Journal of Nuclear Materials 492 (2017) 239–243

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Immobilization and bonding scheme of radioactive iodine-129 in silver tellurite glass

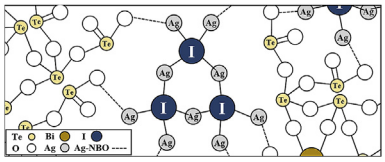
Cheong Won Lee [a], Jae-Young Pyo [a], Hwan-Seo Park [b], Jae Hwan Yang [b], Jong Heo [a, *]

[a] Division of Advanced Nuclear Engineering, Department of Materials Science & Engineering, Pohang University of Science and Technology (POSTECH), 77 Cheongam-ro, Pohang, Republic of Korea
[b] Korea Atomic Energy Research Institute (KAERI), 958 Daedeokdae-ro, Daejeon, Republic of Korea

HIGHLIGHTS

- Chemically durable silver tellurite glass for immobilization of ^{129}I was developed.
- Silver tellurite glass can contain up to 11.21 wt% of iodine.
- There's no significant volatilization of iodine (<5%) during the vitrification.
- Local structure of iodine in silver tellurite glass is similar to β-AgI.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 31 January 2017
Received in revised form
14 May 2017
Accepted 19 May 2017
Available online 22 May 2017

Keywords:
Sequestration
Silver tellurite glass
Radioactive iodine
Vitrification
XAS

ABSTRACT

Silver tellurite glasses with melting temperatures < 700 °C were prepared to immobilize the ^{129}I that normally volatilizes during high-temperature melting. Glasses have densities of 6.31 ± 0.1 g/cm^3 and glass transition temperatures of 165 ± 3 °C that provide thermal stability at the disposal site. Iodine waste loading in glasses was as high as 12.64 wt% of all metallic elements and 11.21 wt% including oxygen. Normalized elemental releases obtained from the product consistency test were well below US regulation of 2 g/m^2. Iodines are surrounded by four Ag^+ ions forming $[Ag_4I]^{3+}$ units that are further connected to tellurite network through bonds with non-bridging oxygens.

1. Introduction

^{129}I is a radioactive isotope that is generated during the fission reactions inside nuclear power plants, and can also be released during reprocessing of spent nuclear fuel [1]. ^{129}I has a long half-life (~1.57 × 10^7 y), high solubility and mobility in water, and high volatility, so immobilization of ^{129}I is a significant objective in management of nuclear wastes [2]. Most of ^{129}I is collected in the form of AgI on the surface of Ag-activated zeolite filters as the ^{129}I moves through the off-gas treatment process. Silver ions capture I with good efficiency, and AgI has low solubility in water [3]. However, AgI must be firmly immobilized inside a chemically-stable matrix to prevent it from re-entering the environment by evaporation or chemical reactions.

Ceramic waste forms were made from AgI-containing sorbents and ceramic matrix using hot isostatic pressing (HIPing) to sequester ^{129}I. Although volatilization of iodine was minimized during the processing, remained as adsorbents without making any chemical bonding with the matrix [4,5]. Silver phosphate glasses have been investigated for immobilization of AgI wastes [6–8]. AgI content [AgI] in glasses can be increased to 60 mol%. In this case, the

* Corresponding author. Tel.: +82 54 279 8651; fax: +82 54 279 8653.
E-mail address: jheo@postech.ac.kr (J. Heo).

http://dx.doi.org/10.1016/j.jnucmat.2017.05.024
0022-3115/

Table 1
Nominal and analyzed compositions of the glass (wt.%).

Starting Chemicals		Nominal composition	Elements excluding oxygens	Nominal composition	Analyzed composition
TeO_2		41.29	Te	37.18	35.99 ± 0.85
Ag_2O		25.69	Ag (combined)	38.16	39.38 ± 0.84
Bi_2O_3		11.33	Bi	11.45	11.99 ± 0.40
AgI	Ag	9.97	–	–	–
	I	11.72	I	13.21	12.64 ± 0.02
Total		100.00	Total	100.00	100.00

glass transition temperature decreased to ~55 °C for below the control temperature (<150 °C) at the deep geological disposal sites [9]. Therefore, the glass waste forms should have T_g > 150 °C to avoid changes in flow properties or crystallization behavior in glasses [10]. Addition of 2 wt% of Al_2O_3 or Bi_2O_3 to silver phosphate glasses can improve their chemical durability but usually leads to crystallization [8]. Borosilicate glasses are not suitable for vitrification of ^{129}I because of their high melting temperatures (>1000 °C) and low iodine solubility of <1 wt% [11].

Several ionically-conductive glass systems that use TeO_2-, V_2O_5- and MoO_3-based glasses have been developed [12–15]. In all of these glasses, preparation of homogeneous glasses with high ionic conductivities requires high [AgI]. These glasses can bear up to 80 mol% AgI, and therefore may provide applications in immobilization of ^{129}I. We have focused on glasses in the tellurite TeO_2-Ag_2O-AgI system, with addition of Bi_2O_3 to increase the chemical durability [16]. Tellurite glasses normally show good chemical durability [17], and are therefore, suitable waste forms for immobilization of ^{129}I. Melting temperatures of tellurite glasses (<700 °C) are low enough to prevent excessive volatilization of AgI during melting. The goal of this study was to develop new glass waste forms to sequester AgI wastes generated by pyrochemical processing of spent fuels. TeO_2-based glasses prepared can accommodate >10 wt% I, and show good chemical and thermal durabilities. Chemical bonding status of I with the glass network was investigated using X-ray absorption spectroscopy (XAS). The oxidation state of I is −1; it forms a bond with Ag^+ with coordination of ~4, which is similar to that in borosilicate and borate glasses [18,19].

2. Experimental methods

The glass (Table 1) was prepared by weighing and mixing powders of TeO_2, Ag_2O, Bi_2O_3 and AgI (with purities > 99%). Batches were melted at 700 °C for 30 min in alumina crucibles in ambient atmosphere, then the melts were quenched by pouring onto brass molds in air. X-ray fluorescence (XRF, PANalytical axios minerals) spectroscopy was used to analyze the glass composition quantitatively. Density was measured at room temperature by the Archimedes method using diethyl phthalate as a medium. T_g was determined using a differential thermal analyzer (DTA, Shimadzu DTG/TA-60) at a heating rate of 10 °C/min.

To evaluate the chemical durability of the glass, a product consistency test (PCT) was performed following the procedures described in American Society for Testing and Materials (ASTM) [20]. Glasses were crushed using mortar and pestle and sieved to collect powders with diameters of 75–150 μm. Powders were ultrasonically washed with deionized water (DIW) and ethanol to remove fine particles and impurities, then dried at 90 °C for 12 h. Samples (1.5 g) of powders were immersed in 15 mL of DIW in a Teflon vessel and kept at 90 ± 2 °C for 7 days in an oven. The solution was filtered through a syringe with a 0.45-μm filter. Concentrations of elements in the solution were analyzed using inductively coupled plasma mass spectroscopy (ICP-MS, NexION 350D, Perkin-Elmer SCIEX). Normalized elemental releases [g/m^2] were calculated as

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

where c_i is concentration of element i in the solution [ppm = g/m^3 in deionized water], f_i is mass fraction of element i in the glass, and A/V is ratio of the glass powder surface area to solution volume [m^{-1}]. A/V is 849 m^{-1} when density of glass is 6.31 g/cm^3.

Iodine K-edge X-ray absorption spectra were collected at beam line 10C of the Pohang Light Source (PLS) at the Pohang accelerator laboratory, South Korea. Spectra were collected in fluorescence mode with a Si (1 1 1) monochromator crystal. Spectra of crystalline standards (AgI, KI, KIO_3) were collected to adjust the Iodine K-edge energy E_0 = 33,169 eV, then spectra of the glasses were recorded from 200 eV below the iodine K-edge to 1000 eV above the edge. Spectra thus collected were processed using Athena software to remove background and noise, then radial

Table 2
Concentration [C (ppm)] and normalized elemental releases [r (g/m^2)] of elements from the glass after the 7-day PCT.

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

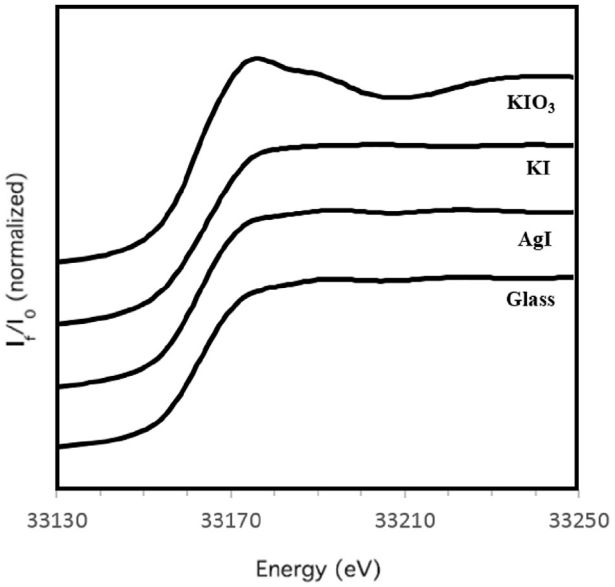


Fig. 1. Iodine K-edge XANES spectra of three crystalline materials and silver tellurite glass.