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Vitrification of the ^{129}I Generated from Reprocessing Using Silver Tellurite Glass

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1. Introduction

^{129}I is one of the radioactive nuclide generated from reprocessing technology [1]. Its waste treatment is significant issue, because of its long half-life (~1.57 x 10^7 yrs), high solubility and mobility in water, and high volatility [2]. ^{129}I were mainly trapped as a AgI form in off-gas treatment system. Because of its high loading capacity and efficiency to trap the gaseous iodine, and AgI is very low soluble in pure water [3].

Silver tellurite glasses were used for fast ion conducting glass and it can contain large amount of iodine [4]. Also, tellurite glasses have low melting temperature and good chemical durability. Therefore, silver tellurite glasses were suitable waste form to vitrify the ^{129}I

Oxidation state and local environment of iodine in the silver tellurite glass was analyzed using X-ray absorption spectroscopy (XAS). Then the expected structure could be assumed by XAS data.

2. Experimental procedure

2.1. Preparation of the silver tellurite glass

The nominal composition and the analyzed composition of the glass were listed in Table I. This nominal composition was mixed by TeO_2 (Kojundo, 99.9%), Ag_2O (Kojundo, 99%), Bi_2O_3 (Kojundo, 99.9%) and AgI (Alfa aesar, 99%). Batch mixtures were heated in alumina crucibles at 700 °C for 30 min and quenched by pouring melt between two brass molds in the air.

Table I: The nominal composition and the analyzed composition of the silver tellurite glass by XRF

Element	Nominal composition		Analyzed composition
	(mol%)	(wt.%)	(wt.%)
TeO_2	53.00	41.29	40.30 ± 0.95
Ag_2O	23.00	25.69	27.21 ± 0.58
Bi_2O_3	5.00	11.33	11.82 ± 0.39
AgI	19.00	-	-
Ag	-	9.97	9.50 ± 0.01
I	-	11.72	11.17 ± 0.02
Totals	100.00	100.00	100.00

2.2. Characterization

Composition of the silver tellurite glass was analyzed by X-ray fluorescence (XRF, PANalytical axios minerals). Ag and I contents in the AgI were assumed that molar ratio of non-oxide Ag and I was 1:1. Density was measured by Archimedes method. Glass transition temperature (T_g) was analyzed using differential thermal analysis (DTA, Shimadzu DTG/TA-60) with a heating rate of 10 °C/min.

2.3. Chemical durability test

Chemical durability of the silver tellurite glass was evaluated by product consistency test (PCT). The glasses were crushed and sieved -100 to +200 mesh (75-150μm). The glass powders were ultrasonically washed with deionized water (DIW) and ethanol to remove fines and impurities. 1.5 g of powders were soaked in 15 mL of DIW in a Teflon vessel and kept at 90 ± 2 °C for 7 days. The leachate was filtered using 0.45 μm filter syringe. Concentration of elements in the leachate were measured using inductively coupled plasma mass spectroscopy (ICP-MS, NexION 350D, Perkin-Elmer SCIEX).

2.4. Oxidation state and local environment

Iodine K-edge XAS spectra were collected by beam line 10C at the Pohang light source (PLS), Pohang accelerator laboratory. XAS data were collected in the fluorescence mode, and Si (1 1 1) monochromator crystals were used. The crystalline standards (AgI, KI, KIO_3) spectra were initially collected to adjust E_0 value, then glass spectra were collected. Iodine K-edge is 33,169 eV (E_0) and it scanned from 200 eV below the edge to 1000 eV above the edge.

3. Results

3.1. Quantitative analysis of the glass

The analyzed composition of the glass was similar with the nominal compostion. And the iodine loading was 11.17 wt.%, as shown in Table I. Then the retention of iodine was 95%. It indicates that iodine were't seriously volatilized during the vitrification.

3.2. Chemical durability

Normalized elemental releases, r_i (g/m^2), were calculated by following formula:

$$r_i = \frac{C_i}{f_i(A/V)} \quad (1)$$

C_i is concentration of *i*th element in the leachate (ppm), f_i is the mass fraction of *i*th element in the glass (unitless), and A/V is ratio of the glass surface area to solution volume (m^{-1}). A/V value of the silver tellurite glass is 849 m^{-1}, calculated from the glass density, 6.31 g/cm^3. The results were listed in Table II.

The normalized release of the all elements were lower than 4.0 X 10^{-2} g/m^2, much lower than US regulation, r_i = 2 g/m^2. These results indicate that silver tellurite glass has very good corrosion resistivity.

Table II: Concentration C_i (ppm) and normalized elemental releases r (g/m^2) of the glass from 7-day PCT

Element	Concentration (ppm)	Normalized elemental releases (g/m^2)
Te	10.9	3.9 X 10^{-2}
Ag	2.3 X 10^{-2}	8.0 X 10^{-5}
Bi	2.6 X 10^{-3}	3.0 X 10^{-5}
I	6.2 X 10^{-2}	6.5 X 10^{-4}

3.3. Glass transition temperature

Glass transition temperature of the silver tellurite glass was 165 °C. It is higher than constraint temperature of 100 °C for the disposal site []. If the surrounding temperature rises over T_g, unexpected crystallization or phase separation will be occurred in the glasses.

According to the results about iodine retention, chemical durability and glass transition temperature, silver tellurite glasses were suitable wasteform for long-term waste treatment.

3.4. Oxidation state

Iodine K-edge X-ray absorption near edge structure (XANES) spectra of 3 crystalline standards (KIO_3, KI, AgI) and the silver tellurite glass were normalized to compare edge features. Iodine XANES spectra can be divided into two groups by comparison of obviously different features. As shown in Fig. 1, KIO_3, represented by iodate (IO_3^-), spectrum have a peak at 33,178 eV with following strong oscillation. In contrast, KI and AgI, represented by iodide (I^-), spectra have suppressed peak with following weak oscillation. Normalized XANES spectrum feature of the silver tellurite glass was almost identical with iodide crystalline standards. As a result, oxidation state of iodine in the silver tellurite glass was -1

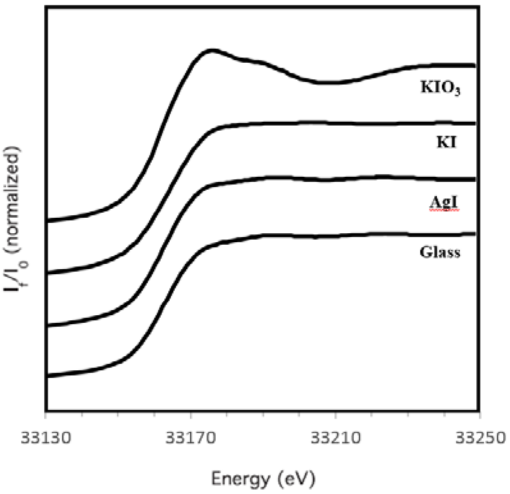

Fig. 1. Iodine K-edge XANES spectra of crystalline standards (KI, AgI and KIO_3) and the silver tellurite glass

3.5. Local environment

The processed $k^2\chi(k)$ data of the silver tellurite glass were very similar with AgI, as shown in Fig. 2. These similarity shows high possibility of the I-Ag bonding in the glass.

$k^2\chi(k)$ data were converted into radial distribution function (RDF) data for fitting, k-range of 3-9.5 Å^{-1}. Structure parameters (coordination number n, radial distance r and mean square disorder σ^2) were obtained by fitting RDF data. Initially, β-AgI (wurzite = tetrahedral) crystal structure parameters were input to fit AgI RDF data. Then, r and n values that refered AgI RDF data were varied to obtain reasonable structure parameters of the silver tellurite glass. I-Ag structure in the glass were fourfold coordination, slightly distorted and the bonding length was shorter than β-AgI crystal (Table III). RDF data of both AgI and the silver tellurite glass were well fitted with structure model.

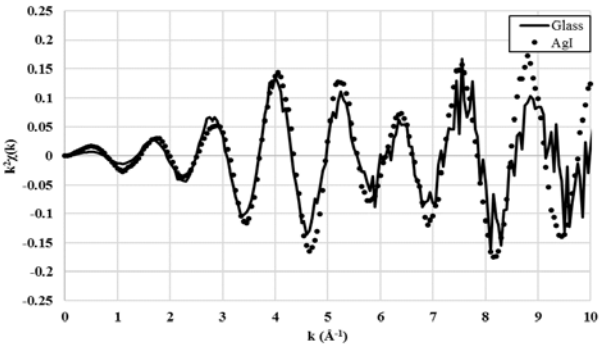

Fig. 2. $k^2\chi(k)$ spectra of AgI (dot) and the glass (line)

Table III. Iodine K-edge EXAFS fitting results about AgI and the glasses.

Sample	n (atoms)	r (Å)	r-factor	σ^2 (Å^2)
AgI	4	2.81	0.004	0.00845
Glass	3.75	2.75	0.018	0.01134

3.6. Expected structure model

Iodine K-edge XAS fitting data of the silver tellurite glass indicate that the local environment of iodide is fourfold coordinated Ag and its structure is tetrahedra. Therefore, 3 Ag from IAg_4 tetrahedra connect with iodide and nearby non-bridging oxygen (NBO) and 1 Ag only connect with iodide (Fig. 3).

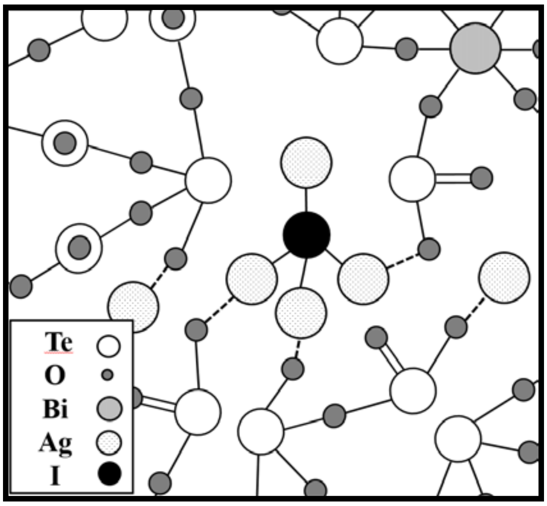

Fig. 4. Proposed structural model of the silver tellurite glass

4. Conclusion

The silver tellurite glass was developed to immobilize radioactive ^{129}I from reprocessing technology. Iodine loading was 11.17 wt.% and 95% of iodine remained during the melting. PCT results were much lower than US regulation. Glass transition temperature was 165 °C, higher than constraint temperature of the disposal site. Therefore, the silver tellurite glass was appropriate wasteform for long-term disposal.

Iodine K-edge XANES data indicate that oxidation state of iodine in the silver tellurite glass was -1. Ag^+ is the nearest atom of iodine and its structure is fourfold coordinated.

5. Acknowledgement

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