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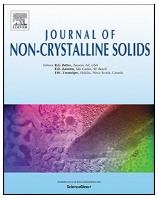

Glass formation and short-range order structures in the BaS + La_2S_3 + GeS_2 system

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ABSTRACT

Infrared (IR) optical materials have enabled a broad range of optical sensing and measurement applications in the mid-wave and long-wave IR. Many IR transmitting glasses are based on covalently-bonded selenides and tellurides, such as As_2Se_3 and $GeTe_2$, which typically have relatively low glass transition temperatures (T_g) on the order of 200 to 350 °C. Many applications have working temperatures above the T_g of these materials, which compels the development of new IR materials. This work studies the underlying short-range order (SRO) structure and glass formability of a new family of ionically-bonded sulfide glasses, $x\text{BaS} + y\text{La}_2\text{S}_3 + (1-x-y)\text{GeS}_2$, to develop high T_g optical materials with a broad IR transmission range. These sulfide glasses were produced by melting sulfide materials inside evacuated and sealed carbon-coated silica ampoules at 1150 °C for 12 h and quenching to room temperature to form glass. Glass samples were then characterized by IR and Raman spectroscopies and differential thermal analysis (DTA). It was found that by increasing the modifier concentration, the predominantly Ge^4 SRO units, the superscript defines the number of bridging sulfur (BS) ions in the tetrahedral network found in GeS_2 glasses, are ultimately converted to Ge^0 units at > 40 mol% network modifier content through the generation of non-bridging sulfur (NBS) ions. These molecular ionic units still form a glassy network, with some of the highest reported T_g values to date for a pure sulfide glass. This suggests that this composition has strong ionic bonds between negatively-charged tetrahedral SRO units and the positively-charged modifier cations. While the glass network is depolymerized in the high modifier content glasses though the formation of a high concentration of molecular ionic Ge^0 SRO groups, they are, nevertheless, homogeneous glassy materials that exhibit the largest T_g and ΔT (difference between crystallization temperature, T_c, and T_g) values of glasses in this system, making them the optimal glasses for high T_g IR optical components, including, potentially, refractory IR optical fibers.

1. Introduction

The increasing global demand for energy continues to challenge the energy sector, as the need for increased energy production are balanced against the urgency to reduce green-house gas emissions. The long-term strategy includes advancing renewable energy sources such as solar, wind, and hydroelectric power; however, there will continue to be a dependence on fossil fuels in the form of natural gas, coal, and oil [1]. One way to ease the transition from fossil fuel consumption to renewable energy harvesting, is to expand commercial nuclear energy production. This approach could lead to decreased fossil fuel consumption, while extending the timeline needed to bring renewable energy production online. Advanced Small Modular Reactors (AdvSMRs) are one emerging strategy being proposed by the nuclear power community [2]. The AdvSMR designs are modular and small size, which may reduce the capital investment costs and, potentially, construction savings through factory fabrication. However, new technical challenges accompany the many attractive features offered by AdvSMR designs. Many of the AdvSMR designs operate at much higher temperatures than light-water reactors and require instrumentation to withstand harsh, in-vessel environments arising from unconventional, chemically aggressive coolants and unique reactor system configurations. For example, molten salt reactors operate at temperatures of ≥ 400 °C [2]. A recent research study of the LiF + NaF eutectic liquid coolant showed strong oxidation of chromium and corrosion of tungsten in steel alloys, from dissolved oxygen and fluorine, leading to structural component weakening and corrosion [3]. Coolant contamination by oxide and ferric ions was also shown to increase this effect.

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One potential solution is to monitor impurities using absorption spectroscopy, where an IR-transmitting fiber guides light from the reactor headspace to an IR spectrometer located outside the reactor vessel [4]. From there, the collected IR spectra can be referenced to a baseline spectra and characterized to determine what additional chemical species are present. IR spectroscopy analyzes characteristic vibrations within the IR spectrum, i.e., $\tilde{\nu} = 4000$ to $100\,\mathrm{cm}^{-1}$ or $\lambda = 2.5$ to $100\,\mu\mathrm{m}$, of chemical species inside the reactor chamber. The approach could provide chemical sensing, within a high-temperature AdvSMR reactor, to monitor coolant impurities that are indicative of structural corrosion. This concept could also be applied to many other research and industrial applications for monitoring high-temperature chemical processes.

One of the most well-known groups of IR-transmitting materials for these types of applications are the chalcogenide glasses [5]. Interest in this glass subset has grown for decades, spurred by the development of new IR measurement technologies [6,7]. IR-transparent chalcogenide glasses typical transmit light much further into the IR spectrum, as compared to their oxide counterparts, and have been a popular material for IR waveguide fabrication [8]. The structure-property relationships for both oxide and chalcogenide glasses have been extensively investigated to engineer better materials [9–13]. IR optical materials development has primarily focused on extending IR transmission window by combining heavy elements to form glasses based on glass-forming components such as As_2S_3 [14–16], As_2Se_3 [15,17], and $GeTe_2$ [18,19]. These larger cations and anions vibrate further in the long-wave IR, allowing greater transmission at longer wavelengths [6,8]. This glass family is suitable for IR waveguide, amplifier, and laser designs for many applications, such as biomedical and space exploration [7,20], because of the extended IR transparency, excellent glass forming abilities, and solubilities for rare earth elements.

While selenide and telluride glasses transmit IR light well, they soften at relatively low temperatures, typically $T_g < 400\,^{\circ}\mathrm{C}$, due to weak covalent bonding. These covalent glasses bond through sharing electrons, and their valence electrons are weakly bound, which often leads to low T_gs between 250 and 350 °C [14,15,17]. Conversely, ionically-bonded chalcogenide glasses like the $Ga_2S_3 + La_2S_3$ [21,22] and $La_2S_3 + GeS_2$ [21,23] systems tend to have T_gs $> 500\,^{\circ}\mathrm{C}$, leading to a family of IR optical materials that can operate at elevated temperature. Optimizing these compositions as well as investigating similarly-bonded sulfides could help develop and innovate chemical sensor technology.

Just a few studies have explored higher T_g ionic chalcogenide glasses based on the $La_2S_3 + Ga_2S_3$ and $La_2S_3 + GeS_2$ systems [22,23]. For example, Risbud and Kumta [23] examined the thermal stability and microstructure in the binary system of $x\mathrm{La_2S_3} + (1-x)\mathrm{GeS_2}$, where glasses can be formed between $x = 0$ to 50 mol%. They studied the two eutectic compositions of $7.5\mathrm{La_2S_3} + 92.5\mathrm{GeS_2}$ and $40\mathrm{La_2S_3} + 60\mathrm{GeS_2}$, and found that these glasses had T_gs of 420 and 510 °C and thermal stability gaps, $\Delta T = T_c - T_g$, where T_c is the crystallization temperature, of 140 and 280 °C, respectively. At the time, these glasses had the highest known T_g values in a sulfide glass family. While these glasses exhibited higher operating temperatures and sufficient thermal stability (to avoid rapid crystallization on cooling the molten liquid to the glassy state), it was found that the glasses phase separated at low La_2S_3 content. For example, in the $7.5\mathrm{La_2S_3} + 92.5\mathrm{GeS_2}$ composition, 6 to 88 nm phase separated droplets were observed by TEM microscopy. Unfortunately, chemical analysis was not carried out on the separate phases, although they reported that other researchers found that GeS_2-rich glasses tended to phase separate into a GeS_2-rich phase [24]. At higher levels of the modifier La_2S_3, the $40\mathrm{La_2S_3} + 60\mathrm{GeS_2}$ composition was found to quench to a homogenous single-phase glass with excellent thermal stability that was suitable for IR optics.

Takebe et al. [22] further showed that other compositions in the $La_2S_3 + Ga_2S_3$ system also offer relatively high T_gs up to 555 °C and ΔT up to 125 °C. They noted that doping these glasses with oxygen allowed for even better glass formation, because the glasses resisted crystallization at higher temperatures for longer periods of times; however, the oxygen dopant did reduce the IR transparency. This work concluded that pulling optical fibers of both the pure and the oxide-doped glasses was feasible. The oxide analogues would draw into a fiber much more efficiently, but the optical fiber would have lower IR transparency due to Ga—O and La—O bonds.

In the work described here, the structures of new ionically-bonded sulfide glasses modified with heavy cations were investigated. Our motivation to select the $x\mathrm{BaS} + y\mathrm{La_2S_3} + (1-x-y)\mathrm{GeS_2}$ system was three-fold. First, while oxide glasses can operate at elevated temperature, non-bridging oxygen (NBO) hole centers are often induced when these glasses are exposed to nuclear radiation [25–27]. These hole centers limit the optical transmission of the glasses, as they absorb light in the ultraviolet-visible (UV–vis) region. Secondly, an ionic glass system was chosen over traditional covalently-bonded chalcogenide glasses such as As_2S_3 and As_2Se_3, because the ionic glasses have higher T_gs and thus can operate at $T > 400\,^{\circ}\mathrm{C}$ [14,15]. Lastly, BaS and La_2S_3 were added as modifiers to a base GeS_2 glass to provide an ionic bonding scheme. The heavy Ba^{2+} and La^{3+} cations also have large ionic radii, 1.03 Å and 1.3 Å [28], respectively, for octahedral coordination, leading to slow interatomic vibrations deep in the long-wave IR. The ionic nature and heavy atoms of this system were hypothesized to give a relatively large IR transmission window and high T_g for a sulfide-based glass. These glasses strike a compromise between highly IR transparent but low T_g selenides and high T_g but IR absorbing oxide glasses, as they transmit IR light down to $1000\,\mathrm{cm}^{-1}$ and operate at $T > 400\,^{\circ}\mathrm{C}$.

The base GeS_2 glass has been well studied. GeS_2 glass has a T_g of 450 °C [29] and is composed of repeating tetrahedral $GeS_{4/2}$ units [30]. These units are predominately bonded at the corners to other $GeS_{4/2}$ tetrahedra, often labeled as Ge^4 (the superscript describes the number of bridging sulfurs, BS), making up a fully connected three-dimensional structure. As modifiers, e.g., CaS, Li_2S, Na_2S, are added, the fully-bridging tetrahedral structure begins to depolymerize with the formation of non-bridging sulfurs (NBS). The bonds between the tetrahedra are broken to charge compensate for the cation addition, and the sulfur from the modifier is donated to the structure to allow complete tetrahedra to remain intact [10]. All of the typical structural units found in GeS_2 glasses can be found in Fig. 1.

While typically the breaking of bonds leads to a decrease in T_g, the $40\mathrm{La_2S_3} + 60\mathrm{GeS_2}$ composition that Kumta reported on had a 60 °C higher T_g compared to GeS_2 glass [23]. This suggests that an overall strengthening of bonds occurs with La_2S_3 additions, as it takes more energy to soften the material. To gather a better understanding of how to increase the T_g and broaden the IR transmission window, we investigated the local bonding structures and thermal characteristics of these materials.

2. Experimental methods

2.1. Sample preparation

The handling of the sulfide materials used in these studies was done inside high-purity nitrogen and argon gloveboxes where the O_2 and H_2O levels were consistently < 5 ppm. As high-purity GeS_2 is expensive and not widely available, it was synthesized for this work. Sixty-gram stoichiometric batches of germanium and sulfur powders (Arcos Organics, 99.999%) were loaded into a silica ampoule. Each ampoule consisted of neck and bulb sections made of silica tubing with 30-cm length and a wall thickness of 2 mm. The neck section with an inner diameter 10 mm was fused to the bulb section with an inner diameter 34 mm to make up the full ampoule.

The batched ampoule was connected to a vacuum system and evacuated to 8 Pa (60 mTorr) for 2–4 h. before sealing the neck potion