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Horizontal gradient freeze growth of $AgGaGeS_4$ and $AgGaGe_5Se_{12}$

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Abstract

$AgGaGeS_4$ and $AgGaGe_5Se_{12}$ are promising new nonlinear optical crystals for frequency-shifting 1-μm solid state lasers into the mid-infrared (2–12 μm) spectral range. The quaternary compounds were synthesized by vapor transport in sealed ampoules from high purity elemental starting materials, and crystals were grown by the horizontal gradient freeze technique in transparent furnaces. $AgGaGe_5Se_{12}$ exhibited incongruent melting behavior, and small optical samples extracted from an as-grown polycrystalline boule had high scattering losses. $AgGaGeS_4$ growth was far more favorable, resulting in a crack-free single crystal measuring 19 mm in diameter and >80 mm in length with as-grown 2.05-μm absorption losses $<0.05\,cm^{-1}$. The measured laser damage threshold of an uncoated $AgGaGeS_4$ crystal at 2.05 μm was $1.1\,J/cm^2$, and room-temperature measurements of thermal diffusivity, heat capacity, and thermal conductivity yielded values of $0.224\,mm^2/s$, 0.448 J/g/K, and 0.399 W/mK respectively, for the sulfide.

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1. Introduction

Significant advances in mid-infrared nonlinear optical (NLO) crystals have been made in recent years due to the growing importance of laser applications in the 2–12 μm spectral range [1]. However, there remains a need for improved NLO materials that can efficiently shift the output of 1.06-μm solid-state Nd-lasers to wavelengths beyond 4 μm (which is the practical limit of oxide-based crystals). The chalcopyrite $AgGaS_2$ is one of the few crystals that meets this requirement, but it is plagued by a low laser damage threshold that severely limits its usefulness. The selenide analog $AgGaSe_2$ has a higher damage threshold but has insufficient birefringence for phase matching a 1.06-μm pump source.

Two new quaternary compounds have recently been reported which overcome these limitations: $AgGaGeS_4$ [2] and $AgGaGe_5Se_{12}$ [3]. $AgGaGeS_4$ can be viewed as a solid solution in the system $AgGaS_2$–GeS_2: the 50:50 mixture forms a compound with orthorhombic (mm2) symmetry that is phase-matchable for Nd-laser pumping and offers a larger bandgap and higher damage threshold than $AgGaS_2$. Similarly, $AgGaGe_5Se_{12}$ is an orthorhombic compound in the $AgGaSe_2$–$GeSe_2$ system: in this case a larger shift in band gap is accompanied by a large birefringence (~0.16) that extends the phase-matching range to allow pumping at laser wavelengths of 1-micron and below.

In order to more accurately assess the usefulness of these materials for mid-IR laser frequency conversion, we conducted preliminary synthesis and growth experiments based on our established techniques for other sulfide [4] and selenide [5] crystals. The resulting samples were characterized in terms of optical absorption, laser damage threshold, and thermal conductivity.

2. Synthesis and growth experiments

2.1. $AgGaGeS_4$

$AgGaGeS_4$ was synthesized by loading 5 9's sulfur into the end of a 25 mm I.D. × 32 mm O.D. × 16-in ampoule, followed by a quartz "choke" and a PBN-coated graphite

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boat filled with stoichiometric amounts of 6-nines Ag shot, 7-nines liquid Ga, and 40-Ω-cm Ge chunk. The ampoule was evacuated, sealed with a quartz plug, and partially loaded (with the sulfur and choke extending out past the end of the furnace) into a two-zone tube furnace fitted with an isothermal liner (a sodium-filled Inconel heat pipe). The furnace was heated at 300 °C/h to 950 °C, and the ampoule was gradually pushed deeper into the furnace to allow more and more sulfur to transport and react with the molten material in the boat. After 3 h the ampoule was completely in the furnace and allowed to equilibrate for 4 h before cooling to room temperature at 300 °C/h. Single crystal growth was performed using the horizontal gradient freeze technique in a two-zone transparent furnace, which lends itself to the growth of new materials since the solid–liquid interface and seeding process can be viewed directly [6]. The synthesized charge and boat were reloaded into a 9-in quartz growth ampoule and heated to set points of 850 and 835 °C. The measured axial gradient was 3.5 °C/cm and the solid–liquid interface temperature was 834 °C (slightly below the 845 °C melting point reported by Badikov et al. [7]). The set points were raised by 12 °C to completely melt the charge to allow liquid to flow into the empty seed well, then the cold zone temperature was dropped by 52 °C to rapidly quench the material in the seed well, then quickly raised by 50 °C to partially melt back the material in the seed well. Once equilibrated, cooling of both zones commenced at 0.2 °C/h (corresponding to a growth rate of 0.6 mm/h) until the charge was fully crystallized, followed by cooling at 35 °C/h to room temperature.

The resulting crystal, shown in Fig. 1, was outstanding for a first attempt at a new material. The first 80 mm of growth were single and crack-free, beyond which the appearance of multiple phases resulted in polycrystallinity and cracking. The as-grown crystal was translucent, which is consistent with the formation of second-phase precipitates observed in $AgGaS_2$ (and $AgGaSe_2$) due to an off-stoichiometric congruency and retrograde solubility of Ga_2S_3 (Ga_2Se_3) [8]. These scattering centers can be eliminated in the ternary chalcopyrites by post-growth annealing in contact with ~1 wt% excess Ag_2S (Ag_2Se) at ~50 °C below the melting point for 2 weeks, and we expect that similar procedures can be applied to $AgGaGeS_4$ (and $AgGaGe_5Se_{12}$) to improve transparency. Note also that these scattering losses are responsible for an apparent band-edge shift to longer wavelengths resulting in the crystal's orange color (scatter-free samples should be yellow in appearance with a band edge of 2.78 eV).

2.2. $AgGaGe_5S_{12}$

Crystal growth of the quaternary selenide proved to be somewhat more problematic. The synthesis itself was straightforward: stoichiometric amounts of 6-nines Ag shot, 7-nines liquid Ga, 40-Ω-cm Ge chunk, and 5-nines Se (pre-purified by vacuum distillation at 650 °C) were loaded into a 24-mm-diameter × 9-in long PBN boat, vacuum encapsulated in a heavy-walled ampoule, loaded into a single-zone tube furnace fitted with an isothermal liner, and heated at 100 °C/h to 650 °C, 30 °C/h–940 °C, equilibrated for 10 h, and cooled at 300 °C/h to produce an 84-g charge. The charge was then loaded into a PBN boat with a seed well, encapsulated, and heated in the transparent HGF growth furnace at 350 °C/h to setpoints of 740 °C (hot zone) and 715 °C (cold zone) respectively, resulting in an axial gradient of 3.65 °C/cm. A very rough solid–liquid interface typical of incongruent melting was observed, and the interface temperature indicated a melting point of 711 °C (compared with 713 °C reported by Petrov et al. [3]). Once a stable interface was established in the seed well, cooling commenced at a rate of 0.2 °C/h for 10 days (to yield a growth rate of 0.55 mm/h) followed by cooling at 35 °C/h to room temperature. The resulting crystal, shown in Fig. 2, was polycrystalline and cracked, but still of sufficient quality to extract some small optical samples for characterization.

Fig. 1. $AgGaGeS_4$ crack-free single crystal grown by the HGF technique.

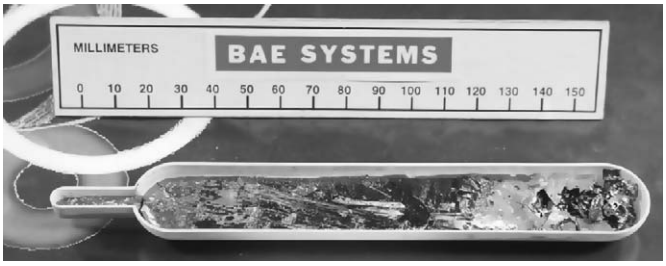

Fig. 2. $AgGaGe_5Se_{12}$ grown by the HGF technique.

3. Fabrication and characterization

3.1. Optical absorption

Several samples were cut from the $AgGaGeS_4$ crystal and polished for optical characterization. Two initial 2-mm-thick samples, irregularly shaped, were polished for damage testing while two larger 8 × 8 mm square samples were fabricated for optical absorption ($t = 3.85$ mm) and