



# Infrared-transparent glass ceramics: An exploratory study



John S. McCloy<sup>a,\*</sup>, Brian J. Riley<sup>b</sup>, David A. Pierce<sup>b</sup>

<sup>a</sup> Washington State University, Pullman, WA 99163, United States

<sup>b</sup> Pacific Northwest National Laboratory, Richland, WA 99352, United States

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## ABSTRACT

In this work, the vision and need for a fully ceramized long-wave infrared (LWIR)-transmitting glass ceramic have been articulated. Three sulfide systems were explored including two with La<sub>2</sub>S<sub>3</sub> in hopes of imparting strong bonds from this refractory sulfide, and two containing GeS<sub>2</sub> in hopes of widening the glass-forming region. Attempts were made to produce glasses in the Ga<sub>2</sub>S<sub>3</sub>-La<sub>2</sub>S<sub>3</sub>-(ZnS,CaS) system, the GeS<sub>2</sub>-La<sub>2</sub>S<sub>3</sub> system, and the GeS<sub>2</sub>-Ga<sub>2</sub>S<sub>3</sub>-CdS system. Water quenching produced glasses of Ga<sub>2</sub>S<sub>3</sub>-La<sub>2</sub>S<sub>3</sub>-CaS and GeS<sub>2</sub>-Ga<sub>2</sub>S<sub>3</sub>-CdS. Microstructural and thermal analyses were used to explore nucleation and growth in these systems and infrared transmission and mechanical hardness showed potential for LWIR window use. The GeS<sub>2</sub>-Ga<sub>2</sub>S<sub>3</sub>-CdS system showed good LWIR transmission and pre-crystallized hardness superior to chemical vapor deposited ZnS. The Ga<sub>2</sub>S<sub>3</sub>-La<sub>2</sub>S<sub>3</sub> glasses did not appear to be viable candidates at this time due to a small temperature window between crystallization and glass transition temperatures and problems with oxygen contamination in the La<sub>2</sub>S<sub>3</sub> source. Suggestions are made for two alternative methods for producing fully ceramized LWIR-transmitting glass ceramics.

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## 1. Introduction

For many years, chemical vapor deposited (CVD) ZnS has been the benchmark for long-wave infrared (LWIR)-transmitting materials, and various attempts have been made to develop ceramic materials with improved engineering properties [1]. Attempts to best ZnS, however, have thus far failed, and ZnS is still the ideal material for combined thermo-mechanical and optical performance [2]. Yet, drive for improvement continues, since mechanical durability of ZnS is sub-optimal, and reduced cost is always desirable. Several candidate polycrystalline ceramics have been developed with the intent of replacing ZnS, but no material has been successful, due to poor thermal properties, degraded optical transparency, or excessive cost [1,3].

The aforementioned contenders for replacing ZnS as a durable LWIR ceramic invariably were produced with traditional ceramic powder processing or CVD. A potential alternative for making durable LWIR ceramics may lie in the use of a glass-ceramic process for making nanocomposites. Compared to traditional powder ceramic processing, glasses and glass ceramics are typically easier to form and have equal or greater potential for process scaling. By definition, glass ceramics are multiphase polycrystalline materials that were once amorphous glasses produced using one of several traditional glass-forming processes. These glasses are then cooled and subsequently heat-treated through a proscribed schedule to enable controlled nucleation and growth of crystalline phases. Durable LWIR-transmitting ceramics could conceivably

be produced from such glasses, provided that the ultimate crystalline phases are themselves LWIR transparent and are sufficiently small such that scattering due to refractive index mismatch is minimized. Ideally, glass ceramics that have crystallized fully should provide the best hardness and fracture toughness. Various applications have been proposed for infrared-transmitting glass ceramics including bulk optical elements [4,5], far-infrared transmitting optical fibers [6], devices utilizing nonlinear optical behavior [7,8], and inorganic scintillators for high energy detectors [9–11].

This paper summarizes previous work on infrared glass-ceramic systems and justifies the selection of a few candidate systems for LWIR glass ceramics. Additionally, preliminary studies are presented for making glasses in three systems containing Ga<sub>2</sub>S<sub>3</sub> and/or GeS<sub>2</sub>, including glass-forming ability, microstructure, thermal properties, infrared transmission, and mechanical hardness. Finally, the suitability of these systems for future work on LWIR glass ceramics is discussed.

## 2. Background and approach

### 2.1. Previous work on IR glass-ceramic systems

The goal of the current work is to evaluate glass ceramics in search of a product with potentially superior mechanical strength and LWIR transparency compared to CVD ZnS. It is assumed that such a glass ceramic should be fully crystalline (except minor glassy phase at grain boundaries typical of ceramics) with grain size <100 nm. Glass ceramics meeting these requirements have thus far been produced only in a few oxide systems, notably Al-(La, Gd, Y)-Zr-O (grain size ~100 nm) [12]

\* Corresponding author.

E-mail address: [john.mccloy@wsu.edu](mailto:john.mccloy@wsu.edu) (J.S. McCloy).

and Ba–Al–O (grain size 500–5000 nm) [13]. One oxide system previously investigated specifically for use as a bulk ceramic window for the midwave infrared (MWIR, 3–5  $\mu\text{m}$ ) is based on Ba–Ga–Ge–O glasses [5] containing a small volume fraction of  $\text{BaGe}_4\text{O}_9$  crystals [4]. Many other glass ceramic oxides are commercially important, but these generally consist of a glassy matrix embedded with a low to medium volume fraction (<40%) of <100 nm crystals. Examples include aluminosilicates such as mullite, cordierite, and  $\beta$ -quartz derivatives (e.g.,  $\beta$ -eucryptite), and others such as oxyfluorides and spinel [14–16].

Chalcogenide-based glass ceramics show the best promise for durable LWIR-transmitting ceramics, but systems based on heavy pnictides such as arsenic should be considered as well [3]. Since weaker chemical bonding is associated with improved transparency further into the infrared [1,17], materials based on Se and Te will have improved LWIR or far-IR transmission, but inferior mechanical properties to analogous materials based on S. However, selenide and telluride precursors typically have higher purity, as sulfur raw material is typically contaminated with oxygen, carbon, and metal-oxygen bonds [18] and these impurity species absorb strongly in MWIR and/or LWIR regions [19]. Ba–Ga–Ge–X systems (where X = S, Se), analogous to the aforementioned oxides, have been proposed with heavier chalcogens acting to increase the infrared transmission cut-off wavelength but decrease the compositional area for glass formation [20].

All sulfide glass-ceramic systems reported in the literature thus far have consisted of a majority glass phase with a minority of small crystallites. Some glass ceramics, more properly *glasses containing crystals*, are made inadvertently upon quenching when exploring the compositional dependence of glass-formation in a particular system. Some glass ceramics based on S have been deliberately designed to improve hardness, but again, these typically contain low volume fractions of crystals. The exemplar systems are traditional chalcogenide (sulfide) glasses based on  $\text{GeS}_2$  plus  $\text{Ga}_2\text{S}_3$  or  $\text{Sb}_2\text{S}_3$  [21,22], sometimes including alkali halides [6,23–25]. When an alkali halide such as CsCl is included, it is normally the crystalline phase in the glass ceramic, although rarely other phases such as  $\alpha$ - $\text{Ga}_2\text{S}_3$  are shown to precipitate [26,27].

## 2.2. Candidate LWIR glass-ceramic systems

Based on a literature review, systems containing the glass-forming components  $\text{Ga}_2\text{S}_3$  and/or  $\text{GeS}_2$  were determined to be the most promising, and thus were investigated experimentally. The expectation was that the addition of the highly refractory  $\text{La}_2\text{S}_3$  would improve mechanical properties and result in a strong ceramic when crystallized.

The Ga–La–S (GLS) glass composition is commercially available and used for fiber lasers [28]. Glass-formation in GLS is favored when  $R = \text{Ga} / (\text{Ga} + \text{La})$  is between 0.5 and 0.8, by mole [29]. Tailoring the glass with rare-earths, other than La, is possible with a reduction in the glass-forming region. Additionally,  $\text{Ga}_2\text{S}_3$  with sulfides of Ge, Sn, Pb, and Bi is reported to form glass [29]. Oxygen impurities are common in GLS glasses, producing an absorption band in the LWIR near 8.5  $\mu\text{m}$  [30,31]. Later work has indicated that oxygen impurities in  $\text{La}_2\text{S}_3$  precursor materials are at least partially responsible for the large glass-forming region of GL(O)S [28,29]. By itself, GLS may not have sufficient LWIR transparency as the 1-mm thickness cut-off (50% transmission) is  $\sim 10 \mu\text{m}$ , hence other components may be needed to stretch the LWIR cut-off wavelength, as GLS transmission may be limited by  $\text{Ga}_2\text{S}_3$  vibrations [32]. However, some crystalline phases containing elements in GLS are known to have longer LWIR transmission cut-offs of  $> 12 \mu\text{m}$ , including  $\text{CaLa}_2\text{S}_4$ ,  $\text{ZnGa}_2\text{S}_4$ , and oxygen-free  $\text{La}_2\text{S}_3$  [28,33–35]. The current study targets glasses with high enough concentrations of Zn and/or Ca such that these crystalline phases, in addition to Ga–La–S phases (of which many different crystalline phases exist [36]), might form.

Germanium sulfide can form a glass on its own [37] with a low glass transition temperature ( $\sim 338 \text{ }^\circ\text{C}$ ) [38] compared to GLS glass ( $\sim 620 \text{ }^\circ\text{C}$ ) [29], making it attractive for processing as a flux during glass melting.  $\text{GeS}_2$  reportedly makes a glass in the binary with  $\text{La}_2\text{S}_3$  [37], and when

combined with  $\text{Ga}_2\text{S}_3$ , additional glasses can be formed with multiple sulfides, including  $\text{La}_2\text{S}_3$  [28],  $\text{CdS}$  [39],  $\text{CaS}$  [40],  $\text{SrS}$  [40],  $\text{Ag}_2\text{S}$  [41], and  $\text{In}_2\text{S}_3$  [32,42], as well as halides like CsCl [26]. The glass-forming regions of representative members of these systems are illustrated in Fig. 1. Compared to  $\text{Ga}_2\text{S}_3$ ,  $\text{GeS}_2$  is a better glass-former, so making initially crystal-free glasses should be easier even when slow quenching in air. Systems containing  $\text{GeS}_2$  should have good LWIR transmission but inferior mechanical properties relative to systems without  $\text{GeS}_2$  due to the weak Ge–S bonds [1,17].

The  $\text{GeS}_2$ – $\text{La}_2\text{S}_3$  glass binary was of particular interest due to the possibility of strong La–S bonds. The phase diagram from Kumta and Risbud [43] based on data from Sarsikov et al. [44] is redrawn in Fig. 2, showing a predicted glass forming when  $\text{GeS}_2$  is 50–100 mol%. The approach in the current work is to choose a composition region with two solid phases, make a glass with this composition, and then heat-treat it to form the two crystalline phases. This is a similar approach to that taken for the MWIR nanocomposite optical ceramic system of  $\text{Y}_2\text{O}_3$ – $\text{MgO}$  [45]. The two targeted crystalline phases of Ge–La–S, assumed to be very similar in refractive index, were  $\text{La}_2\text{Ge}_5\text{S}_{12}$  and  $\text{La}_4\text{Ge}_3\text{S}_{12}$ . Monoclinic  $\text{La}_2\text{Ge}_5\text{S}_{12}$  (2–1–5) is reportedly unstable  $< 600 \text{ }^\circ\text{C}$ , decomposing into solid  $\text{La}_2\text{S}_3$  and gaseous  $\text{GeS}_2$  [46]. The  $\text{GeS}_2$ -rich phase was previously thought to be  $\text{La}_2\text{Ge}_2\text{S}_7$  (2–2–7) [44] but later suggested to be  $\text{La}_4\text{Ge}_3\text{S}_{12}$  (4–3–12) [46]. In theory then, a glass with the composition of 55 mol%  $\text{GeS}_2$  and 45 mol%  $\text{La}_2\text{S}_3$  could crystallize into roughly equal fractions of  $\text{La}_4\text{Ge}_3\text{S}_{12}$  and  $\text{La}_2\text{Ge}_5\text{S}_{12}$ . Only two specific glasses in this system are known from the recent literature: a heat-treated 60 mol%  $\text{GeS}_2$  glass crystallized  $\beta$ - $\text{La}_2\text{S}_3$ , with the  $\text{GeS}_2$  and some  $\text{La}_2\text{S}_3$  thought to remain in residual glass and a  $\text{GeS}_2$ -rich glass, containing 92.5 mol%  $\text{GeS}_2$ , instead produced only  $\text{La}_4\text{Ge}_3\text{S}_{12}$  [43]. This existing data illustrates that formation of the  $\text{La}_2\text{Ge}_5\text{S}_{12}$  compound may be difficult, as had been previously suggested [46].

## 3. Experimental methods

### 3.1. Raw materials analysis

All chemicals used in this work were high purity powders (Table 1). Upon receipt, they were stored in a nitrogen glovebox to prevent oxygen contamination ( $\text{O}_2/\text{H}_2\text{O} < 0.1 \text{ ppm}$ ; M-Braun, Inc., Stratham, NH). Chemicals were subsequently subjected to a phase-purity analysis with X-ray diffraction (XRD). Note that it was not determined what fractions of the sulfide precursors were crystalline versus amorphous. The results of the phase purity test are shown in Table 1. Several items

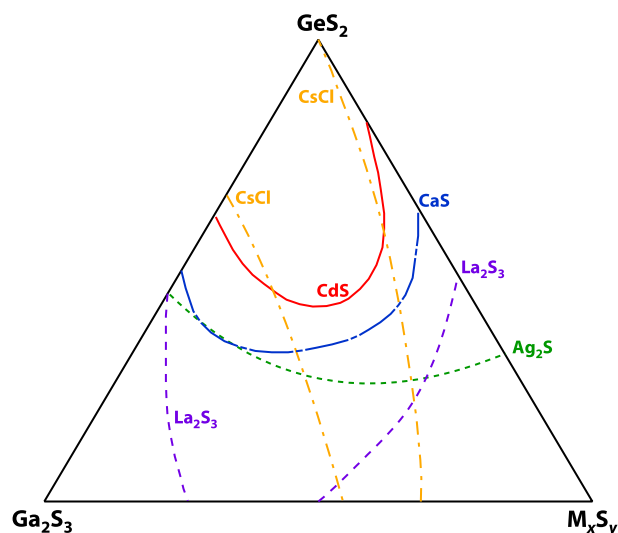


Fig. 1. Glass-forming regions (in moles) in the  $\text{GeS}_2$ – $\text{Ga}_2\text{S}_3$ –Z systems, where Z =  $\text{La}_2\text{S}_3$ ,  $\text{CdS}$ ,  $\text{CaS}$ ,  $\text{Ag}_2\text{S}$ , or  $\text{CsCl}$ .

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