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The Investigation on Mid-Far Infrared Nonlinear Crystal $AgGaGe_5Se_{12}$ (AGGSe)

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Abstract: 3–5, 8–14 μm mid-far infrared (MF-IR) coherent lights generated by nonlinear optical (NLO) crystals are crucial for many industrial and military applications. $AgGaGe_5Se_{12}$ (AGGSe) is a promising NLO candidate because of its good optical performance. In this paper, the large AGGSe single crystal of 35 mm diameter and 80 mm length was obtained by the seed-aided Bridgman method. The crystalline quality was characterized with X-ray diffraction, rocking curve, transmission spectrum. The FWHM of the (210) peak was about 0.05° and the IR transmission was about 60% (1–10 μm, 6 mm thick). Additionally, it performed well in 8 μm frequency doubling, with a maximum output power of about 41 mW, corresponding to an optical-to-optical conversion efficiency of 3.2%. The laser induced damage threshold (LIDT) value was about 200 MW/cm^2 (1.06 μm, 20 ns, 1 Hz).

Keywords: nonlinear infrared optical crystal; $AgGaGe_5Se_{12}$ crystal; Bridgman growth method

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1. Introduction

In recent years, 3–5, 8–14 μm mid-far infrared (MF-IR) laser sources have drawn increasing attention due to their potential applications in the fields of industry and the military, such as atmospheric monitoring, remote sensing, and IR countermeasures [1,2]. The nonlinear optical (NLO) frequency conversion is an effective and promising approach to obtain tunable MF-IR coherent light. Here, the NLO crystal is regarded as one of the core components in this system. At present, many MF-IR NLO crystals such as $AgGaS_2$, $AgGaSe_2$, $ZnGeP_2$, $CdSiP_2$, OP-GaAs, OP-GaP, $BaGa_4S_7$, and $BaGa_4Se_7$ have been developed and widely used [3–7].

$AgGaGe_5Se_{12}$ (AGGSe), as a new type of NLO crystal, was first discovered by VV Badikov in the $AgGaSe_2$-$nGeSe_2$ solid solutions systems with n = 5 [8]. AGGSe has wide spectral region (0.6–16.5 μm) and band gap (2.2 ev), large LIDT (220 MW/cm^2, 1.06 μm, 15 ns, 1 Hz) [9–11]. Additionally, it can achieve 3–5, 8–14 μm mid-far infrared wavelength, be pumped by commercially available 1.06 μm Nd:YAG or 0.8–1.0 μm Ti:Sappire lasers, with the type of second harmonic generation (SHG) [11,12], optical parametric amplification (OPA) [13], and also for difference frequency generation (DFG) [14]. It may offer some advantages over commercial crystals $AgGaS_2$, $AgGaSe_2$ if high crystal quality could be achieved.

However, up to now, only a few attempts have been reported regarding the growth, fabrication and application of AGGSe crystals; probably due to the high equilibrium partial pressure and high volatility of Se, micro-cracks induced by large anisotropy thermal expansion, stoichiometric twins and variation, obtaining large-sized and high-quality AGGSe single crystals is still a considerable challenge [14–17].

In this paper, we report the recent progress in the growth of single AGGSe crystals in our laboratory. Finally, the high-quality AGGSe crystals were grown routinely with the

dimension size 35 mm in diameter and 80 mm in length. The related optimized growth parameters were chosen and discussed, and the certain properties, including the X-ray diffraction, rocking curve, SHG laser experiment and LIDT were also tested.

2. Materials and Methods

2.1. Poly-Crystalline Prepared

The AGGSe poly-crystalline was prepared via a directed high temperature solid-state reaction technique. High purity elements Ag, Ga Ge, Se (EMei Semiconductor Co. Ltd., Leshan, China) with 5–9's and 6–9's grade were used as starting materials. To obtain uniform and single-phase materials, a suitable heating program was designed in our previous work [9], and 200 g AGGSe poly-crystalline could be obtained in one run. The identity of the obtained sample was tested by powder XRD analysis, and it was in excellent agreement with the calculated pattern on the basis of the single crystal crystallographic data of AGGSe, without any detectable impurity.

2.2. Crystal Growth of AGGSe

2.2.1. Seed Orientation Selected

AGGSe single crystal was grown by seed aided vertical Bridgman method in our laboratory. In [100], [110], [010] and so on, several seed orientations were applied for the crystal growth. For the AGGSe crystal, the largest nonlinear coefficient value was d_{31} in XZ plane (we used the correspondence XYZ = cab between the crystallographic and the principal optic axes [14]). It would be beneficial to grow the crystal along the maximum nonlinear coefficient plane or phase matching (PM) orientation, which is an effective way to fabricate long laser elements by increasing the conversion efficiency. For this reason, the seed orientation is focused on [100] in the process of subsequent crystal growth, and high-quality seeds are selected and are normally used repeatedly for a large number of experiments. The seeds are smaller in diameter (about 5 mm with 50 mm in length) with respect to the final diameter of the grown AGGSe crystal (about 35 mm).

2.2.2. Melting Point (or Seed Melting Point) Ascertained

Due to the opacity of the growth chamber, the AGGSe seed-melt interface during growth procedure cannot be observed. In fact, the thermal environment of the growth chamber and the melting point of crystal are vitally important, and tiny temperature fluctuations could sometimes remelt the entire length of the seed. Normally, the heat transfer between the furnace, crucible, melt and growth chamber should be optimized and fixed, and here the exact AGGSe (seed) melting point is important for the crystal growth. As reported in the reference, the melting point of AGGSe is 713 °C [8], 711 °C [14].

For a guide to crystal growth under our conditions, the melting point of AGGSe had to be further investigated and the thermogravimetric and differential thermal analysis instrument (TG-DTA, Diamond TG/DTA, Perkin-Elmer) was used. Here, about 5 mg of AGGSe crystal sample was measured by the heating rate of 5 °C/min in the temperature range of 30–800 °C. Only one absorption peak occurred at 715.2 °C in the TG-DSC curves (Figure 1).

Then, about 20 g poly-crystalline with a random seed orientation (about 30 mm long) was compacted, evacuated and sealed in a cone-shaped growth quartz. Several S-type thermocouples were fixed at the outside of the ampoule near the seed to measure the temperature accurately. Subsequently, the quartz was placed in a special modified resistance furnace with visual observation hole, which was heated to temperature near 710 °C gradually. The procedure of seed melting could been seen clearly as the temperature arise through the observation hole. Normally, the seed needs to be controlled and partially remelted (≈1 cm) to expose a fresh growth interface. This process is crucial and requires adequate care and rich experience, and the seed melting point of AGGSe was assured as 714.3 °C with a potentiometer under above test condition.

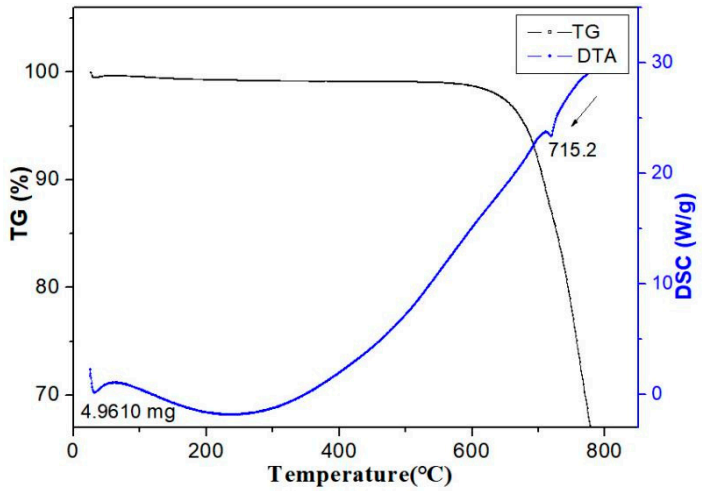

Figure 1. The TG/DSC curves of AGGSe crystal.

2.2.3. Other Growth Parameters Chosen

Different growth parameters, including the crucible pulling down speed, the temperature gradient, the rotation rate and the cooling rate, should be optimized and well controlled over the long AGGSe crystal growth period.

In fact, the growth rates greater than 6 mm per day often produced inclusion globule defects and severe cracking, twins and serious cracks were found in the AGGSe crystal when we attempted to accelerate the growth rate. To keep other experimental parameters invariable, different temperature gradients were also tested. Finally, the low growth rates ($\leq$5 mm/d) and low temperature gradients ($\leq$10 K/cm) were selected, especially in the large size crystal growth procedure, and these probably helped to avoid the thermal stresses due to large changes in diameter from the capillary to the bulk portion.

The effect of a low rotation rate had been evaluated. In the range 0–10 rpm, the rotation of quartz had no effect under the abovementioned growth conditions and the melt and quartz probably move as one body, and the interface shape remained slightly convex to the liquid regardless of the rotational conditions. The higher rotation rate was not studied because of the restrictions of the equipment.

Finally, the above factors had been considered and AGGSe crystal was grown by a seed-aided vertical Bridgman method. The crystal, 20 mm in diameter and 50 mm in length, is shown in Figure 2a. Moreover, by further growth parameter optimization, larger-sized AGGSe crystals with diameters of 30 mm and 35 mm were successfully obtained, as shown in Figure 2b,c. Some typical AGGSe crystal slices and samples 6 mm thick were prepared and are shown in Figure 3a,b. Under the table lamp light, hardly any cracks, precipitates, voids, twins, or micro-bubbles could been seen in the crystal (Figures 2d and 3c).

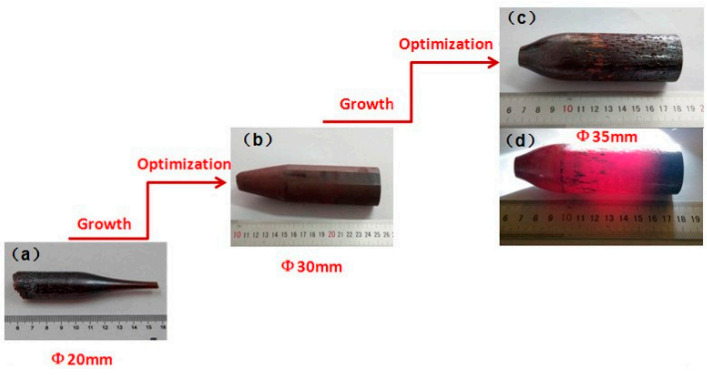

Figure 2. The AGGSe crystals with dimensions of (**a**) Φ20 mm, (**b**) Φ30 mm, (**c**) Φ35 mm and (**d**) Φ35 mm under table lamp light.

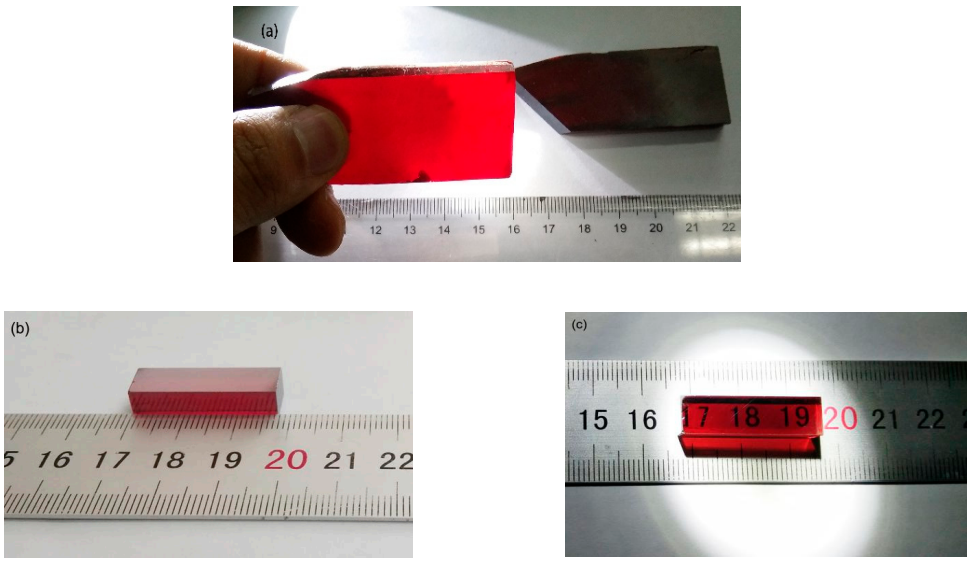

Figure 3. The prepared AGGSe crystal (**a**) slices, (**b**) sample and (**c**) sample under table lamp light with 6 mm thick.

3. Results and Discussion

3.1. Rocking Curve Measurement

The crystalline quality assessment of AGGSe was performed using a Bruker D8 ADVANCE X-ray diffractometer. A sample wafer was cut and mechanically polished on both sides for the rocking curve measurements. The shape of the peak has good symmetry without any sign of peak splitting. The intensity of the diffraction peak was high and the full widths at half maximum (FWHM) of the (210) diffraction peak was about 0.05°.

3.2. Transmission Spectrum Test

The optical transmission properties were recorded by using a UV-vis-NIR spectrophotometer (PerkinElmer Lambda 950, Waltham, MA USA) and a Fourier transform infrared (FTIR) spectrophotometer (Bruker Vertex 70, Berlin, Germany) in the range of 500–2500 nm and 4000–400 cm^{-1} respectively. The sample (Figure 3b) 6 mm thick was polished well on both sides before testing.

Figure 4a,b is the transparency spectrum of the crystal in the whole transparency range—0.63 to 2.5, 2.5 to 16.5 µm—respectively, and the crystal exhibited about 60% in 1–10 µm wavelength without obvious absorption peaks. Figure 4c exhibits the absorption coefficients (calculated according to the Beer–Lambert law with multiple reflections [18]) for the crystal and the value is about 0.06–0.1 cm^{-1} in the 1–10 µm wavelength, indicating the crystal has a fine optical quality.

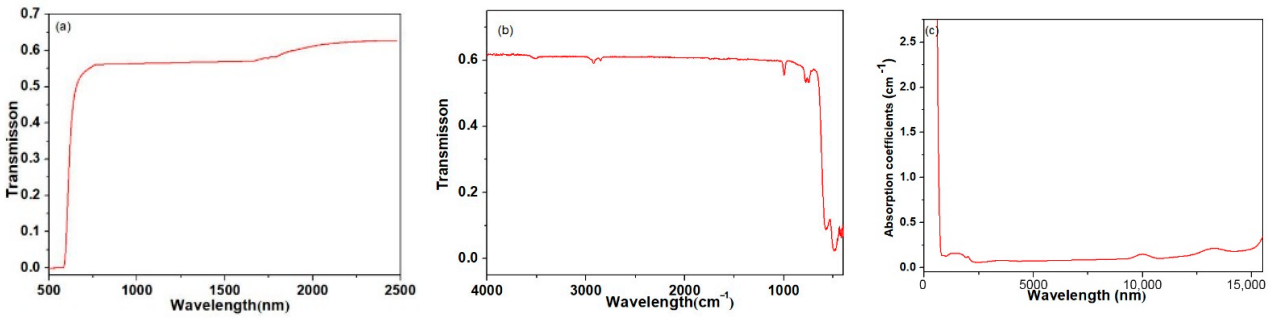

Figure 4. Transparency spectrum of AGGSe crystal (6 mm thick) (**a**) in the range of 500–2500 nm, (**b**) 4000–450 cm^{-1}, and (**c**) the optical absorption spectra in the 950–15,500 nm by calculation.

3.3. SHG Experiment

The experimental setup of the SHG of AGGSe is shown in Figure 5 [12]. Here, the 8.0 μm fundamental wave, with a pulse repetition frequency of 1 kHz, a pulse width of 27 ns, a beam quality $M_x^2 = 1.54$, $M_y^2 = 1.95$, and energy 1.3 mJ per single-pulse, was applied for the SHG experiment, which was obtained by a homemade 2.1 μm Ho, Tm:YLF laser-pumped $ZnGeP_2$ OPO procedure. The pump beam was vertically polarized to meet oo–e interaction. The uncoated AGGSe crystal with a cross face 5.5 × 6.5 mm^2 and length 10 mm, cut angle $\theta = 67.5°$, $\varphi = 0°$, xz plane, was wrapped in indium foil and fixed in a copper heat sink.

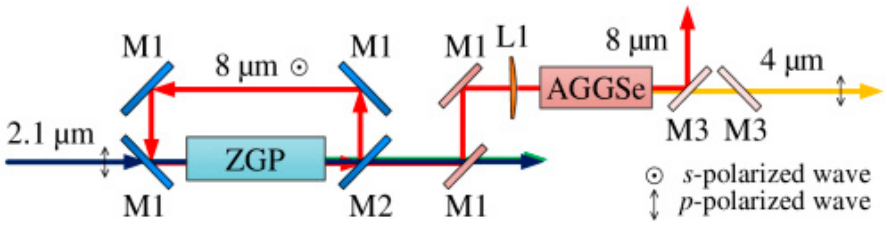

Figure 5. The Experimental setup of AGGSe SHG [12].

When the 8 μm polarized fundamental wave was injected into the AGGSe crystal, by rotating along the y axis of the crystal, the phase-matching angle θ could be changed, and a 4.0 μm laser could be obtained with a maximum output power of about 41 mW, corresponding to an optical-to-optical conversion efficiency of 3.2%. There is a deviation in the phase-matching angle θ of about 0.38° between the maximum output power (67.13°) angle and the calculated angle ($\theta = 67.5°$), which may be caused by the deviation in the crystal cutting, the errors in the Sellmeier Equation and the experimental errors.

3.4. LIDT Measurement

LIDT is one of the most important factors in the evaluation of crystal quality, especially in the use of high energy applications. Here, a standard one-on-one test procedure (ISO11254-1, 2011) was applied to test the crystal AGGSe. The sample shown in Figure 3b was used in this measurement. A commercial 1.06 μm Nd:YAG laser with pulse duration 20 ns, repetition 1 Hz and beam diameter 1.0 mm, was used as a laser source. The power of the laser increased (5 to 20 mJ) and was marked as one group in the crystal. Simultaneously the spots were observed under an optical microscope. Under four groups of experiments, the crystal surface usually damaged was under about 16 mJ per pulse power input. The surface LIDT value of crystal was calculated 200 MW/cm^2. All the above characterizations demonstrate that high-quality crystals were obtained by an optimized seed-aided Bridgman growth method.

4. Conclusions

In summary, using a seed-aided Bridgman growth method, 35 mm in diameter and 80 mm in length AGGSe crystal boule could grow integrated. The test results showed that the crystal has a high crystallinity (FWTH ≈ 0.05°), a low absorption (0.06–0.1 cm^{-1}, 1–10 μm), a fine SHG frequency conversion ability (41 mW, conversion efficiency 3.2%) and a high LIDT value (200 MW/cm^2, 20 ns, 1 Hz).

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