization for the glasses, the values of $\Delta H_v^\circ(\text{NaBO}_2, \text{g})$ are less than those of $\Delta H_v^\circ(\text{Na}_2(\text{BO}_2)_2, \text{g})$. This trend can

be easily understood from the fact that the partial pressures of $\text{NaBO}_2(\text{g})$ are higher than those of $\text{Na}_2(\text{BO}_2)_2(\text{g})$. The value of $\Delta H_v^\circ(\text{Na}, \text{g})$ from Glass-3 is much smaller, as predicted from high partial pressure of $\text{Na}(\text{g})$. The values of $\Delta H_v^\circ(\text{NaBO}_2, \text{g})$ and $\Delta H_v^\circ(\text{Na}_2(\text{BO}_2)_2, \text{g})$ as well as $\Delta H_r^\circ(2\text{NaBO}_2(\text{g}) \rightleftharpoons \text{Na}_2(\text{BO}_2)_2(\text{g}))$ over the glasses are not greatly different from those over $\text{NaBO}_2(\text{s})$ [8], respectively.

Yamanaka et al. [3] have obtained an apparent activation energy for total vaporization rate from a $1\text{Na}_2\text{O}-2\text{B}_2\text{O}_3-2\text{SiO}_2$ glass in which the mole ratio of Na_2O to B_2O_3 is less than unity, to be $273 \text{ kJ} \cdot \text{mol}^{-1}$. Terai and Kosaka [7] have reported that apparent activation energies for total vaporization rates from various borosilicate glasses are obtained to be, in many case, about $210-250 \text{ kJ} \cdot \text{mol}^{-1}$ and that these are in rough agreement with those from $\text{B}_2\text{O}_3(\text{l})$, $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3(\text{l})$ and $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3(\text{l})$ by Cole and Taylor [20]. The values of $\Delta H_v^\circ(\text{Na}, \text{g})$, $\Delta H_v^\circ(\text{NaBO}_2, \text{g})$ and $\Delta H_v^\circ(\text{Na}_2(\text{BO}_2)_2, \text{g})$ obtained in the present work are not apparent activation energies for total vaporization rates under non-equilibrium condition but enthalpies of vaporization for respective vapor species under equilibrium one. Theoretically, the apparent activation energy obtained under non-equilibrium condition should be larger than or equal to the enthalpy under equilibrium. The amount of $273 \text{ kJ} \cdot \text{mol}^{-1}$ obtained by Yamanaka et al. [3] is comparable with the present value of $\Delta H_v^\circ(\text{NaBO}_2, \text{g}) = 276.7 \pm 3.3 \text{ kJ} \cdot \text{mol}^{-1}$ for Glass-2, in which the mole ratio of Na_2O to B_2O_3 is less than unity. In many borosilicate glasses studied by Terai and Kosaka [7], the mole ratio of alkali metal oxides to B_2O_3 is larger than unity. Consequently, the vaporization of atomic alkali metal vapors might occur, thereby lowering the apparent activation energies for

Table 5

Second-law enthalpies of formation ($\text{kJ} \cdot \text{mol}^{-1}$) and dissociation energies ($\text{kJ} \cdot \text{mol}^{-1}$) between Na and BO_2 bonds for $\text{NaBO}_2(\text{g})$, $\text{Na}_2(\text{BO}_2)_2(\text{g})$ and $\text{Na}_3(\text{BO}_2)_3(\text{g})$

	$\text{NaBO}_2(\text{s})$	Glass-1	Glass-2	Glass-3
$\Delta H_f^\circ(\text{NaBO}_2, \text{g})$	-639.2 ± 5.1 ^{a)}	–	–	–
$\Delta H_f^\circ(\text{Na}_2(\text{BO}_2)_2, \text{g})$	$-1509.5-14.4$ ^{b)}	-1536.9 ± 12.8 ^{d)}	-1499.2 ± 13.4 ^{d)}	-1563.0 ± 12.7 ^{e)}
$\Delta H_f^\circ(\text{Na}_3(\text{BO}_2)_3, \text{g})$	-2373.5 ± 28.3 ^{c)}	–	–	–
$D^\circ(\text{Na}-\text{BO}_2)$	462.5 ± 9.8 ^{a)}	–	–	–
$D^\circ(\text{Na}_2(\text{BO}_2)_2)$	1137.5 ± 22.1 ^{b)}	1164.1 ± 21.1 ^{d)}	1126.4 ± 21.5 ^{d)}	1190.6 ± 21.1 ^{e)}
$D^\circ(\text{Na}_3(\text{BO}_2)_3)$	1812.8 ± 37.9 ^{c)}	–	–	–

^{a)} Third-law value at 298 K [8].

^{b)} 1066 K.

^{c)} 1175 K.

^{d)} 1109 K.

^{e)} 1087 K.

total vaporization rates. Indeed, the amounts of 210–250 kJ·mol⁻¹ reported by Terai and Kosaka [7] are somewhat large or comparable with the present value of $\Delta H_v^\circ(\text{Na}, \text{g}) = 210.2 \pm 1.5 \text{ kJ} \cdot \text{mol}^{-1}$ for Glass-3, in which the mole ratio of Na₂O to B₂O₃ is larger than unity.

The enthalpy of formation and the dissociation energy between Na and BO₂ bond for NaBO₂(g) may be derived by combining the enthalpy of vaporization for NaBO₂(g) from NaBO₂(s) [8] with the enthalpy of formation for NaBO₂(s) [21], and further by combining with the enthalpies of formation for Na(g) [22] and BO₂(g) [22], respectively. The combination of $\Delta H_f^\circ(2\text{NaBO}_2(\text{g}) \rightleftharpoons \text{Na}_2(\text{BO}_2)_2(\text{g}))$ and $\Delta H_f^\circ(3\text{NaBO}_2(\text{g}) \rightleftharpoons \text{Na}_3(\text{BO}_2)_3(\text{g}))$ with $\Delta H_f^\circ(\text{NaBO}_2, \text{g})$ [8] and in addition with the enthalpies of formation for Na(g) [22] and BO₂(g) [22] yields the enthalpies of formation and dissociation energies of Na₂(BO₂)₂(g) and Na₃(BO₂)₃(g), respectively. These values are shown in table 5. The values of $\Delta H_f^\circ(\text{Na}_2(\text{BO}_2)_2, \text{g})$ and $D^\circ(\text{Na}_2(\text{BO}_2)_2)$ obtained from the glass samples are almost in agreement with those from NaBO₂(s) [8].

As going from NaBO₂(g) through Na₂(BO₂)₂(g) to Na₃(BO₂)₃(g), the enthalpies of formation and dissociation energies for them become large. The value of $D^\circ(\text{Na}_3(\text{BO}_2)_3)$ is approximately 1.5 times as large as that of $D^\circ(\text{Na}_2(\text{BO}_2)_2)$. Chemical structures of Na₂(BO₂)₂(g) and Na₃(BO₂)₃(g) molecules have been known to be four-member cyclic and six-member one, respectively [18,23], that is, the number of the bonds between Na and BO₂ is four for Na₂(BO₂)₂(g) and six for Na₃(BO₂)₃(g). Consequently, an additivity rule is held between $D^\circ(\text{Na}_2(\text{BO}_2)_2)$ and $D^\circ(\text{Na}_3(\text{BO}_2)_3)$.

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