

# Self-Diffusion of $^{22}\text{Na}$ and $^{137}\text{Cs}$ in Simulated Nuclear Waste Glass \*

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The knowledge of self-diffusion of various elements is important for understanding and elucidating the long-term dissolution of the nuclear waste glass. The self-diffusion coefficients of Na and Cs in P0798 simulated nuclear waste glass have been measured by an ion beam sputter-sectioning technique using the radioactive isotopes  $^{22}\text{Na}$  and  $^{137}\text{Cs}$ . The temperature dependence of the diffusion coefficients in each temperature range in P0798 glass below the glass transition temperature  $T_g$  can be expressed by the following equations:

$$(428\text{--}574\text{ K}) : D_{\text{Na--below}T_g} = 2.7 \times 10^{-6} \exp(-113 \pm 4 \text{ kJ}\cdot\text{mol}^{-1} / RT) \text{m}^2\cdot\text{s}^{-1}$$

$$(713\text{--}758\text{ K}) : D_{\text{Cs--below}T_g} = 7.1 \times 10^{-5} \exp(-241 \pm 10 \text{ kJ}\cdot\text{mol}^{-1} / RT) \text{m}^2\cdot\text{s}^{-1}$$

The diffusion coefficient of  $^{22}\text{Na}$  was about ten orders of magnitude larger than that of  $^{137}\text{Cs}$  at 573 K. The large difference in the diffusion coefficients is explained in terms of the ion size effect, the mixed-alkali effect and lower concentration of Cs compared with Na in P0798 glass.

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**Keywords:** simulated nuclear waste glass, self-diffusion, radioactive isotope  $^{22}\text{Na}$  and  $^{137}\text{Cs}$ , ion beam sputter-sectioning, glass transition temperature, leaching tests, ion size effect, mixed-alkali effect

## 1. Introduction

High-level waste (HLW), which is a by-product of reprocessing of spent nuclear fuel, contains radionuclides with long half-lives, and it should be safely isolated from the human environment for very long periods of time so as to protect the environment from any harmful effects. In the case of HLW, radionuclides are immobilized in a borosilicate glass matrix in stainless steel fabrication containers. The vitrified waste is sealed in a disposal metallic container and disposed of deep underground, far removed from the human environment.<sup>1)</sup>

The vitrified waste is one of engineered barriers, which retard the release and migration of radionuclides from the disposal system to groundwater. So it is considered as one of important subjects to assess release rate of radionuclides from vitrified waste contacted with water. To date many leaching tests have been conducted on various conditions by research institutes all over the world, and several models<sup>2-5)</sup> have been proposed based on those results.

The mechanism of elemental release from glass by diffusion was investigated from the 1960s to the early 1980s.<sup>6)</sup> Doremus<sup>7)</sup> proposed a model for the release of alkali ions from alkali silicate glass. This model describes the mechanism of elemental release by diffusion between hydrogen ion and alkali ion. Lanford *et al.*<sup>8)</sup> estimated a diffusion coefficient of sodium by applying the model by Doremus to elemental depth profile of sodium in leached soda-lime glass, and they found that the value was consistent with the self-diffusion coefficient derived from the tracer diffusion experiment. Thus the self-diffusion coefficients are closely related to the elemental release from glass contacted with water, and it is indispensable to obtain precise data of self-diffusion coefficients for assessment of release rate of radionuclides.

As to HLW disposal, the radionuclides with long half-lives are what we have to consider. Among long half-lived radionuclides in the vitrified waste, cesium-135 (half-life 2.3 m.y.) is the only soluble nuclide, and it is considered that cesium is released according to alteration of vitrified waste. Sodium is often used as an indicator of glass alteration because of its large amount in vitrified waste, but the difference of leaching behavior between cesium and sodium are not clear. Hence, in the first place, it is important to develop a model of radionuclide release and to clarify the difference of leaching behavior between cesium and sodium. Yamanaka *et al.*<sup>9)</sup> reported a self-diffusion coefficient of sodium in a simulated vitrified waste, P0798, which was obtained by tracer diffusion experiments with a grinding technique. On the other hand, there is no measured values for self-diffusion coefficients of cesium in the same glass. In this paper, we report the result of the measured self-diffusion coefficients of sodium and cesium in the P0798 glass by using tracer diffusion experiments with an ion beam sputter-sectioning technique, and discuss a relation between self-diffusion coefficients and leaching behavior.

## 2. Experimental Procedure

Simulated nuclear waste glass P0798 was used as samples whose size was  $10 \times 5 \times 1 \text{ mm}^3$ . Table 1 shows the chemical composition of the simulated nuclear waste glass P0798. The contents of glass frit in the simulated nuclear waste glass was about 75 mass% in which main components were  $\text{SiO}_2$  (46.6 mass%) and  $\text{B}_2\text{O}_3$  (14.2 mass%). The waste component was about 25%. The sample surface was ground with emery papers (#500-#1500) and was finally polished with 1 micron meter diamond paste to obtain mirror polished surface. The radioactive isotopes  $^{22}\text{Na}$  and  $^{137}\text{Cs}$  were used for tracers. The radioactive isotopes,  $^{22}\text{Na}$  and  $^{137}\text{Cs}$  were purchased from E. I. Du Pont de Nemours & Co. Inc. in the forms

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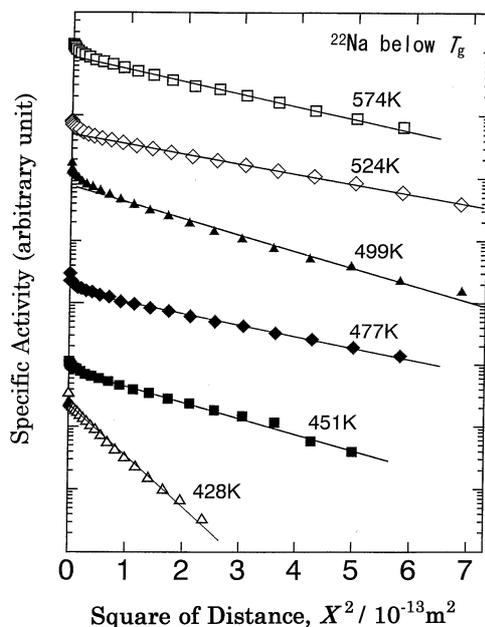
Table 1 Chemical composition of simulated nuclear waste glass (P0798).

Glass frit		Waste	
SiO <sub>2</sub>	46.60 (mass%)	Na <sub>2</sub> O	10.00 (mass%)
B <sub>2</sub> O <sub>3</sub>	14.20	P <sub>2</sub> O <sub>5</sub>	0.30
Al <sub>2</sub> O <sub>3</sub>	5.00	Fe <sub>2</sub> O <sub>3</sub>	2.04
Li <sub>2</sub> O	3.00	ZrO <sub>2</sub>	1.46
Na <sub>2</sub> O		Sm <sub>2</sub> O <sub>3</sub>	0.29
K <sub>2</sub> O		MoO <sub>3</sub>	1.45
CaO	3.00	Cs <sub>2</sub> O	0.75
ZnO	3.00	SrO	0.30
Total	74.80	BaO	0.49
		MnO <sub>2</sub>	0.37
		RuO <sub>2</sub>	0.74
		PdO	0.35
		CeO <sub>2</sub>	3.34
		Pr <sub>8</sub> O <sub>11</sub>	0.42
		Nd <sub>2</sub> O <sub>3</sub>	1.38
		<i>etc.</i>	1.52
		Total	25.20

of sodium chloride in pH 5 H<sub>2</sub>O solution, and cesium chloride in 0.5 kmol/m<sup>3</sup> hydrochloric acid, respectively. First the radioactive isotope was dropped onto the tungsten boat and then was dried. The radioactive isotope was evaporated to glass by heating the boat through a direct current in vacuum of  $5 \times 10^{-4}$  Pa in order to deposit the isotope onto the samples.

T-T-T diagram of the simulated nuclear waste glass P0798 was determined from the result of X-ray diffraction by Kawamura.<sup>10</sup> The glass transition temperature  $T_g$  of the P0798 glass was determined 763 K. According to the T-T-T diagram, isothermal diffusion annealing time is limited. If the anneal is continued even after the crystallization occurs, the diffusion behaviour should not be in simple amorphous phase. In the experiments, all the isothermal diffusion annealing times were chosen shorter than the time the crystallization occurs.

The specimens deposited with the isotope were wrapped with tantalum foil and was sealed in a quartz tube in vacuum of  $5 \times 10^{-4}$  Pa. The capsule was inserted in an electrical resistivity furnace. On the other hand, the diffusion annealing of  $^{22}\text{Na}$  above 499 K was carried out for short diffusion-annealing time because of large diffusion coefficient. For such shorter anneal a quartz tube was evacuated by a turbomolecular pump until  $10^{-5}$  Pa and then was heated by an infrared furnace. The diffusion anneals were carried out at given temperatures controlled to within  $\pm 1$  K. The diffusion-annealing time was corrected taking into consideration the heating and cooling times. After the diffusion anneals, the specimens were sectioned by the ion-beam sputter-sectioning apparatus.<sup>11</sup> The sputtering rate was adjusted to be 0.4 nm/s. The 450–600 keV activity for  $^{22}\text{Na}$  and 600–724 keV activity for  $^{137}\text{Cs}$  were measured by a well-type  $\gamma$ -ray scintillation spectrometer (Aloka Auto well  $\gamma$ -system, ARC-301B).

Fig. 1 Penetration profiles for diffusion of  $^{22}\text{Na}$  in the simulated nuclear waste glass below  $T_g$ .Table 2 Diffusion coefficients of  $^{22}\text{Na}$  in the simulated nuclear waste glass below  $T_g$ .

Phase	Temperature (K)	Annealing time (s)	Diffusion coefficients ( $\text{m}^2 \cdot \text{s}^{-1}$ )
below $T_g$	574	$4.80 \times 10^2$	$(1.13 \pm 0.02) \times 10^{-16}$
	524	$3.05 \times 10^3$	$(2.16 \pm 0.02) \times 10^{-17}$
	499	$7.27 \times 10^3$	$(5.36 \pm 0.09) \times 10^{-18}$
	477	$6.17 \times 10^4$	$(9.35 \pm 0.13) \times 10^{-19}$
	451	$2.48 \times 10^5$	$(1.67 \pm 0.03) \times 10^{-19}$
	428	$2.60 \times 10^5$	$(5.14 \pm 0.05) \times 10^{-20}$

### 3. Experimental Results

#### 3.1 Concentration profiles of $^{22}\text{Na}$ in the simulated nuclear waste glass

The initial condition for diffusion sample is equivalent to an infinitely thin source in a semi-infinite cylinder. The diffusion-penetration profiles conform well to the thin film solution of the diffusion equation,

$$C(x, t) = M/(\pi Dt)^{1/2} \exp(-x^2/4Dt) \quad (1)$$

where  $C(x, t)$  is the tracer concentration at a depth  $x$  after a diffusion interval  $t$ ,  $D$  is the tracer diffusion coefficient, and  $M$  is the initial amount of a tracer at the surface.

Figure 1 shows the penetration profiles for the diffusion of  $^{22}\text{Na}$  of the nuclear waste glass below glass transition temperature  $T_g$ . All diffusion profiles were Gaussian without serious surface hold-up or noticeable non-Gaussian. These penetration profiles were analyzed by using a least square fitting to eq. (1). The diffusion coefficients obtained at each temperature are compiled in Table 2.

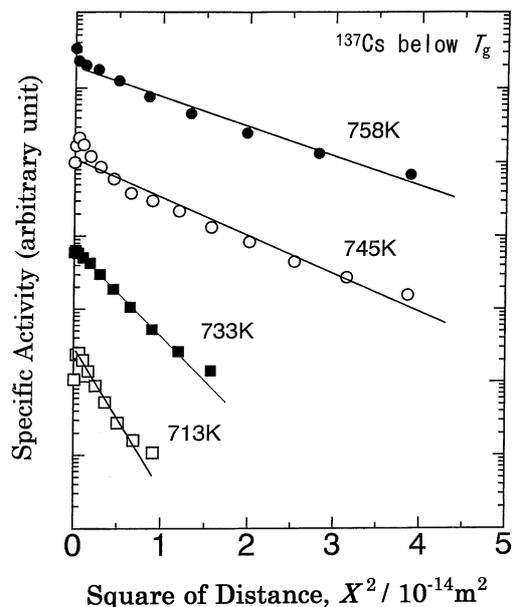


Fig. 2 Penetration profiles for diffusion of  $^{137}\text{Cs}$  in the simulated nuclear waste glass below  $T_g$ .

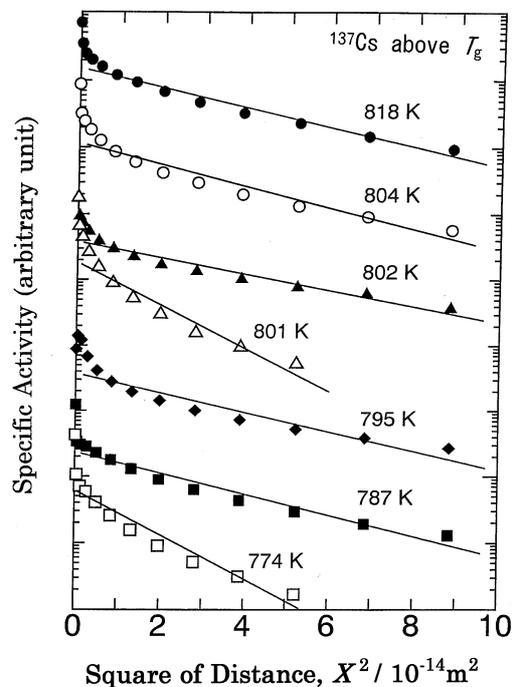


Fig. 3 Penetration profiles for diffusion of  $^{137}\text{Cs}$  in the simulated nuclear waste glass above  $T_g$ .

### 3.2 Concentration profiles of $^{137}\text{Cs}$ in the simulated nuclear waste glass

Figure 2 shows the concentration profiles of  $^{137}\text{Cs}$  in the simulated nuclear waste glass below  $T_g$ . Figure 3 shows the concentration profiles of  $^{137}\text{Cs}$  in the simulated nuclear waste glass above  $T_g$ . These profiles were non-Gaussian at near surface. It was considered that  $^{137}\text{Cs}$  tracer was hold-up at the surface of the samples. In this report the  $^{137}\text{Cs}$  diffusion coefficient was evaluated from the slope of these straight lines of Fig. 2 and Fig. 3. The diffusion coefficients obtained at each temperature are compiled in Table 3.

Figure 4 shows the annealing-time dependence of self-

Table 3 Diffusion coefficients of  $^{137}\text{Cs}$  in the simulated nuclear waste glass below and above  $T_g$ .

Phase	Temperature (K)	Annealing time (s)	Diffusion coefficients ( $\text{m}^2 \cdot \text{s}^{-1}$ )
below $T_g$	758	$1.54 \times 10^6$	$(1.73 \pm 0.06) \times 10^{-21}$
	745	$2.06 \times 10^6$	$(9.68 \pm 0.41) \times 10^{-22}$
	733	$2.15 \times 10^6$	$(4.21 \pm 0.05) \times 10^{-22}$
	713	$3.53 \times 10^6$	$(1.60 \pm 0.04) \times 10^{-22}$
above $T_g$	818	$1.13 \times 10^4$	$(6.39 \pm 0.30) \times 10^{-19}$
	804	$5.58 \times 10^4$	$(1.18 \pm 0.08) \times 10^{-19}$
	802	$8.00 \times 10^4$	$(1.02 \pm 0.07) \times 10^{-19}$
	801	$2.64 \times 10^4$	$(1.06 \pm 0.08) \times 10^{-19}$
	795	$1.56 \times 10^4$	$(4.69 \pm 0.38) \times 10^{-20}$
	787	$2.40 \times 10^4$	$(2.82 \pm 0.14) \times 10^{-20}$
	774	$4.27 \times 10^5$	$(8.38 \pm 0.48) \times 10^{-21}$

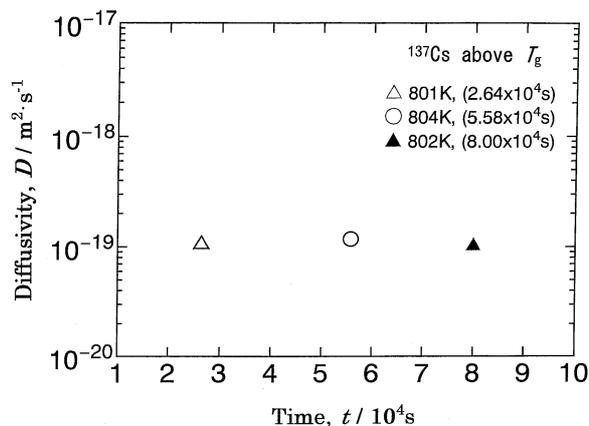


Fig. 4 Annealing time dependence of diffusion coefficients of  $^{137}\text{Cs}$  in the simulated nuclear waste glass above  $T_g$ .

diffusion coefficient of  $^{137}\text{Cs}$  in the simulated nuclear waste glass above  $T_g$ . The diffusion coefficient was not changed at the various annealing-time at the same annealing temperature. Thus, the diffusion measurement of the simulated nuclear waste glass was reproducible with enough accuracy.

### 3.3 Temperature dependence of diffusion coefficients of $^{22}\text{Na}$ and $^{137}\text{Cs}$ in the simulated nuclear waste glass

Figure 5 shows the temperature dependence of diffusion coefficients of  $^{22}\text{Na}$  and  $^{137}\text{Cs}$  in the simulated nuclear waste glass P0798. The temperature dependence of the diffusion coefficients of  $^{22}\text{Na}$  in the simulated nuclear waste glass follows the Arrhenius equation, which is expressed as below the glass transition temperature  $T_g$  (428–574 K):

$$D_{\text{Na-below}T_g} = 2.7 \times 10^{-6} \exp(-113 \pm 4 \text{ kJ} \cdot \text{mol}^{-1} / RT) \text{m}^2 \cdot \text{s}^{-1}$$

The temperature dependence of the diffusion coefficients of  $^{137}\text{Cs}$  in the simulated nuclear waste glass also follows the Arrhenius equation. The temperature dependence of the diffusion coefficients of  $^{137}\text{Cs}$  is expressed as below the glass transition temperature  $T_g$  (713–758 K):

$$D_{\text{Cs-below}T_g} = 7.1 \times 10^{-5} \exp(-241 \pm 10 \text{ kJ} \cdot \text{mol}^{-1} / RT) \text{m}^2 \cdot \text{s}^{-1}$$

above the glass transition temperature  $T_g$  (774–818 K):

$$D_{\text{Cs-above}T_g} = 5.3 \times 10^{13} \exp(-502 \pm 19 \text{ kJ} \cdot \text{mol}^{-1} / RT) \text{m}^2 \cdot \text{s}^{-1}$$

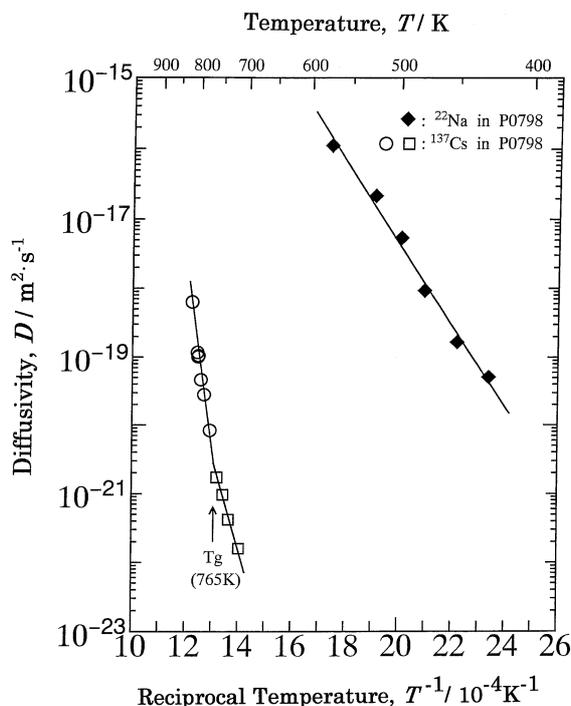


Fig. 5 Temperature dependence of diffusion coefficients of  $^{22}\text{Na}$  and  $^{137}\text{Cs}$  in the simulated nuclear waste glass.

The diffusion coefficients above  $T_g$  were much higher than those extrapolated from the data below  $T_g$ .

#### 4. Discussion

##### 4.1 Temperature dependence of diffusion coefficients of $^{22}\text{Na}$ and $^{137}\text{Cs}$ in the simulated nuclear waste glass

Figure 6 shows the temperature dependence of diffusion coefficient of  $^{22}\text{Na}$  and  $^{137}\text{Cs}$  in the simulated nuclear waste glasses P0798<sup>9)</sup> and HB-II'<sup>12)</sup> Yamanaka *et al.*<sup>9)</sup> measured the diffusion coefficient of  $^{22}\text{Na}$  in P0798 glass by the grinding method. The temperature dependence of the diffusion coefficient of  $^{22}\text{Na}$  in P0798 glass can be described by the Arrhenius equation: Yamanaka *et al.* (573–743 K):

$$D_{\text{Na-below } T_g} = 1.4 \times 10^{-5} \exp(-123 \pm 2 \text{ kJ} \cdot \text{mol}^{-1} / RT) \text{ m}^2 \cdot \text{s}^{-1}$$

While the activation energy determined by Yamanaka *et al.* is a little larger than that by the present work, the difference in the diffusion coefficients between them is quite small.

Yamashita *et al.*<sup>12)</sup> also reported the diffusion behaviour of  $^{22}\text{Na}$  and  $^{137}\text{Cs}$  in the simulated nuclear waste glass HB-II' (composition: Glass frit: 42.6%  $\text{SiO}_2$ , 8.3%  $\text{B}_2\text{O}_3$ , 1.2%  $\text{Li}_2\text{O}$ , 1.2%  $\text{Na}_2\text{O}$ , 7.5%  $\text{MgO}$ , 2.5%  $\text{ZrO}_2$ , 6.7%  $\text{Al}_2\text{O}_3$ , Waste oxides: 10.1%  $\text{Na}_2\text{O}$ , 0.2%  $\text{Rb}_2\text{O}$ , 1.6%  $\text{Cs}_2\text{O}$ , 18.1% others (mass%)). Yamashita *et al.*<sup>12)</sup> measured the diffusion coefficient of  $^{22}\text{Na}$  and  $^{137}\text{Cs}$  in the simulated nuclear waste glass by the grinding method and the etching method used 5% HF water solution, respectively. The measured diffusion coefficients of  $^{22}\text{Na}$  were one order of magnitude larger than that by the present work and Yamanaka *et al.* This discrepancy was considered to be attributed to difference in the content of  $\text{B}_2\text{O}_3$  which was about 6 mass% smaller than that in the P0798 glass.<sup>9)</sup> However, each activation energies were similar values.

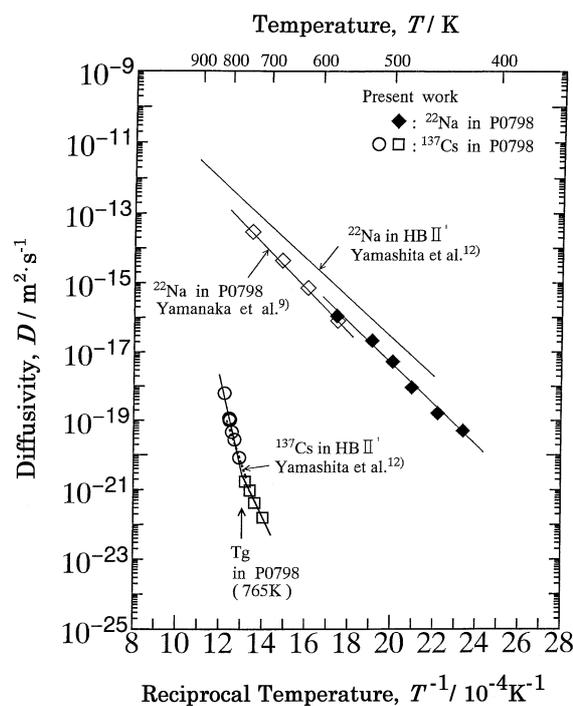


Fig. 6 Temperature dependence of diffusion coefficients of  $^{22}\text{Na}$  and  $^{137}\text{Cs}$  in the simulated nuclear waste glasses (P0798) and (HB-II').

The diffusion coefficients of  $^{137}\text{Cs}$  in HB-II' glass measured below the glass transition temperature are similar to those by the present work. However, while the diffusion parameters by Yamashita *et al.* were the pre-exponential factor  $D_0$   $2.8 \times 10^3 \text{ m}^2 \cdot \text{s}^{-1}$  and the activation energy  $Q$  about  $350 \text{ kJ} \cdot \text{mol}^{-1}$ , those in the present work were evaluated to be  $D_0$   $7.1 \times 10^{-5} \text{ m}^2 \cdot \text{s}^{-1}$  and  $Q$  about  $241 \text{ kJ} \cdot \text{mol}^{-1}$ . Such large difference reflects on low value of the diffusion coefficient at lower temperature. For example, the diffusion coefficient at 367 K (in this case assuming the temperature of subterranean water) evaluated from the diffusion parameters  $Q$  and  $D_0$  was eight orders of magnitude different. These large different diffusion parameters were considered to be due to difference in the component of  $\text{B}_2\text{O}_3$ . Since the self-diffusion coefficient of  $^{137}\text{Cs}$  was extremely low, the concentration depth profiles must be measured accurately. The ion beam sputter-sectioning technique is more accurate than the etching method used 5% HF water solution as a sectioning technique. Therefore, the different activation energy is also considered to be attributed to the different sectioning method.

##### 4.2 Diffusion behavior of $^{137}\text{Cs}$ above and below glass transition temperature $T_g$

As shown in Fig. 6, the self-diffusion coefficients of  $^{137}\text{Cs}$  in P0798 glass above  $T_g$  were much higher than those extrapolated from the data below  $T_g$ . Such a tendency is known on the oxide glass.<sup>13,14)</sup> In the present work, the diffusion parameters of  $^{137}\text{Cs}$  in P0798 glass were evaluated to be the pre-exponential factor  $D_0$   $7.1 \times 10^{-5} \text{ m}^2 \cdot \text{s}^{-1}$  and the activation energy  $Q$   $241 \text{ kJ} \cdot \text{mol}^{-1}$  below  $T_g$ , and the pre-exponential factor  $D_0$   $5.3 \times 10^{13} \text{ m}^2 \cdot \text{s}^{-1}$  and the activation energy  $Q$   $502 \text{ kJ} \cdot \text{mol}^{-1}$  above  $T_g$ . We will discuss these different diffusion parameters above and below  $T_g$ . It is well known that the viscosity of oxide glass continuously decreases with in-

creasing temperature from the glass transition temperature to the liquid solution. While a single jump process takes place in the amorphous phase below the glass transition temperature, more cooperative motion may occur in the supercooled liquid phase above the glass transition temperature due to the lower viscosity.<sup>15-17)</sup> Thus, it is considered that the similar phenomenon occurs in the diffusion behavior of <sup>137</sup>Cs above and below the glass transition temperature  $T_g$  in P0798 glass.

### 4.3 Large difference in self-diffusion coefficients between <sup>22</sup>Na and <sup>137</sup>Cs

The self-diffusion coefficients of <sup>22</sup>Na and <sup>137</sup>Cs obtained in the present work are  $1.3 \times 10^{-16} \text{ m}^2 \cdot \text{s}^{-1}$  and  $7.6 \times 10^{-27} \text{ m}^2 \cdot \text{s}^{-1}$  at 573 K, respectively and the difference between them is about ten orders of magnitude. The activation energy for Cs diffusion,  $241 \text{ kJ} \cdot \text{mol}^{-1}$ , is about twice as much as that for Na diffusion,  $113 \text{ kJ} \cdot \text{mol}^{-1}$ .

“Handbook of Glass Properties”<sup>18)</sup> shows the pre-exponential factors and activation energies for diffusion of Na and Cs in a  $16.7(1-x)\text{Na}_2\text{O}-16.7x\text{Cs}_2\text{O}-83.3\text{SiO}_2$  (mol%) glass, where the parameter “ $x$ ” is the mole ratio of Na and Cs in a glass. The diffusion coefficients of Na and Cs at 573 K were estimated from these data. In case of  $x = 1$ , the diffusion coefficient of Na is three orders of magnitude smaller than that of Cs. On the other hand, in case of  $x = 0$ , the diffusion coefficient for Na diffusion is eight orders of magnitude larger than that of Cs. As  $x$  approaches 0, the activation energy of Na becomes smaller, whereas that for Cs diffusion becomes larger. In case of  $x = 0$ , the activation energy of Cs is twice as much as that of Na. The phenomena of these types, in which coexisting alkali ions affect to each mobility, can be explained by a mixed alkali effect. The mixed alkali effect is a phenomenon that the mobility of the alkali ion is extremely decreased by the addition of the other alkali ion into the alkali silicate glass. This phenomenon is prominent in the case that a glass contains large amount of alkali or the difference in atomic weight between alkali elements is large.<sup>19)</sup>

Although the composition of the above-mentioned glass is different from P0798 glass, it is considered that the same phenomenon can occur in P0798 glass. As shown Table 1, the contents of Na and Cs are 10 mass% and 0.75 mass%, respectively. The content of Na is 80 times as much as that of Cs. This ratio is almost the same case of  $x = 0$ . Furthermore, P0798 glass contains many other alkali and alkaline earth elements, such as Li, Ca, Sr and Ba, and thus, the mixed alkali effect could be significant. From these implications, we suggest that the large difference in the self-diffusion coefficient between Na and Cs is related to the mixed alkali effect and also due to large difference in ionic radius between Na and Cs.

### 4.4 Consideration of relation between self-diffusion coefficient and leaching behavior

Regarding the leaching behavior from glass, many studies have been conducted up to date, and most of them were explained the elemental release by glass matrix dissolution or the selective leaching of soluble elements, such as Na, Cs and B, caused by ion exchange with hydrogen.<sup>2-7)</sup>

Deionized water or silica saturated water was used as leaching solutions for the experiments. In the deionized water the

glass matrix dissolution and selective leaching caused by diffusion between soluble elements and hydrogen ions can proceed simultaneously. On the other hand, the selective leaching proceeds dominantly in the silica saturated water, because the glass matrix dissolution is negligible under the silica saturated conditions.

Doremus<sup>7)</sup> proposed a model that the leaching of the soluble elements from the glass is controlled by diffusion between soluble elements and hydrogen ions. This model is supported by the following study conducted by Lanford *et al.*<sup>8)</sup> They measured the elemental depth profiles of sodium and hydrogen in the surface of soda-lime glass leached in the deionized water, and found that the self-diffusion coefficients estimated from depth profiles were consistent with those derived from the tracer diffusion experiment. Furthermore, Inagaki *et al.*<sup>4)</sup> conducted the leaching experiment of powdered P0798 glass in deionized water at 363 K for periods of  $1.12 \times 10^4$  ks. They suggested that the long-term leaching mechanism for Li, B, Na and Mo was explained by diffusion, because the elemental release of those elements was shown as a function of the square root of time. The elemental release of Cs is significantly small compared with other soluble elements, and they considered that Cs was removed from glass surface layer by solution. Mitsui *et al.*<sup>20)</sup> conducted the leaching experiment of platy P0798 glass in silica saturated water at 363 K for periods of  $3.46 \times 10^4$  ks. They analyzed the elemental depth profiles of various elements in the surface of glass leached for  $3.46 \times 10^4$  ks. The SIMS and TEM analyses showed that the glass had no signs of the glass matrix dissolution. The difference in the diffusion coefficients between Na and Cs is one order of magnitude at most.

It is suggested from these examples that the leaching behavior of Cs varies depending on the experimental conditions. In this paper we discuss a relation between the leaching behavior and the self-diffusion coefficient based on experimental results of Mitsui *et al.*<sup>20)</sup> The diffusion coefficients at 363 K are estimated from the present results of diffusion experiments of Na and Cs in P0798 glass to the followings:

$$D_{\text{Na}} = 1.5 \times 10^{-22} \quad (\text{m}^2 \cdot \text{s}^{-1})$$

$$D_{\text{Cs}} = 1.5 \times 10^{-39} \quad (\text{m}^2 \cdot \text{s}^{-1})$$

The difference in the values is 17 orders of magnitude, and it is far from that estimated from the result of leaching experiment. This suggests that the leaching behavior of Cs cannot be explained by the self-diffusion coefficient in unleached glass. Then we consider why the leaching behavior of Cs is far from estimate based on self-diffusion coefficient.

In a leaching experiment, Li, B, Mo and Na leach faster than Cs and  $\text{H}_3\text{O}^+$  ions regardless of the same valence. The composition of the glass surface changes significantly and, the matrix changes from unleached glass to leached layer before Cs leaches. As a result, firstly as mentioned in Sec. 4.3, it is considered that the diffusion coefficient increases, since the composition ratio of Na and Cs changes so that  $\text{Na}/(\text{Na} + \text{Cs})$  becomes smaller. Secondly, it is considered that the diffusion coefficient of Cs increases in the leached layer, since some defects are introduced near the glass surface owing to hydration of  $\text{H}_3\text{O}^+$  ions with the glass so that short-circuit diffusion takes place.

As described above, there might be two causes to explain the increase of diffusion coefficient of Cs in the leached glass. We can explain the leaching behavior of Cs by using self-diffusion coefficient of Cs in leached glass. Further investigations to obtain the self-diffusion coefficient of Cs in leached glass and to analyze the microstructure of the leached glass are necessary in order to clarify a relation between self-diffusion coefficient and leaching behavior.

## 5. Conclusion

The self-diffusion coefficients of Na and Cs in the simulated nuclear waste glass P0798 have been measured by an ion beam-sputter sectioning technique using radioactive isotopes  $^{22}\text{Na}$  and  $^{137}\text{Cs}$ . The results were as follows.

(1) The self-diffusion coefficients of  $^{22}\text{Na}$  in the P0798 glass below the glass transition temperature  $T_g$  (428–574 K) were obtained, which follows the Arrhenius equation.

$$D_{\text{Na-below}T_g} = 2.7 \times 10^{-6} \times \exp(-113 \pm 4 \text{ kJ}\cdot\text{mol}^{-1}/RT) \text{ m}^2\cdot\text{s}^{-1}$$

(2) The self-diffusion coefficients of  $^{137}\text{Cs}$  in the P0798 glass below the glass transition temperature  $T_g$  (713–758 K) was obtained, which are expressed by the Arrhenius equation.

$$D_{\text{Cs-below}T_g} = 7.1 \times 10^{-5} \times \exp(-241 \pm 10 \text{ kJ}\cdot\text{mol}^{-1}/RT) \text{ m}^2\cdot\text{s}^{-1}$$

Moreover, the self-diffusion coefficient of  $^{137}\text{Cs}$  in the P0798 glass above  $T_g$  (774–818 K) were obtained, which yields the pre-exponential factor  $5.3 \times 10^{13} \text{ m}^2\cdot\text{s}^{-1}$  and the activation energy  $502 \text{ kJ}\cdot\text{mol}^{-1}$ .

(3) The  $^{22}\text{Na}$  diffusion coefficient was about ten orders of magnitude larger than  $^{137}\text{Cs}$  diffusion coefficient. The activation energy for  $^{137}\text{Cs}$  for diffusion was two times larger than that for  $^{22}\text{Na}$  in the P0798 glass. The large difference in the diffusion coefficients and the activation energies are explained in terms of the ion size effect, the mixed-alkali effect and lower Cs concentration compared with Na in P0798 glass.

(4) The  $^{137}\text{Cs}$  diffusion coefficient predicted from the Arrhenius equation was 17 order of magnitude smaller than that of  $^{22}\text{Na}$  in the P0798 glass at 363 K. On the other hand, the difference in the diffusion coefficient of Na and Cs predicted from the leaching test in the P0798 glass at 363 K is only one order of magnitude. It is difficult to evaluate the leaching behavior of Cs in P0798 glass from  $^{137}\text{Cs}$  diffusion coefficient in the sound P0798 glass. In view of the above mentioned, it is considered that Cs diffusion coefficient in the leached layer in the P0798 glass is significantly larger than the  $^{137}\text{Cs}$  diffusion coefficient in the sound P0798 glass.

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