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RESEARCH ARTICLE

Growth of large size $AgGaGeS_4$ crystal for infrared conversion

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Abstract Single crystals of $AgGaGeS_4$ (AGGS) were grown in a modified Bridgman furnace with 25 mm in diameter and 70 mm in length. The transmission spectra of as-grown AGGS slices were measured on a Hitachi 270 – 30 spectrophotometer, the fabricated device crystal was 5 mm×5 mm×3.5 mm in dimension and its absorption was 0.04–0.15 cm^{-1}. Frequency doubling of 2.79 and 8 μm laser radiation were investigated using fabricated device crystals with thicknesses of 3.5 and 2.7 mm respectively.

Keywords crystal growth, Bridgman technique, $AgGaGeS_4$ (AGGS), frequency doubling

1 Introduction

The middle infrared (IR) 3–12 μm range is of great importance in many applications due to the transparency windows (3–5 μm and 8–12 μm sub-ranges) in the atmosphere. A variety of nonlinear materials have been developed for frequency conversion from near IR to 3–12 μm spectral ranges [1–3]. As pumping sources for frequency conversion 1.064 μm Nd:YAG and (0.7–1.1 μm) Ti:sapphire lasers are the most desirable. Nd:YAG lasers possess high power, good optical parameters, and have been widely distributed and used in mobile systems, which permits us to design a wide band of 3–12 μm sources of coherent radiation. In turn, frequency conversion of Ti:sapphire laser is also desirable for designing middle IR tunable femtosecond sources. However, most middle IR nonlinear crystals ($CdGeAS_2$, $ZnGeP_2$, $AgGaSe_2$, CdSe, etc.) are not transparent or have big loss, or can not be phase matchable at the near IR regions. $AgGaS_2$ can be used with the pumping source of 1.064 μm Nd:YAG lasers, but it has low thermal conductivity and low damage threshold, leading to a lack of high-energy $AgGaS_2$ frequency converter operating at 3–12 μm range.

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Recently, single crystals of $AgGaGeS_4$ (AGGS) crystal [4–6] has been paid much attention because of its unique properties, such as wide spectral region (0.5–11.5 μm), low absorption (typically in 0.01–0.05 cm^{-1} at 1.064 μm), suitable birefringence ($\Delta n \approx 0.06$), and high resistance to high-energy irradiation (230 $MW \cdot cm^{-2}$) et al., which make it one of the most prospective current materials for frequency conversion in the middle IR 3–12 μm range. It can be pumped with Nd:YAG and Ti:sappire lasers for optical parametric oscillation (OPO), optical parametric amplification (OPA), difference frequency generation (DFG), and also for harmonic generation of 9.2–11 μm CO_2 lasers.

Up to now, various methods have been used for the growth of AGGS crystal, such as Bridgman-Stockbarger method and horizontal gradient freeze technique [7,8]. These are all important growth methods. However, major obstacles still exist in the growth of large single crystals while the higher equilibrium partial pressures of Ge(g) and S(g) along the liquids, and in addition, stoichiometric variation, second-phase precipitates, high dislocation density and twins are still difficult to avoid in AGGS crystal growth. Therefore, it is yet very useful to perfect the growth technique for AGGS crystal.

In this article, we report on a modified Bridgman-Stockbarger method for the growth of large single AGGS crystal under carefully controlled thermal conditions with seed orientation. Certain optical properties, especially frequency conversion ability of fabricated AGGS device crystals grown by this method, have been tested in detail.

2 Crystal growth

High purity elements Ag, Ga, Ge, and Se with 5–9's and 6–9's grade were used as the starting materials. The calculated amounts of the elements were placed in carbon-coated quartz ampoules, which were then evacuated to 10^{-6} Tor and sealed. Synthesis was carried out in a two-zone tube furnace. Reaction temperature was set at 950°C and soak time for exceeding 15 h. After cooled to

the room temperature, the synthesized alloy was collected and ground into powder.

Then, a slice of AGGS single crystal (obtained by spontaneous nucleation before this experiment) with certain seed orientation was put into a carbon-coated quartz growth crucible with a cone-shaped bottom. The quartz crucible was then evacuated and sealed. Growth was carried out in a conventional vertical tube furnace at the rate of 0.5–1.2 mm/h, with a temperature gradient of 30°C/cm typically at the interface. The growth procession was finished 2 weeks later, and then the ampoule was cooled slowly to the room temperature. An integral, crack-free crystal of AGGS with 25 mm in diameter and 70 mm in length in yellow color was successfully obtained. The photograph of as-grown crystal is displayed in Fig. 1.

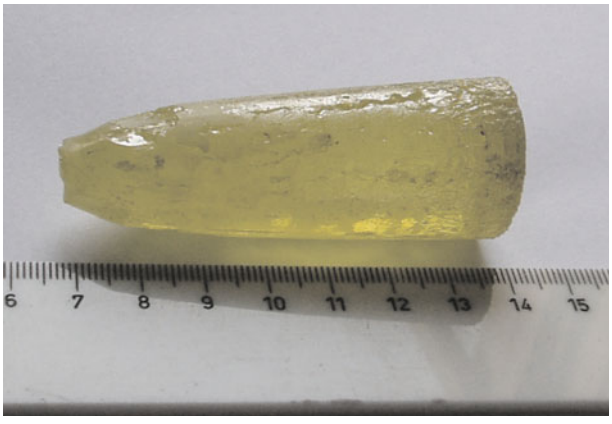

Fig. 1 Photograph of as-grown AGGS boule

The phase and the crystallographic of the products were characterized by X-ray diffraction (XRD) pattern, which was recorded with a Shimadzu XRD-6000 X-ray diffractometer equipped with Cu Kα radiation ($\lambda = 0.15406$ nm); the scanning rate of $0.05° \cdot s^{-1}$ was applied to record the pattern in the 2θ range of 10°–70°. Transmittance spectra were measured by a Hitachi 270 – 30 spectrophotometer at the room temperature model.

3 Characterization

3.1 XRD analysis

A little block of single-crystal sample was ground into powder and its XRD pattern was recorded as shown in Fig. 2, which showed the presence of the characteristic of reflectiveness with orthorhombic phase AGGS. The XRD pattern indicates that the as-prepared products have high crystallinity. The cell parameter is calculated to be $a = 1.2029 \pm 0.002$ nm, $b = 2.2911 \pm 0.002$ nm, and $c = 0.6876 \pm 0.004$ nm, which is also in agreement with the values of $a = 1.2028$ nm, $b = 2.2918$ nm, and $c = 0.6874$ nm reported [JCPDS 72–1912].

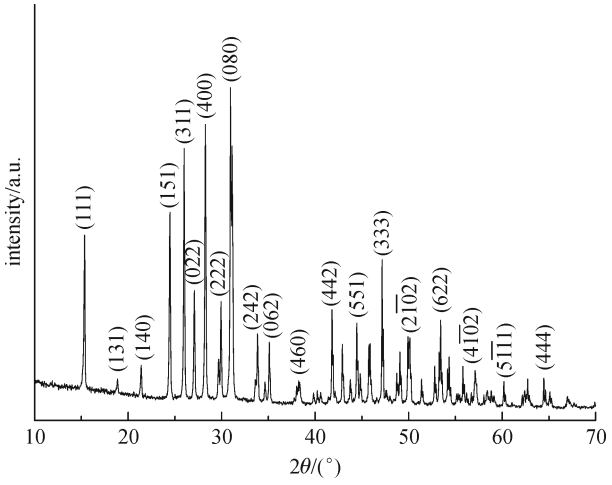

Fig. 2 XRD pattern of synthesized polycrystalline, which was agreed well with card for AGGS of JCPDS 72–1912

In order to further confirm the crystallinity of the as-grown AGGS crystal, a slice of 6 mm×6 mm×3 mm in size was fabricated with (400) face. The XRD spectrum is shown in Fig. 3(a), with no peaks be observed except (400) and (800). Figure 3(b) is the typical XRD rocking curve of the as-prepared sample, from which we can see that the intensity of the diffraction peak is high, and the shape of the peak has good symmetry. The full width at half maximum (FWHM) is about 0.018°. All these have demonstrated that the crystal has a high crystallinity.

3.2 Visible light inspection and IR transmission tests

The short cut-off wavelength of AGGS crystal is about 0.5 μm, therefore, the internal quality of the crystal could be checked roughly with naked eyes. Figure 4 exhibits the image of a single crystal with the letters "AGGS" after polishing. It is free of voids, twins, phase precipitates and in a pale yellow color.

Spectrophotometer was employed to verify the crystal's transmission property. Figure 5(a) shows the transmittance spectrum of AGGS single crystal slice with a thickness of 3.5 mm without any coating. It has a wide transparent spectral range (about 0.5–12.4 μm), and the infrared transmission is above 62% in the region from 2 to 10 μm.

The optical absorption coefficient was calculated utilizing the following equation [9] based on the above measured data of the transmission spectra.

$$\alpha = -\frac{1}{L}\ln\left(\left\{\left[\frac{(1-R)^2}{2TR^2}\right]^2 + \frac{1}{R^2}\right\}^{1/2} - \left[\frac{(1-R)^2}{2TR^2}\right]^2\right),$$

where L is the thickness of the sample, T is the transmission, and $R = (n-1)^2/(n+1)^2$ is the Fresnel power reflection coefficient. The calculated values (Fig. 5(b)) exhibit clearly absorption coefficients for the

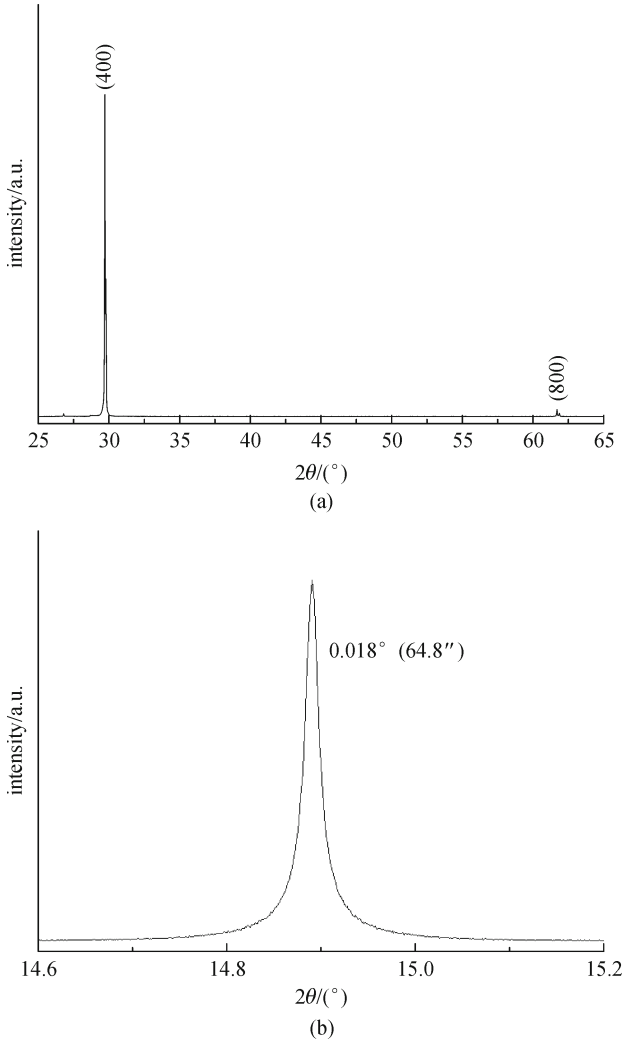

Fig. 3 (a) XRD spectrum of (004) faces ; (b) rocking curve of (004) face

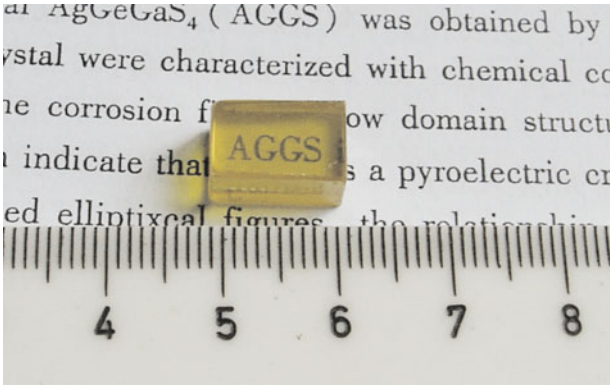

Fig. 4 Image of single crystal upper letters "AGGS"

crystal (about 0.04–0.15 cm^{-1}), indicating a fine optical quality of the crystal.

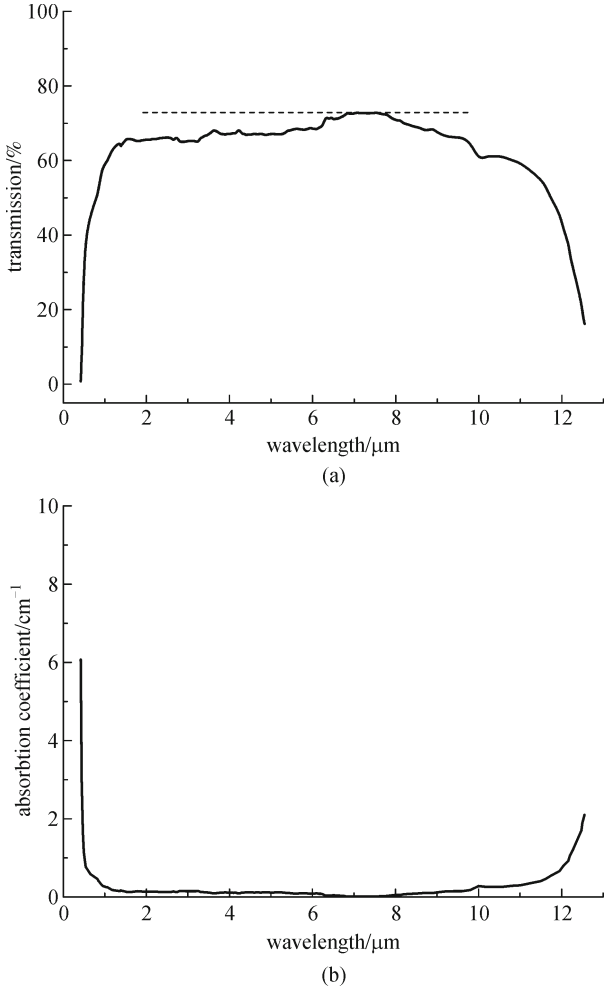

Fig. 5 (a) Transparency measured with unpolaried light of AGGS slice with thickness of 3.5 mm (broken line indicates reflectivity limit); (b) optical absorption spectrum in region of 0.5–12.5 μm

4 Second harmonic generation

We fabricated two AGGS device crystals for the experiments of second harmonic generation (SHG) in type I phase-matching in the *XZ* plane: One is for 2.79 μm Er^{3+},Cr^{3+}:YSGG laser radiation, and the other for 8.0 μm radiation from a Ho,Tm:YLF laser pumped $ZnGeP_2$ OPO source. The end faces of crystals were optically polished but uncoated.

4.1 2.79 μm SHG

2.79 μm Er^{3+},Cr^{3+}:YSGG laser (repetition 5–10 Hz, energy 20–30 mJ, pulse width 40–50 ns) is used as a pump source. The fabricated crystal is measured 9 mm×12 mm×3.5 mm (thickness) cut at $\theta = 56°$ in the *XZ* plane. The pump beam is vertically polarized to meet the oo-e interaction. By rotating the crystal in the horizontal plane, we obtain the peak output of doubling frequency for

phase-matching, which is measured 14 μJ at 23 mJ input of fundamental frequency.

4.2 8.0 μm SHG

8 μm radiation from a Ho,Tm:YLF laser pumped $ZnGeP_2$ OPO source is used as fundamental input at repetition of 10 kHz. AGGS device crystal is measured 7 mm× 7 mm×2.7 mm cut at $\theta = 43.5°$ in the *XZ* plane. Maximum output of 4015 nm radiation attained is 10 mW at fundamental input power of 930 mW.

The resulting tuning points are shown in Fig. 6. We observe that phase-matching angles (43.1°, 54.8°) are very close to the ones which are theoretically predicted by Petrov et al. [6]. Furthermore, even the lasers input energy is lowered to 5 mJ and 100 mW, double-frequency light can still be found. All these indicated that AGGS crystal grown in our lab possesses a high-frequency conversion ability.

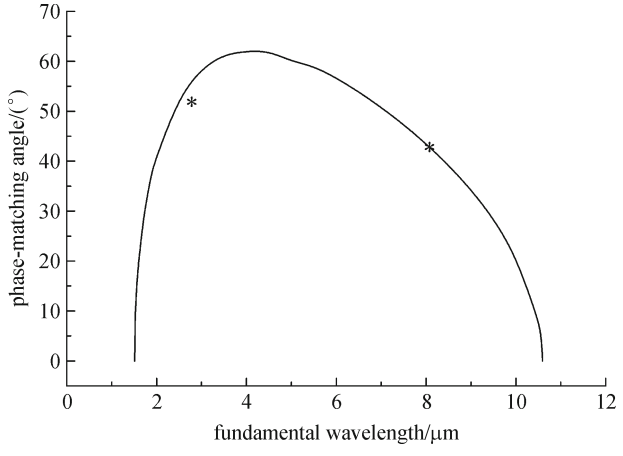

Fig. 6 Angular tuning characteristics of second harmonic generation in AGGS crystal for type I phase-matching in *XZ* plane (solid curve is theoretical prediction obtained from Sellemeier coefficients reported by Petrov et al. [6], and stars * represent our experiment measured values for SHG of 2.79 and 8.0 μm, respectively)

5 Conclusions

Single crystals of AGGS had been successfully grown under carefully controlled thermal conditions. Cracking was avoided through modifying the Bridgman furnace and optimizing the growth parameters.

Transparency of the as-grown crystal was quite good, and such a device crystal as 5 mm×5 mm×3.5 mm was obtained with the absorption in the range of 0.04–0.15 cm^{-1}.

The results of SHG experiments with very thin device crystals imply that AGGS crystal should have a potential in high-power applications by using long interaction crystal length owing to its higher optical damage threshold.

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