Heat-resistivity and Local Structure of New Nuclear Waste Glass Composed of Calcium Aluminate and Lead Phosphate

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Aluminophosphate glass with a batch composition of $30\text{CaO} \cdot 15\text{Al}_2\text{O}_3 \cdot 5\text{Fe}_2\text{O}_3 \cdot 25\text{PbO} \cdot 25\text{P}_2\text{O}_5$ was prepared as a potential host for the high-level nuclear wastes. This "base glass" consists of highly heat-resistant $60\text{CaO} \cdot (40-x)\text{Al}_2\text{O}_3 \cdot x\text{Fe}_2\text{O}_3$ glass and water-resistant lead metaphosphate glass, $\text{Pb}(\text{PO}_3)_2$, which is known to have $\sim 10^8$ times higher water-resistivity than conventional borosilicate glass. Two crystallization temperatures (T_c) of 650–671 and 668–693 °C were determined from the differential thermal analysis (DTA) of the "base glass". Large activation energies of 4.2 and 4.9 eV were obtained from a Kissinger plot of the T_c values. Nuclear waste "model glass" containing 10 stable isotopes with the mass numbers of 90–100 (Sr, Y, Zr, Nb, Mo) and 135–145 (Ba, La, Ce, Pr, Nd) also shows high heat-resistivity. ^{57}Fe Mössbauer spectrum indicates that Fe(III) and Fe(II) are ionically bonded to distorted PO_4 tetrahedra at the sites of network modifier.

Key Words: nuclear waste glass, calcium aluminate, lead phosphate, heat-resistivity, chemical durability, crystallization of glass, Mössbauer spectrum, differential thermal analysis, electron probe X-ray microanalyzer

1. Introduction

For the stable storage of high-level nuclear wastes for more than several thousands years, development of chemically and physically stable solid materials are required. Borosilicate glass, which is familiar to chemists, has been investigated for this purpose and several application studies have already been carried out. A great amount of radiation and heat emitted from the fission products of ^{235}U and transuranium elements are reported to destruct the host matrix for the nuclear wastes. It is considered that high heat-resistivity is a primary requisite to the actual nuclear waste hosts.

Among several oxide glasses, aluminate glass has extremely high heat-resistivity^{1)–4)}. Activation energies (E_a) of the crystallization of $60\text{CaO} \cdot 40\text{Al}_2\text{O}_3$, $60\text{CaO} \cdot 35\text{Al}_2\text{O}_3 \cdot 5\text{Fe}_2\text{O}_3$ and $60\text{CaO} \cdot 27\text{Al}_2\text{O}_3 \cdot 13\text{Fe}_2\text{O}_3$ glasses were determined to be 5.6–6.0, 4.3–4.6 and 4.2–4.9 (± 0.3 –0.4) eV, respectively¹⁾. E_a values of $60\text{CaO} \cdot 10\text{BaO} \cdot 30\text{Al}_2\text{O}_3$, $60\text{CaO} \cdot 10\text{BaO} \cdot 17\text{Al}_2\text{O}_3 \cdot 13\text{Fe}_2\text{O}_3$ and $60\text{CaO} \cdot 10\text{BaO} \cdot 15\text{Al}_2\text{O}_3 \cdot 15\text{Fe}_2\text{O}_3$ glasses were estimated to be 5.9, 3.8 and 3.9 (± 0.3) eV, respectively²⁾. It is noted that the E_a value of $60\text{CaO} \cdot 10\text{BaO} \cdot 30\text{Al}_2\text{O}_3$ glass (5.9 eV) is equal to that of $60\text{CaO} \cdot 40\text{Al}_2\text{O}_3$ glass (5.6–6.0 eV). These values are equal to a sum of Ca–O (1.4 eV) and Al–O bond energies (4.4 eV), suggesting that simultaneous cleavage of Ca–O and Al–O bonds triggers the crystallization. $60\text{CaO} \cdot 10\text{BaO} \cdot 17\text{Al}_2\text{O}_3 \cdot 13\text{Fe}_2\text{O}_3$ and $60\text{CaO} \cdot 10\text{BaO} \cdot 15\text{Al}_2\text{O}_3 \cdot 15\text{Fe}_2\text{O}_3$

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Fe_2O_3 glasses had smaller E_a values (3.8 – 3.9 eV) than $60 \text{ CaO} \cdot 35 \text{ Al}_2\text{O}_3 \cdot 5 \text{ Fe}_2\text{O}_3$ (4.3 – 4.6 eV) and $60 \text{ CaO} \cdot 27 \text{ Al}_2\text{O}_3 \cdot 13 \text{ Fe}_2\text{O}_3$ glasses (4.2 – 4.9 eV). These smaller E_a value will be associated with a marked decrease in the fraction of Al_2O_3 (15 or 17 mol%), which is an effective heat-resistant material. The extensive replacement of Al_2O_3 by other metal (or non-metal) oxides will cause the degradation of the heat-resistivity. Recently, a marked decrease of E_a was observed in calcium gallate ($\text{CaO} \cdot \text{Ga}_2\text{O}_3$)⁵⁾ and sodium tungstate ($\text{Na}_2\text{O} \cdot \text{WO}_3$)⁶⁾ glasses when a small amount (1 mol%) of Ga_2O_3 and WO_3 was replaced by Fe_2O_3 . It is noteworthy that aluminate glass shows high infrared (IR)-transparency, which may be utilized as IR-regulating glass, optical memory, etc.^{1)–4)}. The high IR-transparency will be favorable for the nuclear waste glass, since the heat involved with the fission products and transuranium elements will be easily dispersed.

It is known that heat-resistivity of phosphate glass is much lower than that of borosilicate glass⁴⁾. Nevertheless, synthetic “phosphate” mineral termed “synrock”, which has a similar composition to monazite, $(\text{Ce}, \text{Y}, \text{La}, \text{Th})\text{PO}_4$, has been developed as a high-level nuclear waste host^{7),8)}. Sales and Boatner⁹⁾ reported that the corrosion-resistivity of lead phosphate glass, $50 \text{ PbO} \cdot 50 \text{ P}_2\text{O}_5$, in hot water (90°C) was improved by a factor of 10^5 by incorporating 9 wt% (extra weight) of Fe_2O_3 into the lead phosphate glass when prepared at 800 – 900°C. Corrosion-resistivity or chemical durability of the lead phosphate glass containing 9 wt% of Fe_2O_3 proved to be higher than that of borosilicate glass by a factor of $\sim 10^3$. This pioneering work by Sales and Boatner⁹⁾ shows that Fe(III) plays a significant role for the stable storage of nuclear wastes in lead phosphate glass. Introduction of alkaline-earth metal or heavy metal oxide into phosphate

glass seems to improve the corrosion-resistivity in hot water. High corrosion-resistivity and high mechanical strength of alkaline-earth phosphate glasses can be anticipated from the fact that glass and glass-ceramics of $\text{CaO} \cdot \text{P}_2\text{O}_5$, e.g., hydroxy-apatite, are authorized as an excellent artificial bone joint, tooth root, etc. in the medical and dental fields.

This paper describes the characterization of aluminophosphate glass with a batch composition of $30 \text{ CaO} \cdot 15 \text{ Al}_2\text{O}_3 \cdot 5 \text{ Fe}_2\text{O}_3 \cdot 25 \text{ PbO} \cdot 25 \text{ P}_2\text{O}_5$, which was prepared as a new host for the high-level nuclear wastes. This “base glass” consists of highly heat-resistant calcium aluminate glass, $60 \text{ CaO} \cdot 30 \text{ Al}_2\text{O}_3 \cdot 10 \text{ Fe}_2\text{O}_3$, and water-resistant lead phosphate glass, $50 \text{ PbO} \cdot 50 \text{ P}_2\text{O}_5$, i.e., lead metaphosphate : $\text{Pb}(\text{PO}_3)_2$. Heat-resistivity of the nuclear waste “base glass” was investigated by differential thermal analysis (DTA). E_a values of crystallization were determined with the Kissinger equation :

$$\ln (T_c^2/\alpha) = E_a/RT_c + \text{const.}, \quad (1)$$

in which T_c , α and R are the crystallization peak temperature (in K), heating rate in DTA and the gas constant, respectively. ^{57}Fe -Mössbauer spectroscopy was applied for evaluating the local structural role of iron in the nuclear waste “base glass”. DTA and Mössbauer techniques were also applied to the nuclear waste “model glass” containing 10 stable isotopes with the mass numbers of 90 – 100 (Sr, Y, Zr, Nb, Mo) and 135 – 145 (Ba, La, Ce, Pr, Nd). These stable isotopes were incorporated into the “base glass” as the simulated fission products of ^{235}U .

2. Experimental

2.1 Preparation of glass

Nuclear waste “base glass”, $30 \text{ CaO} \cdot 15 \text{ Al}_2\text{O}_3 \cdot 5 \text{ Fe}_2\text{O}_3 \cdot 25 \text{ PbO} \cdot 25 \text{ P}_2\text{O}_5$, was prepared by melting the mixture of CaCO_3 , $\text{Al}(\text{OH})_3$, Fe_2O_3 , PbO and

P₂O₅ of guaranteed reagent grade at 1400°C for 3 h in an electric muffle furnace. This melting temperature is lower than that for 60CaO·(40-x)Al₂O₃·xFe₂O₃ glasses, i.e., 1550°C⁽¹⁾⁻⁴⁾, due to the presence of less heat-resistant 50PbO·50P₂O₅ in the mixture. After the fusion, the melt in a platinum crucible was quenched with ice-cold water and homogeneous “base glass” of dark brown (which looked almost black) was prepared. A simulated nuclear waste “model glass” was prepared by melting small pieces of the “base glass” with the powdered reagent mixture (oxide or carbonate) of 11 stable isotopes (Sr, Y, Zr, Nb, Mo, Cs, Ba, La, Ce, Pr, Nd) at 1350°C for 2 h. The simulated nuclear waste is composed of equal numbers of individual atoms, and the weight ratio of the “base glass” to the simulated wastes (reagent mixture) was fixed to 9:1. Technetium (Tc) and xenon (Xe) were excluded from the reagent mixture since the former has no stable isotope and the latter is “gas” at the room temperature.

2.2 Characterization of glass

Crystallization peak temperatures (T_c) and activation energies (E_a) were determined by DTA conducted at heating rates (α) of 5, 10, 15 and 20 K min⁻¹, using powdered α -Al₂O₃ as the standard. Mössbauer spectra were observed by the constant acceleration method with a ⁵⁷Co(Pd) source and a reference of α -Fe foil, which was also used for the velocity calibration (abscissa of the spectrum). Since the samples contain a large amount of Pb and other heavy metals, Mössbauer spectra were measured after diluting the glass powder with powdered boron nitride (BN). Elemental analysis of these samples was performed with the electron probe X-ray microanalyzer (EPMA).

3. Results and Discussion

The EPMA study revealed that the “base glass” had a composition of 40CaO·11Al₂O₃·6Fe₂O₃·14PbO·29P₂O₅, instead of the batch composition of 30CaO·15Al₂O₃·5Fe₂O₃·25PbO·25P₂O₅. Increases of the relative fraction of CaO, Fe₂O₃ and P₂O₅ were observed together with a slight decrease of Al₂O₃ from 15 (batch composition) to 11 mol% (“base glass”). A backscattering electron image (BEI) of the scanning electron microscope revealed the presence of a small amount (a few %) of crystalline particles with a composition of 93Al₂O₃·6.7Fe₂O₃·0.3PbO. These crystalline particles, which precipitated during the sample preparation, seem to have reduced the relative fraction of Al₂O₃ in the “base glass”. The marked decrease of PbO from 25 mol% in the reagent mixture (batch composition) to 14 mol% in the “base glass” will be due to the evaporation during the sample preparation at 1350–1400°C. The EPMA study revealed the absence of cesium (Cs), although it was originally included in the reagent mixture when the nuclear waste “model glass” was prepared. It is known that Cs, Na and Mo are volatile in borosilicate glass system¹⁰⁾. All other elements in the reagent mixture, i.e., Sr, Y, Zr, Nb, Mo, Ba, La, Ce, Pr, Nd, were preserved in the “model glass”, except for a slight weight loss of Mo.

DTA curves of the “base glass” show two exothermic peaks at the crystallization temperatures (T_c) of 650–671°C and 668–693°C (Figs. 1 (a)–(d), depending on the heating rates of 5–20 K min⁻¹). DTA curves of the “model glass”, containing 10 stable isotopes, showed only one exothermic peak at the T_c of 696–724°C (Figs. 1 (e)–(h)) when heated at the rates of 5–20 K min⁻¹. Figures 1 (e)–(h) indicate that the incorporation of 10 elements (Sr, Y, Zr, Nb, Mo, Ba, La, Ce, Pr,

Fig. 1 DTA curves of the nuclear waste "base glass" recorded at heating rates of (a) 5, (b) 10, (c) 15 and (d) 20 K min⁻¹, and those of the nuclear waste "model glass" recorded at heating rates of (e) 5, (f) 10, (g) 15 and (h) 20 K min⁻¹.

Nd) into the "base glass" brings about an improved heat-resistivity by about 30–50°C. It is noted that the T_c values of the "base glass" (650–671 and 668–693 °C) and the "model glass" (696–724 °C) are much lower than those of binary 60 CaO·40 Al₂O₃ glass (926–955 °C)^{1,3)} or 60 CaO·27 Al₂O₃·13 Fe₂O₃ glass (769–814 °C)¹⁾, due to the coexistent PbO and P₂O₅. This result suggests that T_c , softening temperature and even the melting temperature can be regulated by changing the relative fraction of calcium aluminate and lead phosphate. It is noteworthy that "ancient glass" is observed nowadays as it was, in spite that it is essentially alkali silicate glass having lower heat-resistivity and lower corrosion-resistivity than aluminophosphate glass. Therefore, it is expected that we can prepare new nuclear waste glass in which radioactive wastes are stably stored for more than several thousands years.

Activation energy (E_a) of crystallization be-

Fig. 2 Kissinger plots for the crystallization peak temperatures (T_c) of (a) 650–671 °C and (b) 668–693 °C obtained from the DTA curves of the nuclear waste "base glass" (see Figs. 1 (a)–(d)). A Kissinger plot for the T_c values of the nuclear waste "model glass", 696–724 °C (see Figs. 1 (e)–(h)), is illustrated in (c).

comes an important key when determining the heat-resistivity and the stability of glass. Kissinger plots for the "base glass" and "model glass" are illustrated in Fig. 2. All the plots show straight lines with similar slopes, which yield E_a values of 4.9 (Fig. 2 (a)), 4.2 (Fig. 2 (b)) and 3.8 eV (Fig. 2 (c)). Almost comparable E_a values were recently obtained for 60 CaO·35 Al₂O₃·5 Fe₂O₃ (4.3–4.6 eV)¹⁾, 60 CaO·27 Al₂O₃·13 Fe₂O₃ (4.2–4.9 eV)¹⁾, 60 CaO·10 BaO·17 Al₂O₃·13 Fe₂O₃ (3.8 eV)²⁾ and 60 CaO·10 BaO·15 Al₂O₃·15 Fe₂O₃ glasses (3.9 eV). The E_a values of 3.8–4.9 eV obtained in the present study indicate that both the "base glass" and "model glass" behave as a heat-resistant aluminate glass. These E_a values suggest that the average of Al–O bond having a single bond energy of ca. 4.4 eV¹¹⁾ or the simultaneous cleavage of Ca–O and Fe–O bonds triggers the crystallization, as recently observed in aluminate and gallate glasses containing iron^{1),2),5)}.

Mössbauer spectra of the "base glass" and

Fig. 3 Mössbauer spectra of the nuclear waste (a) “base glass” and (b) “model glass” measured at room temperature.

“model glass” are shown in Figs. 3 (a) and (b), respectively. All the Mössbauer parameters are summarized in Table 1. Although the absorption intensity was not high due to the shielding effect of the γ -rays ($E = 14.4$ keV) by the coexistent lead (Pb), Mössbauer spectra evidently showed the absorption peaks due to Fe(III) and Fe(II). Large isomer shift values (δ) of 0.53 (“base glass”) and 0.52 (± 0.01) mm s^{-1} (“model glass”) indicate that Fe(III) ions are ionically bonded to several distorted PO_4 tetrahedra at the sites of network modifier (NWM), as are often observed in several phosphate glasses⁴⁾. The com-

parable δ values of 0.52 and 0.53 mm s^{-1} indicate that Fe(III) ions have essentially the same Fe–O bond length and chemical bond strength, irrespective of the presence of about 10 wt% stable isotopes. The same δ values of 1.02 (± 0.01) mm s^{-1} obtained for Fe(II) ions in the “base glass” and “model glass” indicate that they are surrounded by several PO_4 units at NWM sites.

Quadrupole splitting value (Δ) of Fe(III) increased from 0.86 ± 0.02 mm s^{-1} in the “base glass” to 0.99 ± 0.02 mm s^{-1} in the “model glass” as a result of the dissolution of 10 stable isotopes. This result means a marked increase in the distortion, i.e., a marked decrease in the local symmetry at the Fe(III) sites. At the same time, the linewidth values (Γ) for the Fe(III) increased from 0.61 (“base glass”) to 0.75 (± 0.02) mm s^{-1} (“model glass”), reflecting widely distributed Fe–O bond lengths and O–Fe–O angles. By contrast, Δ (2.45 and 2.49 mm s^{-1}) and Γ (0.68 and 0.63 mm s^{-1}) values of Fe(II) in the “base glass” and “model glass” were almost the same as each other, within the experimental error of ± 0.02 mm s^{-1} . These results indicate that Fe(II) is less sensitive to the local structural change than Fe(III), probably because the chemical (ionic) bond of the former is weaker than that of the latter. (Ionic bond strength of metal ion is proportional to the z/r value, in which z and r are the charge and ionic radius, respectively.)

Table 1 Mössbauer parameters for the nuclear waste “base glass” and “model glass”

Sample	Species	$\delta^{\text{a)}$ (mm s^{-1})	$\Delta^{\text{b)}$ (mm s^{-1})	$\Gamma^{\text{c)}$ (mm s^{-1})	$A^{\text{d)}$ (%)
Base glass	Fe(III)	0.53	0.86	0.61	48.8
	Fe(II)	1.02	2.45	0.68	51.2
Model glass	Fe(III)	0.52	0.99	0.75	60.8
	Fe(II)	1.02	2.49	0.63	39.2

a) Isomer shift w.r.t. α -Fe. b) Quadrupole splitting. c) Linewidth (FWHM). d) Relative absorption area.

It is generally known that metal ions of higher oxidation state is preferentially observed in several oxide glasses when melted at lower temperatures. Table 1 shows that the relative absorption area (A) of Fe(III) in the Mössbauer spectrum is $48.8 \pm 0.5\%$ in the "base glass", while it is $60.8 \pm 0.5\%$ in the "model glass". This will be due to the difference in the melting temperature at which the sample was prepared, i.e., 1400°C for the "base glass" and 1350°C for the "model glass". Table 1 indicates that a part of Fe(II) ions in the "base glass" was oxidized to Fe(III) in the "model glass" when melted at 1350°C . Phosphorus pentoxide (P_2O_5) in oxide glasses plays a role of reducing agent for metal ions⁴). Introduction of about 10 wt% stable elements in the simulated nuclear waste will not be responsible for the oxidation of Fe(II) to Fe(III), since simulated nuclear waste was extraneously added to the "base glass" and hence the Fe(III)/ P_2O_5 ratio in the "model glass" is the same as that in the "base glass". We can conclude from the Mössbauer spectra that the iron in the "model glass" has essentially the same chemical and structural environment as that in the "base glass", except that the former is more distorted than the latter, owing to the simulated nuclear waste. Several metal ions in the simulated nuclear waste will occupy the sites of NWM, as do the Fe(III) and Fe(II), being ionically bonded to distorted PO_4 tetrahedra. This conclusion is consistent with the high heat-resistivity of the "model glass" that was confirmed from the DTA study.

4. Summary

(1) A new nuclear waste "base glass" could be prepared from highly heat-resistant $60\text{CaO} \cdot (40 - x)\text{Al}_2\text{O}_3 \cdot x\text{Fe}_2\text{O}_3$ glass and water-resistant lead metaphosphate glass, $\text{Pb}(\text{PO}_3)_2$.

(2) The "base glass" has high crystallization

peak temperatures (T_c) of $650 - 671$ and $668 - 693^\circ\text{C}$, of which Kissinger plot yields large activation energies (E_a) of 4.9 and 4.2 eV, respectively.

(3) A nuclear waste "model glass" containing 10 stable isotopes (Sr, Y, Zr, Nb, Mo, Ba, La, Ce, Pr, Nd) shows high heat-resistivity with large T_c and E_a values of $696 - 724^\circ\text{C}$ and 3.8 eV, respectively.

(4) Both Fe(III) and Fe(II) preferentially occupy the sites of network modifier (NWM) and are ionically bonded to distorted PO_4 tetrahedra.

(5) Several metal ions in the nuclear wastes will occupy the sites of NWM, as do the Fe(III) and Fe(II).

(6) DTA and Mössbauer spectroscopy proved to be useful tools for evaluating the heat-resistivity and local structure of the nuclear waste glass.

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要 旨

アルミン酸カルシウムとリン酸鉛により構築される新しい放射性廃棄物 ガラスの耐熱性と局所構造

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放射性廃棄物ガラスとして、熱に強い $60\text{CaO} \cdot (40-x)\text{Al}_2\text{O}_3 \cdot x\text{Fe}_2\text{O}_3$ ガラスと、耐水性に優れた $\text{Pb}(\text{PO}_3)_2$ ガラスから成るアルミノリン酸塩ガラスを調製した。示差熱分析 (DTA) から求めた結晶化ピーク温度のキッシンジャープロットから、結晶化の活性化エネルギー (E_a) が 4.2 および 4.9 eV であり、耐熱性に優れた材料であることを実証した。質量数が 90 - 100 (Sr, Y, Zr, Nb, Mo) および 135 - 145 (Ba, La, Ce, Pr, Nd) の安定核種を溶融した放射性廃棄物モデルガラスについても優れた耐熱性を明らかにした。 ^{57}Fe メスバウアースペクトルから、Fe(III) および Fe(II) が骨格の隙間で網目修飾イオン (NWM) として存在し、 PO_4 四面体とイオン結合をしていることを明らかにした。