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The Vaporization of the Various Trace Components from Aluminoborosilicate Glass

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The simultaneous vaporization of dopants in aluminoborosilicate glass was investigated by means of mass spectrometry using a Knudsen cell. The detected chemical species were Na, K, Ni, Zn, Rb, Ag, Te, TeO_2, and Cs in the temperature range of 650—800 °C. Their vapor pressures were 10^{-6}—10^{-4} Pa. The activation energy of vaporization was discussed in relation to the electrostatic force between the vaporizing specie and oxygen. However, lithium, alkali-earth metal elements, alomst all the transition metal elements (such as Fe, Cr, and Ru), and rare-earth metal elements were not detected in the vapor phase, though they were contained in the glass matrix.

The glass is often heated to several hundred degrees in the process of producing and using the enamel, the glass lining, or the glass matrix containing radioactive wastes. It is an important problem how many and what constituents vaporize from the glass. Numerous investigations have been reported.[1-9] They have, however, been concerned with the gross volatility[1-5] and volatility of a specified element.[2,6-9]

In this work, Knudsen's effusion cell and a mass spectrometer were used in order to determine simultaneously about thirty kinds of chemical species vaporizing from the aluminoborosilicate glasses. The volatilities of the detected elements were estimated by mean of a scale of activation energy.

Experimental

Glass Matrices. The glass matrices were SiO_2-Al_2O_3-B_2O_3-Na_2O glasses doped with a single modifier oxide (S-series) and doped with 26—35 kinds of modifier oxides (P-series). The S-series glasses were used in order to estimate the thermodynamic parameters of the vaporization of a certain modifier ion. The experimental data concerning S1 will be excluded hereinafter because neither Sr nor SrO was detected in the vapor from the S1 glass, where the SrO was the modifier oxide. The chemical compositions are shown in Table 1. The S2, S3, and S4 glass matrices were prepared in the weight ratio of $SiO_2 : B_2O_3 : Al_2O_3 : Na_2O : M_xO_y = 1 : 0.312 : 0.0797 : 0.220 : 0.0848$.

The P-series glasses were used to observe the simultaneous vaporization of the various modifier ions from the same matrix. The P5 and P7 glasses were prepared so that their frit compositions are the same as those of the S-series glasses, i.e., the weight ratio was $SiO_2 : B_2O_3 : Al_2O_3 = 1 : 0.326 : 0.0814$, but the weight ratios of the modifier oxides were different. The frit compositions of the P6 and P8 glasses were different from those of the S-series glasses. However, most of the modifier oxides of the P6 glass have a chemical composition analogous to that of the P5 glass. On the other hand the P8 glass is analogous to the P7 glass in the composition of most of the modifier oxides. The chemical compositions are listed in Table 2 in the order of (1) the components of the frit glass, (2) the components doped in the frit glass and detected in the

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Table 1. Composition of S2-S4 Glass Matrices (wt.%)

	S2	S3	S4
SiO_2	59.0	59.0	59.0
B_2O_3	18.3	18.3	18.3
Na_2O	13.0	13.0	13.0
Al_2O_3	4.7	4.7	4.7
Cs_2O	5.0	—	—
La_2O_3	—	5.0	—
TeO_2	—	—	5.0
Sum	100	100	100

Table 2. Composition of Aluminoborosilicate Glass (wt.%)

		P5	P6	P7	P8
I	SiO_2	43.22	47.2	43.47	48.49
	B_2O_3	14.07	13.5	14.15	18.58
	Na_2O	8.42	9.34	10.00	11.30
	Al_2O_3	3.52	2.41	3.54	2.00
II	K_2O	2.01	0.96	—	—
	NiO	0.49	0.49	0.23	—
	ZnO	2.01	0.96	3.03	—
	Rb_2O	0.15	0.15	0.11	0.12
	Ag_2O	—	—	0.02	0.02
	TeO_2	0.26	0.26	0.19	0.18
	Cs_2O	1.02	1.02	0.75	0.84
III	Fe_2O_3	7.41	7.41	2.04	2.96
	Li_2O	3.02	1.93	3.54	1.87
	CaO	2.01	0.96	3.03	1.86
	BaO	0.68	1.64	3.52	0.57
	ZrO_2	2.00	2.00	1.46	2.52
	MoO_3	1.99	1.99	1.45	1.57
	RuO_2	1.02	1.02	0.74	0.86
	CeO_2	1.14	1.14	3.34	1.90
	Nd_2O_3	2.50	2.50	1.38	1.48
	Cr_2O_3, MnO_2, SrO, P_2O_5, Y_2O_3, La_2O_3, Pr_6O_{11}, Sm_2O_3, Rh_2O_3, PdO	Content of each oxide is 0.01—1.0 wt.%.			
	CdO, SnO_2, SeO_2, Eu_2O_3	—	—	0.02 ≀ 0.05	0.02 ≀ 0.05
	Sb_2O_3	—	—	—	0.005

vapor phase, and (3) the components doped in the frit glass but not detected in the vapor phase.

Mass Spectrometry. The instrument used was a JEOL-1A-type mass spectrometer equipped with the Knudsen cell. The conditions of measurement were as follows:

a) Realizable limit of vapor pressure: 10^{-6}—10^{-4} Pa,
b) Deviation of ion current I: ±20%,
c) Mass resolution at m=44: 2200,
d) Ionizing electron: 27.0 kV×100 μA,
e) Potential for accelerating the ions to the electric-magnetic field: 8 kV,
f) Temperature measurement: 400—840 °C by the use of a W5Re/W26Re thermocouple.

A glass sample of about 0.5 g was set in the Knudsen cell and heated step by step, such as: room temperature $\xrightarrow{1.5h}$ 400 °C(1h) $\xrightarrow{40m}$ 500 °C(1h) $\xrightarrow{40m}$ 600 °C(1h) $\xrightarrow{20m}$ 650 °C(1h) $\xrightarrow{20m}$ 700 °C(1h) $\xrightarrow{20m}$ 750 °C(1h) $\xrightarrow{20m}$ 800 °C(1h), or as: room temperature $\xrightarrow{40m}$ arbitrary temperature(1.5h). The steady ion currents were confirmed even after 150m at 700 °C. The weight loss of the glass between before and after heating was 1.5 mg.

Results and Discussion

The Shape of Mass Peak and Correction of the Peak Height. A mass spectrum is constituted of the background (BG) peaks and the sample peaks. Since the BG peaks appear at the positions of almost all the mass numbers, the mass spectrum of BG was used as the mass marker. As the BG molecules are composed of carbon, hydrogen and oxygen, the sample peak appears at a lower mass position than the BG peak when the mass number is the same. The typical shape of a mass peak is illustrated in Fig. 1. It can be seen that the peak height of ^{39}K started to grow at 650 °C and then continued to grow exponentially as the temperature was raised.

The heights of the BG peaks are quite different because of the change in the instrumental constant. Thus, the BG peak heights at every temperatures were normalized at constant values, and the observed heights of the sample peaks were corrected using the normalizing factor.

Establishment of the Steady Flow. The ion currents became constant after 10 min when the temperature of the sample reached the arbitrary value. This means that a steady flow from the Knudsen chamber to the ionizing chamber was established. The difference in pressure between inside and outside the Knudsen cell is calculated by means of Eq. 1, itself derived from the molecular corrision theory and the Maxwellian distribution of velocities[10,11]

$$P - P_{out} = G(2\pi RT/M)^{1/2}/(Ut), \quad (1)$$

where P: Pressure inside the Knudsen cell,
P_{out}: Pressure outside the Knudsen cell, i.e., in the ionizing chamber,
G: Effusion loss through the orifice of area U in an experimental time t,
T: Temperature in the Knudsen cell,
M: Molar weight of the effusion species.

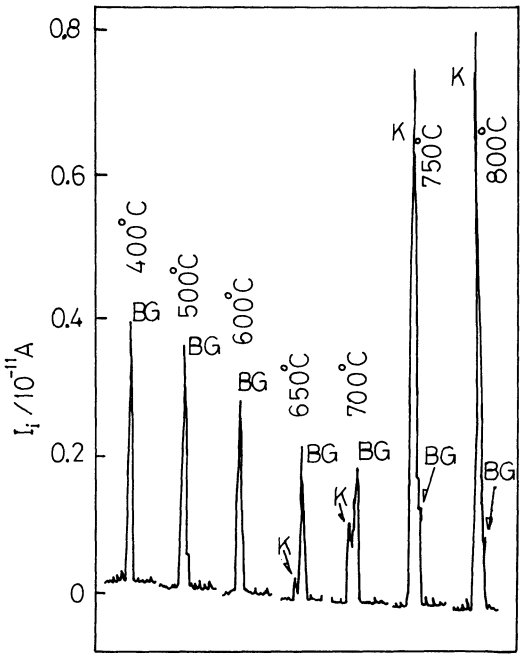

Fig. 1. Change of the mass peak pattern at m=39 for P6 glass matrix. BG: Back Ground, K: Potassium.

In view of the facts that the mean molar weight of various effusing species M is 100 g/mole and that t=4h because the effusion rate G/t increases steeply beyond 700 °C, and using the experimental values of G=1.5 mg, T=1000 K, U=0.25^2 π mm^2 and P_{out}=2×10^{-5} Pa, P=0.38 Pa was obtained. P=0.38 Pa corresponds to 3.1×10^{-9} mol from the ideal gas law, and it is comparable with the effusing rate per second G/t=1.0×10^{-9} mol s^{-1}. Thus a rapid but steady effusion and a similar vaporization were recognized.

Vaporizing Species and the Volatilities. The assignment of the chemical species was based on the agreement of the ion-beam current ratio with the natural abundance of isotopes. No parent-daughter relation was found between Na, NaO, Na_2O, and Na_2, or between Cs, CsO, and Cs_2O, by recording the ionization efficiency curves in the range of the ionizing voltage from 4 to 33 kV. Thus, it is presumed that the chemical formulae of the assigned ions are identical with those of the evaporating species.

The species vaporizing from every glass were Na, K, Rb, and Cs, but Li was not vaporized from any glass. Nickel and Zinc were vaporized from the P5 and P7 glasses, but not from the P6 glass. Tellurium was vaporized as Te from the P5, P6 and S4, while it was vaporized as Te and TeO_2 from the P7 and P8 glasses. The other modifier ions were not detected in the vapor phase of any glass. None of the network-former ions (Al, B, or their oxides) were detected in the vapor phase below 840 °C. The vaporizing species and the ion-beam currents observed are summarized in Table 3.

The ratios of the ion-beam current IT vs. the molar fractions of the positive ion in the glass matrix X are

Table 3. Observed Ion-Beam Currents ($\times 10^{-11}$ A) at Various Temperatures

	T/K	^{23}Na	^{39}K	^{58}Ni	^{64}Zn	^{85}Rb	^{107}Ag	^{130}Te	^{133}Cs	^{130}Te^{16}O$_2$
P5	933	0.4	1.0	2.4	0	.0	—	0	0.99	0
	962	1.3	3.2	8.7	0	0	—	0	1.7	0
	990	2.25	5.8	8.3	0.5	0.20	—	0.25	3.2	0
	1020	2.5	6.4	9.0	0.51	0.30	—	0.47	2.8	0
	1050	2.6	5.2	10.9	1.38	0.43	—	0.71	4.8	0
	1083	7.1	11.6	15.8	2.24	0.49	—	1.09	6.2	0
P6	989	3.77	1.88	0	0	0	—	0	1.54	0
	1022	3.66	2.42	0	0	0.535	—	0	2.53	0
	1050	5.83	4.36	0	0	0.893	—	0	12.6	0
	1077	12.6	7.69	0	0	0.654	—	0.128	8.21	0
	1110	19.3	13.6	0	0	1.61	—	0.313	15.7	0
P7	928	1.14	—	6.26	0	0.306	0.163	0	1.51	0
	960	1.11	—	14.6	0	Missed	0	0	4.6	0.043
	986	4.87	—	36.6	0	0.444	0.444	0	5.93	0.212
	1025	10.2	—	39.9	0.286	1.21	0.73	0.508	17.6	0.478
	1077	25.9	—	143	0.894	2.50	1.20	1.10	30.2	1.46
P8	930	0.881	—	—	—	0	0	0	0.610	0
	971	3.84	—	—	—	0	0	0.060	4.31	0
	1011	5.76	—	—	—	0.244	0.550	0.227	7.70	0
	1039	10.1	—	—	—	1.12	1.03	0.458	9.39	0
	1086	46.2	—	—	—	1.92	2.40	0.782	19.0	1.01
S2	933	0	—	—	—	—	—	—	0.06	—
	970	0	—	—	—	—	—	—	0.13	—
	1005	0.09	—	—	—	—	—	—	1.2	—
	1043	0.45	—	—	—	—	—	—	5.9	—
	1073	1.2	—	—	—	—	—	—	10.0	—
S3	930	0								
	979	0.016								
	1025	0.090								
	1057	0.34								
	1105	2.6								
S4	1001	0.061	—	—	—	—	—	0	—	—
	1030	0.341	—	—	—	—	—	0.120	—	—
	1060	0.807	—	—	—	—	—	0.532	—	—
	1095	2.95	—	—	—	—	—	1.11	—	—
	1110	4.8	—	—	—	—	—	1.88	—	—

Table 4. The Ratios of (Ion Current IT)/(Molar Fraction in the Glass X) at 800 °C (μA·K/mol%)

	S2	S3	S4	P5	P6	P7	P8
Li	—	—	—	0	0	0	0
Na	0.64	0.04	0.08	0.43	0.78	1.66	1.67
K	—	—	—	2.91	7.46	—	—
Rb	—	—	—	9.30	17.2	53.0	41.2
Cs	0.78	—	—	17.2	21.8	133	68.8
Ag	—	—	—	—	—	259	400
Ni	—	—	—	2.0	0	9.14	—
Zn	—	—	—	0.016	0	0.005	—
Te	—	—	0.004	0.13	0.047	0.18	0.14

shown in Table 4. The IT/X varies by several orders in magnitude with the different ions in the same glass. This means that the vaporization is incongruent. Supposing that the IT/X is a scale of the volatility, and that the species are confined to monovalent ions, silver is the most volatile; subsequently volatility order of Cs>Rb>K>Na follows silver. The exptremely high value of IT/X for silver is attributably to the rapid diffusion. The volatility of alkali metal ions is correlated with the ionic radius.

Thermodynamic Considerations. The total vapor pressure in the Knudsen cell was previously estimated as P=0.38 Pa. The partial pressure of the i-th ion P_i is proportional to the ion current I_i.[11]

$$P_i = I_i Tk/(\sigma_i S_i), \quad (2)$$

where k: Istrumental coefficient,
σ_i: Ionization cross-section,
S_i: Sensitivity coefficient of the secondary-electron multiplier.

In practice, the I_i and T are observed by means of mass spectrometry, but the estimation of the σ_i and S_i is impossible. Accordingly, the values of P_i are not

Table 5. Arrhenius Plots of the Ion-Current IT(AK); $\log(IT) = -a/T + b$

	S2		S3		S4	
	a	*b*	*a*	*b*	*a*	*b*
Na	17808	9.716	19416	9.973	19116	9.972
Te	—	—	—	—	16356	7.064
Cs	18440	9.318	—	—	—	—

	P5		P6		P7		P8	
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*
Na	7389	−0.3437	12840	5.056	10520	3.238	10740	3.486
K	6296	−1.082	10620	2.769	—	—	—	—
Ni	4766	−2.345	—	—	9098	2.616	—	—
Zn	8675	0.3754	—	—	10969	2.168	—	—
Rb	5304	−3.327	5627	−2.758	6867	−1.239	6551	−1.643
Ag	—	—	—	—	6344	−1.964	9772	1.420
Te	7705	−0.796	14505	5.148	7540	−0.9272	7145	−1.494
Cs	5579	−1.997	9774	2.027	9184	2.116	9463	2.134
TeO_2	—	—	—	—	11840	3.211	—	—

Table 6. Activation Energy ΔH_i^* (kJ mol^{-1}) and Network-Formers' Content (mol%)

	P5	P6	P7	P8	S2	S3	S4
Na	141.5	246	201.4	205.6	341.0	371.8	366.0
K	120.6	203	—	—	—	—	—
Ni	91.3	>300	174.2	—	—	—	—
Zn	166.1	>300	210.0	—	—	—	—
Rb	101.6	107.7	131.5	125.4	—	—	—
Ag	—	—	121.5	187.1	—	—	—
Te	147.5	278	144.4	136.8	—	—	313.2
Cs	106.8	187.2	175.8	181.2	353.2	—	—
$\sum_i X(i)$ (i=Si, B, Al)	60.53	63.99	60.87	67.90	77.86	78.04	78.02

determined by the use of Eq. 2.

Suppose that an *i*-th component in the glass matrix has an activation energy of vaporization, ΔH_i^*. The ΔH_i^* is, as well known, a coefficient of the Arrhenius plot of the vapor pressure:

$$\frac{d \ln P_i}{d(1/T)} = \frac{-\Delta H_i^*}{R} \tag{3}$$

By substituting Eq. 2 in Eq. 3, we obtain:

$$\frac{d \ln(I_i T)}{d(1/T)} = \frac{-\Delta H_i^*}{R} \tag{4}$$

The plots of $\ln(I_i T)$ vs. $1/T$ showed linear lines. The coefficients of lines *a* and *b* were calculated by means of the least-squares method, they are summarized in Table 5. The ΔH_i^* values were evaluated from the *a* value and Eq. 4. They were listed in Table 6. Tables 4 and 6 indicate that the volatility of Na, Te, or Cs in the S2, S3, and S4 (S-series) glasses is obviously smaller than in the P5, P6, P7, and P8 (P-series) glasses. This is attributable to the fact that the network-former ions in the S-series glass are richer than in the P-series glass: i.e., the sum of the molar fractions of Si, B, and Al in the S-series glass was about 78 mol%, while that in the P-series glass was 61—68 mol%.

From another point of view, the activation energies of monovalent modifier ions in the same glass decrease and then increase as the ionic radius increases. If the activation energy were exactly the energy needed for release from the electrostatic force between M^+ and O^{2-}, the activation energy would decrease monotonously as the ionic radius increased. Thus, another energy which increases with the increase in the ionic radius must be included in the activation energy. The high registivity of Cs against movement has been reported after the measurement of the self-diffusion coefficient. For instance, the values in $M_2O \cdot SiO_2$ glass at 500 °C are 5.8×10^{-10} cm^2 s^{-1} for M=Cs, while 2.3×10^{-8} cm^2 s^{-1} for M=Na.[13,14] It was assumed that the additional energy is elastic energy and is proportional to the cube of the ionic radius;

$$\Delta H_i^* = \Delta H_{i,\text{coul}}^* + \Delta H_{i,\text{elas}}^*, \tag{5}$$

$$\Delta H_{i,\text{coul}}^* = N\frac{2e^2\alpha}{r_o + r_i} = \frac{A}{r_o + r_i}, \tag{6}$$

$$\Delta H_{i,\text{elas}}^* = \text{Dr}_i^3. \tag{7}$$

As the Madelung constant is used to calculate the lattice energy, $\Delta H_{i,\text{coul}}^*$ is a product of $2e^2/(r_o+r_i)$ by a constant α. Thus, a simple expression, $A/(r_o+r_i)$, was obtained. It was previously noted that the observed

Table 7. Calculated and Observed Activation Energy ΔH_i^* (kJ mol^{-1})

i	r_i+r_o[a]	P5 $A=321.0$, $D=-0.244$				P6 $A=555.1$, $D=-6.89$				P7 $A=378.7$, $D=6.153$				P8 $A=455.6$, $D=1.13$			
		Calcd			Obsd	Calcd			Obsd	Calcd			Obsd	Calcd			Obsd
	nm	coul	elas	sum		coul	elas	sum		coul	elas	sum		coul	elas	sum	
Na^+	0.224	143	0	143	142	248	−4	244	246	169	4	173	201	203	1	204	206
Ag^+	0.255	—	—	—	—	—	—	—	—	148	9	157	122	179	2	181	187
K^+	0.278	115	−1	114	121	200	−18	182	203	—	—	—	—	—	—	—	—
Rb^+	0.292	110	−1	109	102	190	−24	166	108	130	22	152	132	156	4	160	125
Cs^+	0.303	106	−1	105	107	183	−30	153	187	125	27	152	176	150	5	155	181

a) Shannon's effective ionic radius of 6-coordinated ion; $r_o=0.140$ nm.[15]

ΔH_i^* showed different values depending on the mol% of the network-former ion: Si, B, and Al. The total mol% of the modifier cations and the middle ions in the P-series glasses were 32—39 mol%. This quantity is sufficient to determine the values of $\Delta H_{i,coul}^*$. It follows that a more precise chemical composition may also be effective. The A and D constants were calculated for the respective glass by the least-squares method, using the data of ΔH_i^* and Shannon's effective ionic radius.[15] The contributions of the electrostatic energy and the elastic energy to the total activation energy was summarized in Table 7. Almost all the $\Delta H_{i,calc'd}$ values are in agreement with the $\Delta H_{i,obs'd}$ values, but (1) the $\Delta H_{i,calc'd}$ values for every glass showed a monotonously decreasing curve with increase in r_o+r_i, and (2) the negative sign of D for the P5 and P6 glasses is unreasonable physically. The other functions, such as $A/(r_o+r_i)+B\exp[-(r_o+r_i)C]+Dr_i^3$ and $A/(r_o+r_i)+Dr_i^2$, gave quite unreasonable values of A, B, or C. The calculation based on the simple assumption suggested that the electrostatic energy is the major portion, while the elastic energy is a minor portion, of the activation energy.

Conclusion

When an aluminoborosilicate glass matrix is heated up to near the softening point, Na, K, Ni, Zn, Rb, Ag, Te, TeO_2, and Cs are detected in the vapor phase. The activation energy of vaporization was calculated from the Arrhenius plot of the observed ion currents.

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