

Initial Assessment of the Consolidation of Chalcogels into a Viable Waste Form

Fuel Cycle Research & Development

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U.S. Department of Energy
B.J. Riley and W.C. Lepry
Pacific Northwest National Laboratory
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SUMMARY

This report provides some preliminary data for the consolidation of chalcogen-based aerogels. The chalcogels tested to date at PNNL show great promise as iodine sorbents and preliminary consolidation research shows that they can be melted into a phase-pure glass at moderate temperatures. The preliminary consolidation experiments show that these materials might attack fused quartz so an alternative crucible material will likely need to be used to prevent this. The next steps will be to

- Consider melting other chalcogel chemistries, e.g., Sn-Sb-S, Ge-Sn-S chalcogels
- Consider melting chalcogels with adsorbed iodine to monitor iodine loss during melting
- Optimize the consolidation temperatures to minimize the iodine loss and volatilization

CONTENTS

SUMMARY.....	iii
ABBREVIATIONS AND DEFINITIONS	v
1 INTRODUCTION.....	7
2 METHODS.....	9
2.1 Gel Synthesis	9
2.2 Consolidation.....	10
3 RESULTS.....	11
4 CONCLUSIONS.....	13
5 ACKNOWLEDGEMENTS.....	15
6 REFERENCES.....	17

FIGURES

Figure 1. Glass formation tendency in Sn-Ge-S chalcogenide glasses (Ruffolo and Boolchand, 1985).	8
Figure 2. Progression of making Sn ₂ S ₃ chalcogels.	9
Figure 3. (left) As-measured and silica equivalent specific surface area as a function of degas temperature and (right) SEM micrograph of Sn-S chalcogel.	10
Figure 4. Progression of chalcogel consolidation in a fused quartz ampoule (as viewed through outer tube).....	11
Figure 5. Optical and SEM micrographs of the heat-treated and polished Cg-17C-2 chalcogel.	11
Figure 6. XRD spectrum of portion of consolidated glass that was not mounted in resin for SEM observations. Minor quartz peaks were observed (Wyckoff, 1926).	12

TABLES

Table 1. Summary of non-Pt chalcogel chemistries (families). *AN: aggregation of nanocrystals; CL: chemical linkage of clusters.....	7
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ABBREVIATIONS AND DEFINITIONS

AN	aggregation of <u>n</u> anocrystals/nanoparticles (chalcogel fabrication method)
CL	<u>c</u> hemical <u>l</u> inkage of clusters (chalcogel fabrication method)
DIW	deionized water
EDS	energy dispersive spectroscopy
<i>M</i>	interlinking metal (used in CL method for chalcogel fabrication)
mmol	millimoles
N/A	not applicable
OAc	acetate (CH_3COO^-)
PNNL	Pacific Northwest National Laboratory
psi	pounds per square inch
SEM	scanning electron microscopy
SSA	specific surface area
XRD	X-ray diffraction

1 INTRODUCTION

A new family of non-oxide, chalcogen-based aerogels, called *chalcogels*, has been reported in the literature (Mohanani et al., 2005; Kalebaila et al., 2006; Bag et al., 2007; Kanatzidis and Bag, 2008; Bag et al., 2009; Bag and Kanatzidis, 2010; Oh et al., 2011; Yuhua et al., 2011b; Yuhua et al., 2011a; Shafaei-Fallah et al., 2011; Riley et al., 2011; Polychronopoulou et al., 2012). These are highly porous semisolids made from a variety of S-, Se-, and/or Te-based building blocks that have selective affinity for various heavy metals and gases (Bag et al., 2007; Bag et al., 2009; Bag and Kanatzidis, 2010). Different methods have been discovered to make these chalcogels including (1) the aggregation of nanoparticles and (2) the chemical linkage of chalcogenido clusters with an interlinking metal (or metals). A comprehensive summary is provided in Table 1 (Riley et al., 2012).

Table 1. Summary of non-Pt chalcogel chemistries (families). *AN: aggregation of nanocrystals; CL: chemical linkage of clusters.

Chemistry (Family)	Method*	Chalcogenido cluster(s)	Interlinking metal(s), <i>M</i>	Reference(s)
(Cd,Zn,Pb)-(S,Se)	AN	N/A	N/A	(Mohanani et al., 2005)
Ge-S	AN	N/A	N/A	(Kalebaila et al., 2006)
(Mo,W)- <i>M</i> -S	CL	(Mo,W)S ₄ ²⁻	Co ²⁺ , Ni ²⁺	(Bag et al., 2009; Shafaei-Fallah et al., 2011)
(Sn,Sb)- <i>M</i> -(S,Se)	CL	Sn ₂ (S,Se) ₆ ⁴⁻ , Sn(S,Se) ₄ ⁴⁻ , SbSe ₄ ³⁻	Sn ²⁺ , Sb ³⁺	(Bag and Kanatzidis, 2010)
Zn-Sn-S	CL	SnS ₄ ⁴⁻ , Sn ₂ S ₆ ⁴⁻ , Sn ₄ S ₁₀ ⁴⁻	Zn ²⁺	(Oh et al., 2011)
Fe-Sn-S	CL	Fe ₄ S ₄ ^{m-} , Sn ₂ S ₆ ⁴⁻	Fe ₄ S ₄ ^{m-} , Sn ₂ S ₆ ⁴⁻	(Yuhua et al., 2011b)
Fe- <i>M</i> -Sn-S	CL	Fe ₄ S ₄ ^{m-} , Sn ₂ S ₆ ⁴⁻	Zn ²⁺ , Sn ²⁺ , Ni ²⁺ , Co ²⁺	(Yuhua et al., 2011a)
Mo-Co- <i>M</i> -S	CL	MoS ₄ ²⁻	Co ²⁺ , Pb ²⁺ , Cd ²⁺ , Pd ²⁺ , Cr ³⁺ , Bi ³⁺	(Polychronopoulou et al., 2012)

At the Pacific Northwest National Laboratory (PNNL), we have been studying these materials as sorbents for the radioiodine evolved during the proposed reprocessing of used nuclear fuel. While the concentrations of iodine are low, the required capture efficiencies are very high at $\geq 99.4\%$ (40 CFR 190, 2012). The initial chalcogel materials tested at PNNL to date show promise as sorbents with $>99\%$ capture efficiencies for low iodine concentrations in air (Riley et al., 2011; Riley et al., 2012).

Unlike the traditional iodine sorbents such as silver-exchanged zeolites, chalcogels do not require “functionalization” to bind the iodine. Silver is a precious metal and toxic per the Resource Conservation and Recovery Act (40 CFR 261, 2012). These make chalcogels an attractive material for removal of iodine from reprocessing off-gases. The mechanism by which chalcogels bind iodine is likely a combination of physisorption and chemisorption, whereas AgI is formed in any Ag-functionalized sorbent.

It has been shown that iodine is soluble in several different chalcogenide glasses and they can accommodate large fractions of iodine into their structure (Heo and Mackenzie, 1989; Wang et al., 2001; Krasteva et al., 1997b; Krasteva et al., 1997a; Seddon and Hemingway, 1991, 1993; Heo et al., 1987; Lin and Ho; Maneglier-Lacordaire et al., 1975; Turyanitsa et al., 1974). Like the other iodine capturing materials being considered (zeolite and silica aerogel), chalcogels have high surface area and porosity, they and require consolidation to collapse the pore structure with heating, for example to make them suitable for disposal. Chalcogels fall into a category of materials called chalcogenides and many chalcogenide compounds can be melted into glasses at moderate temperatures, e.g., typically <700 °C. The primary goal of this brief report is to demonstrate the melting of a chalcogel into a chalcogenide

glass. These melted glasses potentially have high chemical durability. This is in contrast to oxide glasses where halides tend to remain as undissolved salts within the glass network or evolve from the glass surface during melting (Hrma, 2010). The preliminary results reported here fulfill the milestone “M3FT-12PN03030912-Provide an initial assessment of the consolidation of chalcogels into viable waste forms” (FCRD-SWF-2012-000246).

From a glass formation standpoint, the most promising chalcogel chemistries are Sn-S and Sn-Se formulations that include Ge or Sb. Since Zn-Sn-S chalcogels tend to change from an amorphous aerogel to a crystalline material when heated (Oh et al., 2011), we suspect that the Sn-S chalcogels will crystallize as well. Therefore, this system probably requires a glass-forming additive in order to obtain a glassy product, e.g., Ge or Ge-S (Ruffolo and Boolchand, 1985) (Figure 1). Figure 1 shows the glass transition temperature (T_g), crystallization temperature (T_c), and value of ($T_c - T_g$) for the Sn_2S_3 - Ge_2S_3 binary system. The value of ($T_c - T_g$) provides an estimate of ability to make a glass where a larger difference allows for slower quench rates to prevent glass crystallization and from Figure 1, it is evident that increased Sn_2S_3 loadings decrease the glass formability.

It is possible to make a Sn-Ge-S chalcogel with the variety of Ge-S and Sn-S chalcogel precursors discovered to date that include GeS_4^{4-} , $\text{Ge}_4\text{S}_{10}^{4-}$, SnS_4^{4-} , $\text{Sn}_2\text{S}_6^{4-}$, and $\text{Sn}_4\text{S}_{10}^{4-}$ (Melullis and Dehnen, 2007; Bowes et al., 1996; Schiwy et al., 1973; Krebs et al., 1972; Tsamourtzis et al., 2008). Glass formation has been demonstrated in the Sb-Sn-S system with iodine (Turyanitsa et al., 1974). Thus, our focus is on these two systems—Sn-S with added Ge-S powder and Sb-Sn-S. Several techniques are evaluated for consolidating both the as-made and iodine-sorbed chalcogels. These include melting, hot pressing, and spark plasma sintering.

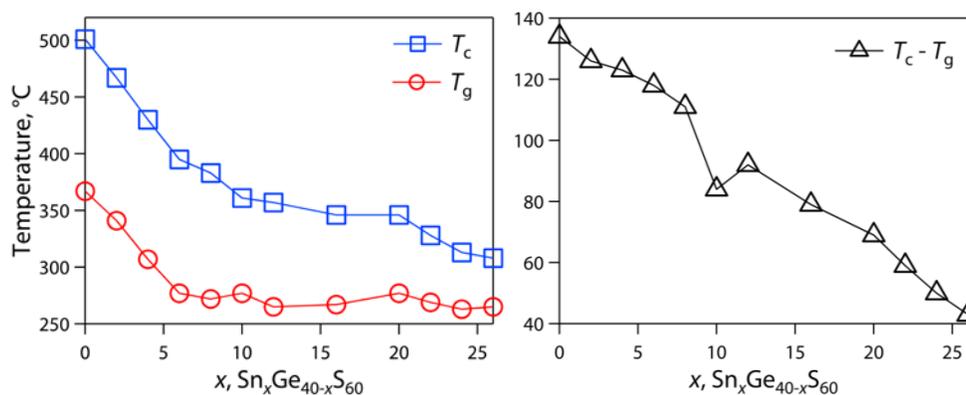
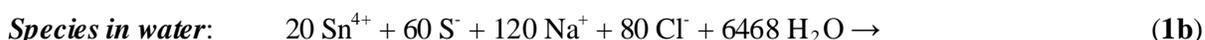
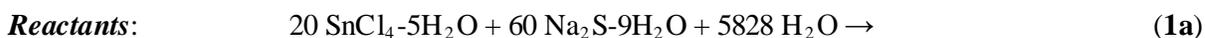


Figure 1. Glass formation tendency in Sn-Ge-S chalcogenide glasses (Ruffolo and Boolchand, 1985).

2 METHODS

2.1 Gel Synthesis and Characterization

The Cg-17C-2 Sn_2S_3 chalcogel was fabricated with solutions of $\text{Na}_4\text{Sn}_2\text{S}_6\cdot 14\text{H}_2\text{O}$ and SnCH_3COO , or tin(II) acetate; hereinafter SnOAc. The $\text{Na}_4\text{Sn}_2\text{S}_6\cdot 14\text{H}_2\text{O}$ was made with the procedure used by Oh et al. (2011) and the SnOAc was purchased from Sigma Aldrich. The $\text{Na}_4\text{Sn}_2\text{S}_6\cdot 14\text{H}_2\text{O}$ compound was made by slowly adding solution (1) containing 20 mmol (7.01 g) of $\text{SnCl}_4\cdot 5\text{H}_2\text{O}$ in 5 mL of deionized water (DIW), to solution (2) containing 60 mmol (14.41 g) of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ in 100 mL of DIW, and mixing. The process of the chemical reaction that took place is presented in Equations 1a–1c where the species present at each step are defined (assuming 100% yield). This mixture was added to ~300 mL of acetone and, after stirring/shaking, a yellow emulsion was observed that eventually resulted in a white precipitate. The solution was kept in the refrigerator for a few days to increase the yield of the precipitate and then the precipitate was vacuum filtered with a Buchner funnel, washed with acetone, and dried in a vacuum desiccator.



To make the chalcogel, a scaled-up version of the process defined by Bag and Kanatzidis for Chalcogel-Sn-2 was followed (Bag and Kanatzidis, 2010). Here, 4 mmol (3.10 g) of $\text{Na}_4\text{Sn}_2\text{S}_6\cdot 14\text{H}_2\text{O}$ was dissolved in 80 mL of formamide and 8 mmol (1.89 g) of SnOAc was dissolved separately in 80 mL of formamide (CH_3NO). Then, the SnOAc solution was slowly added to the $\text{Na}_4\text{Sn}_2\text{S}_6\cdot 14\text{H}_2\text{O}$ solution at which point, the solution turned from a clear (sometimes light blue) to a green, orange, and then dark maroon (see Figure 2). The chemical reaction that took place is presented in Equations 2a–2c where the species present at each step are defined (assuming 100% yield).

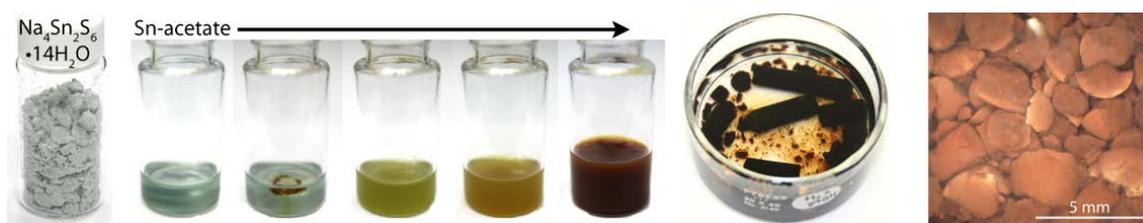
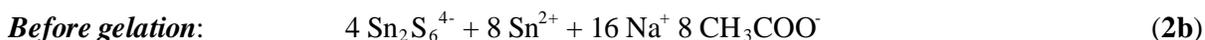


Figure 2. Progression of making Sn_2S_3 chalcogels.

The solution was then poured into polypropylene vials with lids and zero headspace. These were covered with aluminum foil to exclude light, left to gel over the course of 4–5 weeks, after which the gels were removed from the vials, cut into ~3–6 mm pieces, and placed in a 50/50 (v/v) ethanol/DIW mixture to age overnight. The aged gels were washed several times in fresh 50% ethanol to remove the water-soluble byproducts (Equation 2c). This was followed by several washes in 100% ethanol to remove the water.

The washed gels were submerged in fresh ethanol in an autoclave (4762Q, Parr Instruments) and placed in a temperature-controlled water bath at 10°C . A syringe pump (Teledyne ISCO 500D) was used to slowly add liquid CO_2 to a pressure of 6.9×10^6 Pa (1000 psi). This was repeated until approximately 1 to 2 L of liquid CO_2 was flushed through autoclave to replace the ethanol. After the CO_2 drying, the autoclave was left overnight with liquid CO_2 at 1.0×10^7 Pa. The next day, an additional CO_2 wash was

performed and the temperature of the water bath increased to 50 °C. Once the temperature equilibrated, the CO₂ was vented from the autoclave resulting in an aerogel.

After degassing at 25, 60, 100, and 125 °C for 8 h at each temperature, the specific surface areas of these gels measured with nitrogen adsorption/desorption isotherms were 456, 432, 378, and 364 m²/g, respectively (Figure 3). The specific surface areas of this chalcogel decreased with increasing degas temperature. This decrease could be due to the collapse of pore structure during evaporation of residual solvent in the gel network. A picture of a typical Sn₂S₃ chalcogel is also presented in Figure 3.

In order to relate these chalcogels to the more common silica aerogel, a “silica equivalent specific surface area” is often used (Kanatzidis and Bag, 2008). Here, the chalcogel composition is normalized to two anions, e.g., Sn_{2.00}S_{3.00} becomes Sn_{1.33}S_{2.00} and the molecular mass of this compound (222.41 g/mole) is compared to that of SiO₂ (60.08 g/mole) and the silica equivalent specific surface area (SSA) translates to 3.70× that of the values measured with the adsorption/desorption isotherms. These values are plotted on the right y-axis in Figure 3.

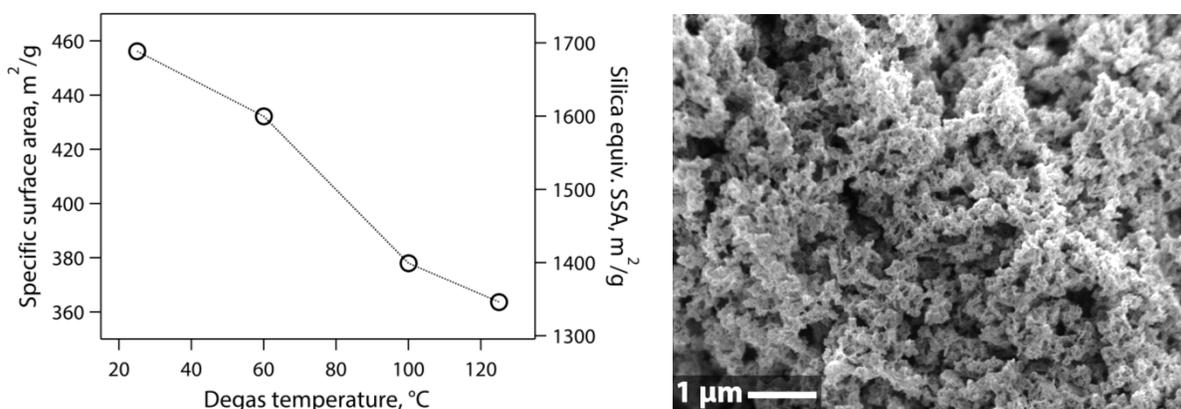


Figure 3. (left) As-measured and silica equivalent specific surface area as a function of degas temperature and (right) SEM micrograph of Sn-S chalcogel.

2.2 Consolidation and Characterization

Before consolidation, the Cg-17C-2 Sn₂S₃ chalcogel was analyzed with scanning electron microscopy (SEM, JEOL 7001F, JEOL, Ltd) and energy dispersive spectroscopy (EDS, AMETEK Apollo XL) to verify the chemistry. The Sn:S ratio was ~2:3, with inclusions of Na, an impurity from the reactants (Equation 2c). The Cg-17C-2 chalcogel was weighed (0.1786 g) and added to a fused quartz tube (10×12 mm along with 0.1464 g GeS₂, resulting in a Sn:Ge = 1, on a molar basis, i.e., $\sim x = 20$ in Figure 1. This tube was added to a secondary tube (22×25 mm) that was evacuated and sealed under vacuum. This assembly was loaded into a Deltech furnace (Deltech, Inc.) and heated to various temperatures, taken out briefly for observation, returned to the furnace, and heated to the next higher temperature. Observations were made at 400, 550, 750, and 830°C. At 830°C, the sample was quenched in water. The inner ampoule was then mounted in resin, cross-sectioned, and polished for SEM/EDS observation.

The portion of the consolidated glass that was not mounted in resin was removed from the quartz tube, ground to a powder in an agate mortar and pestle, and analyzed with X-ray diffraction (XRD). The instrument was a Philips X'Pert with a radius of 190 mm and variable divergence and anti-scatter slits (10 mm irradiated area). The scan range was 5–90° 2θ with 0.03 degree steps and a 2 s count at each step. The phases were identified with JADE® 6 software.

3 RESULTS

Figure 4 shows a progression of the consolidation process. From these pictures it is readily apparent that the sample melted between 550 and 750 °C. A likely processing temperature would be about 750 °C or slightly less. The yellow films observed on the walls of the quartz tube are very thin films of the chalcogenide glass that evaporated but condensed upon cooling (likely < 1 mass% of melt).

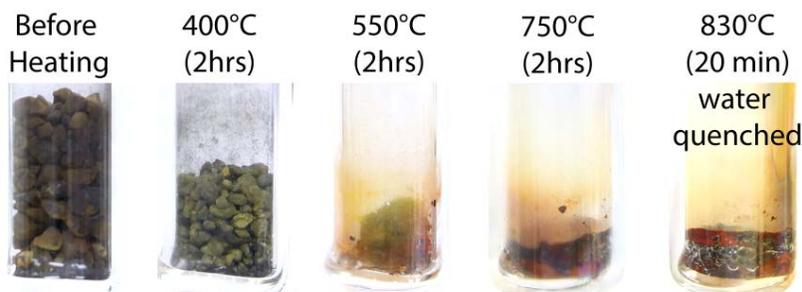


Figure 4. Progression of chalcogel consolidation in a fused quartz ampoule (as viewed through outer tube).

Figure 5 shows a complete and polished cross-section of the bottom portion of the sample quenched from 830 °C. The bright red opaque glass is common to chalcogenides. Quenching the glass and the thermal expansion mismatch between the glass and the quartz likely caused the cracking – the molten glass attacked the fused quartz causing SiO₂ particles to spall from the ampoule wall and into the melt (Figure 5b-d). Future experiments will be conducted with different crucible materials, e.g., alumina. Other than the SiO₂ particles, the glass was completely homogeneous according to backscattered electron imaging and random area EDS analyses.

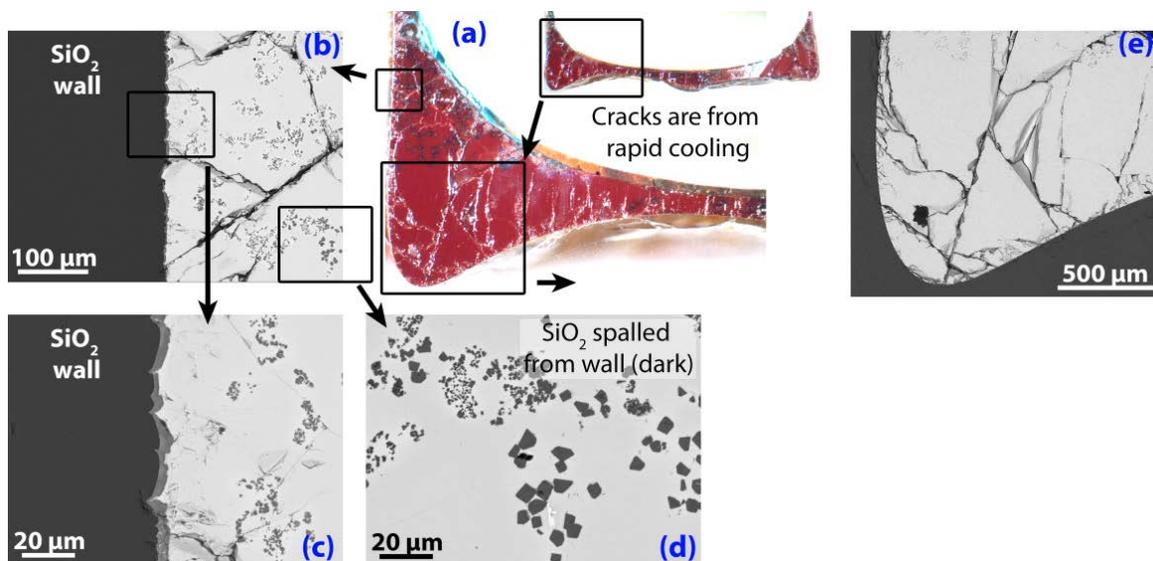


Figure 5. Optical and SEM micrographs of the heat-treated and polished Cg-17C-2 chalcogel.

Figure 6 provides the XRD spectrum of the powdered glass. The results show that XRD from the melted chalcogel has broad maxima characteristic of amorphous materials, e.g., chalcogenide glass. A few weak crystalline peaks were observed that were attributed to the quartz from the wall of the tube.

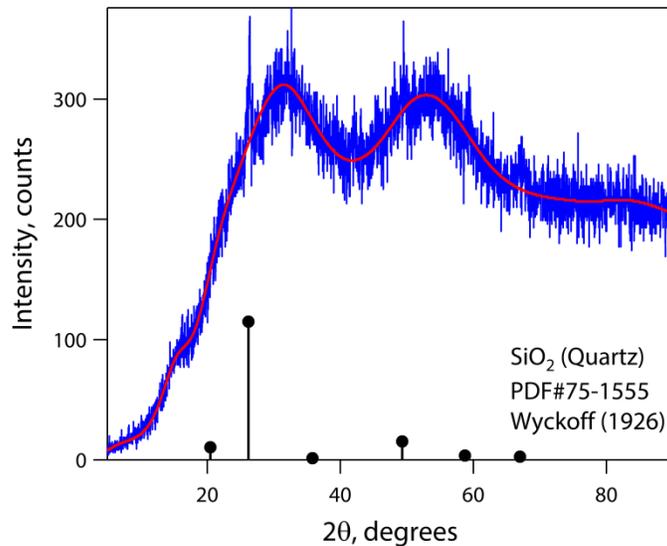


Figure 6. XRD spectrum of portion of consolidated glass that was not mounted in resin for SEM observations. Minor quartz peaks were observed (Wyckoff, 1926).

4 CONCLUSIONS

The chalcogels tested to date at PNNL show great promise as iodine sorbents and preliminary consolidation research shows that they can be melted into a phase-pure glass at moderate temperatures. The preliminary consolidation experiments show that these materials might attack fused quartz so an alternative crucible material may be needed to prevent this. The next steps will be to

- make glasses from other chalcogel chemistries, e.g., Sn-Sb-S, Ge-Sn-S chalcogels
- Melt chalcogels containing iodine to monitor iodine loss
- Optimize the consolidation temperatures to minimize the iodine loss and volatilization

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Open-Framework Chalcogenides $(\text{Me}_4\text{N})_2\text{M}[\text{Sn}_4\text{Se}_{10}]$ ($\text{M} = \text{Mn}^{\text{II}}, \text{Fe}^{\text{II}}, \text{Co}^{\text{II}}, \text{Zn}^{\text{II}}$) Including the First Telluride Member $(\text{Me}_4\text{N})_2\text{Mn}[\text{Ge}_4\text{Te}_{10}]$." *Inorganic Chemistry* **47**(24):11920-29.

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