Synthesis and growth of nonlinear infrared crystal material AgGeGaS$_4$ via a new reaction route

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High quality nonlinear infrared crystal material AgGeGaS$_4$ with size 30 mm diameter and 80 mm length was grown via reaction of raw materials AgGaS$_2$ and GeS$_2$ directly. The as-prepared products were characterized with X-ray powder diffraction pattern and their optical properties were studied by spectroscopic transmittance. The absorption coefficient in the region of 6.8–7.8 μm is as low as 0.02 cm^{-1}, also, frequency doubling for 2.79, 8 μm with different lasers was demonstrated successfully. The reaction conditions are easy to be maintained and controlled, which may provide a new method to produce other high-quality Ag$_x$Ga$_x$Ge$_{1-x}$S$_2$ materials via changing the amount of GeS$_2$.

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1. Introduction

Since the first study of quaternary compounds with the type I–III–IV–VII in the 1960s [1], much effort has been focused on these kind of materials. Many crystals such as AgGaSiSe$_4$, CuGaSnSe$_4$, AgGeGaS$_4$, and AgAlGeSe$_4$ have been studied [2–4]. Due to various reasons, some of them could not grow into single crystals, but the others, especially, AgGeGaS$_4$ (AGGS) crystal has been paid much attention because of its unique structure, special properties, including the capability of using as nonlinear optical element in second harmonic generation (SHG), difference frequency generation (DFG) and optical parametric amplification (OPA) [5–8]. Also, AGGS is the most promising material for parametric light generators in mid-far IR range with Nd:YAG laser radiation pumping due to the weak absorption around 1 μm, high radiative resistance (230 MW/cm^2), and large birefractive index [5].

Traditionally, AGGS was synthesized by vapor transport from high-purity elements in an evacuated sealed ampoules at about 1220 K. Then the as-prepared polycrystalline is placed in a two-zone furnace by using Bridgman–Stockbarger method to growth,

or is grown by the horizontal gradient freeze technique in transparent furnaces [9,10]. These methods are very useful and are of widespread importance. However, there are some limitations in their utility usefulness, e.g. the difficulty in preparation of raw materials, probable introduction of some impurities, needing more energy and requiring much time to grow the single crystal, etc. Therefore, it is a challenge to synthesize and grow the high quality of material at more convenient steps.

In this paper, we described how single-crystal AGGS can be prepared via a new reaction route successfully by using AgGaS$_2$ and GeS$_2$ as raw materials without the preparation of polycrystalline. The reactions were easy to control and maintain. Then, the crystal's optical properties and SHG phase-matching conditions were examined. All the experimental results show that the AGGS crystal had high optical quality and excellent frequency-conversion ability when grown by this method.

2. Experimental procedures

All materials were commercially available and were used without further purification. In a typical experiment, AgGaS$_2$ (159.7 g, 99.99%) and GeS$_2$ (90.3 g, 99.999%) were put together and stirred uniformly, then loaded into a quartz ampoule of

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appropriate shape and size without any coating. The ampoule was sealed and evacuated, and placed into the furnace at the right place. Single crystal was grown using the modified Bridgman–Stockbarger method by spontaneous nucleation.

First, the resistance furnace was set to get a suitable temperature field via three independent heating zones: we raised the upper one to 1010 °C at the rate of 40 °C/h, the middle one to 950 °C and the lower one to 850 °C; maintained these temperatures for about 6 h to make the raw materials react entirely. Then the temperatures were decreased to 820, 800, and 750 °C, and held at these levels for about 48 h. Then, these temperatures were raised to 880, 840, and 780 °C to start the crystal growth. The growth process was performed in a low thermal gradient (<2 °C/cm) phase as this probably helps to prevent cracking of crystal during solidification and phase transformation. The growth process finished 2 weeks later with the growth rate of 5 mm/d, and then the ampoule was cooled slowly to room temperature. An integral and crack-free AGGS single crystal was obtained finally.

The phase and the crystallography of the products were characterized by X-ray diffraction (XRD) pattern, was and the data were recorded using a Shimadzu XRD-6000 X-ray diffractometer equipped with CuKα radiation ($\lambda=0.15406$ nm), and scanning rate of 0.05°/s was applied to record the pattern in the 2θ range of 10–80°. Transmittance spectra were measured on a Hitachi 270-30 spectrophotometer at room-temperature model.

3. Results and discussion

A little block of single-crystal sample was ground into powder and its XRD pattern was recorded, shown in Fig. 1, which showed the presence of reflections characteristic of orthorhombic phase AGGS. The intense peaks indicate that the as-prepared product has high degree of crystallinity. The lattice constants calculated for the sample are $a=1.2028\pm0.001$ nm; $b=2.2909\pm0.002$ nm and $c=0.6878\pm0.002$ nm; which is in agreement with the values of $a=1.2028$ nm, $b=2.2918$ nm and $c=0.6874$ nm, reported by the JCPDS 72-1912.

The typical photograph of the as-prepared single crystal is presented in Fig. 2a. It can be seen that the size of the crystal is about 25 mm in diameter and 80 mm in length. But at the tail, there are some incompact lumpish crystalloids, which probably result from poor crystallization. Fig. 2b is the picture of one typical
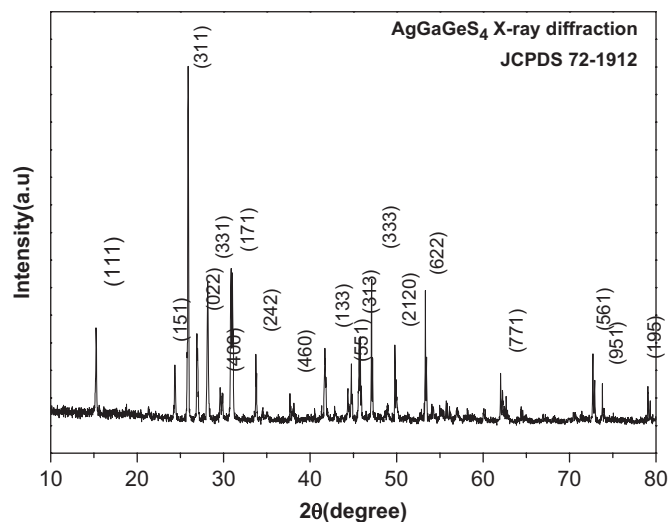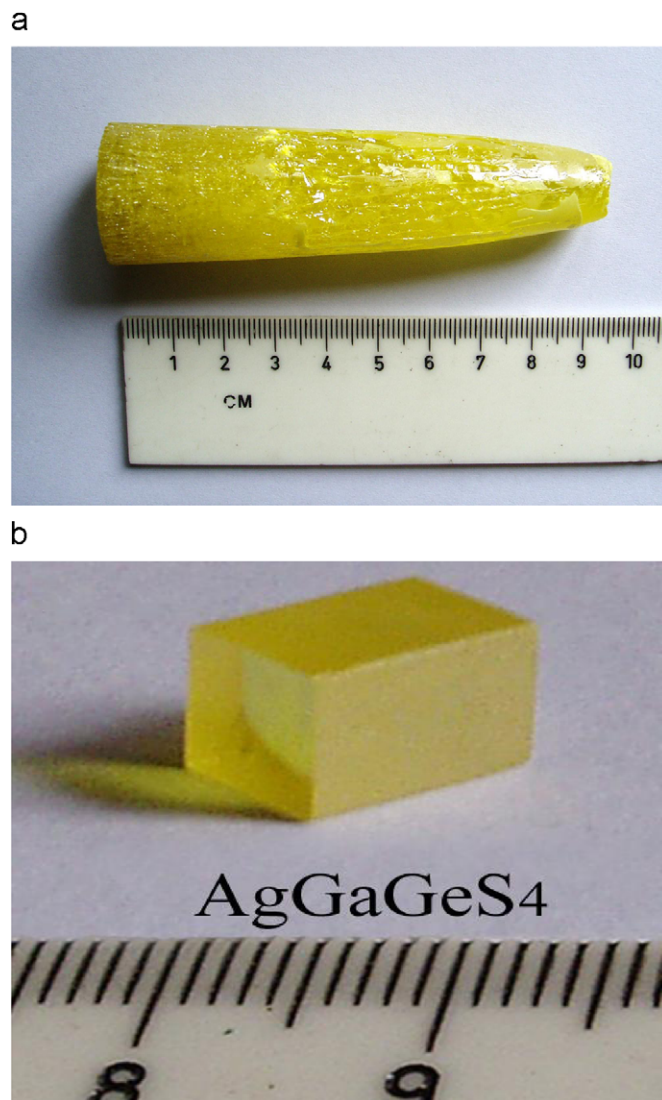

a

b

Fig. 2. The photograph of as-grown AGGS crystal (a) bar and (b) polished crystal element.

polished AGGS element (the dimension $5\times5\times10$ mm³) with pale yellow color, and it is free of voids.

We also prepared two such AGGS crystal elements for the experiments of second harmonic generation, one for 2.79 μm Er^{3+},Cr^{3+}:YSGG laser and the other for 8 μm by using Ho, Tm:YLF laser-pumped $ZnGeP_2$ OPO as pump source. According to the Sellmeier equations provided by Petrov et al. [6], type I XOZ main plain SHG tuning curve of AGGS was calculated first, then the crystals were fabricated with sizes $9\times12\times3.5$ mm³ and $7\times7\times2.7$ mm³ and cut angle $\theta=56°$ and 44°. The accuracy of the orientation is known to be within less than $\pm0.1°$ to each surface. Antireflection coating was not applied.

Before using the crystals for SHG experiments, we first measure their absorption coefficient for the entire transmission range. Fig. 3a shows the transmittance spectrum of a slice AGGS single crystal with thickness 3.5 mm without any coating. It has a wide transparent spectral range (about 0.5–12.4 μm). The transmittance absorption coefficient was calculated (Fig. 3b) utilizing the equation [11]:

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

Fig. 1. The XRD pattern of as-prepared polycrystalline, which indicates orthorhombic phase of AGGS.
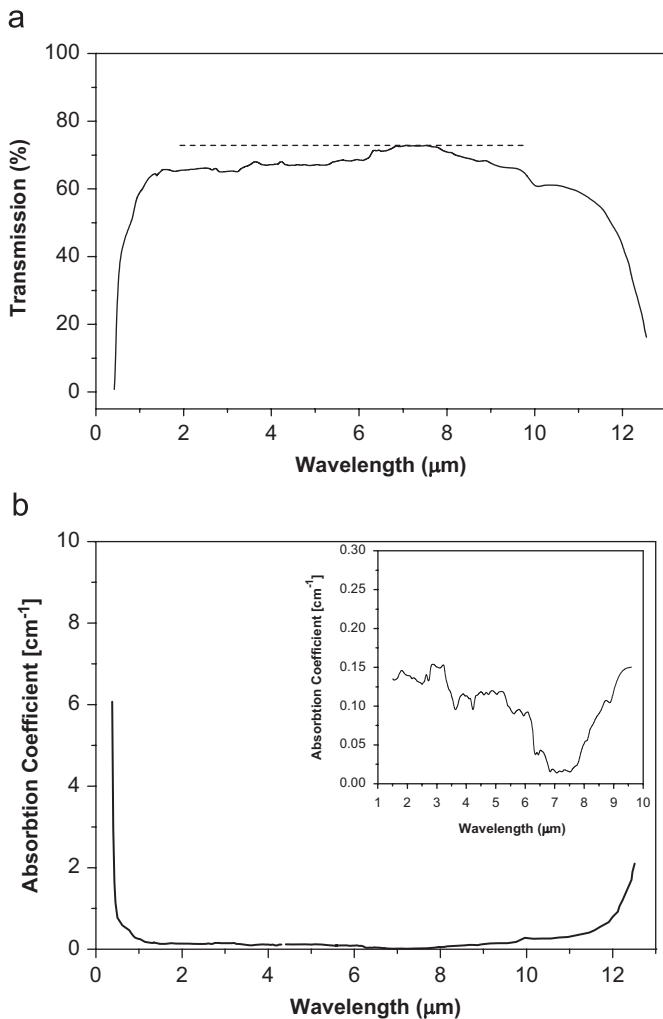
Fig. 3. (a)Transparency measured with unpolarised light of AGGS slice with thickness of 3.6 mm and (b) optical absorption spectrum in the region of 0.5–12.5 μm.

where L is the length of the sample, T is the transmission, and $R=(n-1)^2/(n+1)^2$ is the Fresnel power reflection coefficient. The figure (Fig. 3b, inset) is the magnifying curve from 1.4 to 9.6 μm with the mean absorption coefficient of about 0.15 cm^{-1}. It should be noted that in the region 6.8–7.8 μm the coefficient is as low as 0.02 cm^{-1}, indicating the crystal has fine optical quality.

For the SHG, one Er^{3+}, Cr^{3+}:YSGG laser with a repetition of 10 Hz and a pulse energy of 20 mJ is used as a pump source. The pump beam is vertically polarized to meet oo–e interaction, then the crystal is rotated and energy was measured for 1.395 μm beam and in this crystal it is about 14 μJ. Also, the phase-matching conditions for AGGS crystal SHG at wavelength 8 μm had been studied by using Ho, Tm:YLF laser-pumped ZnGeP$_2$ OPO as pump source (10 KHz, 900 mW), and 4 μm light with 10 mW harmonic energy had been detected.

The resulting tuning points are shown in Fig. 4. We observe that phase-matching angles (43°, 54.8°) are very close to the ones which are theoretically predicted by Petrov. Furthermore, even the lasers input energy lower to 5 mJ and 100 mW, double-frequency
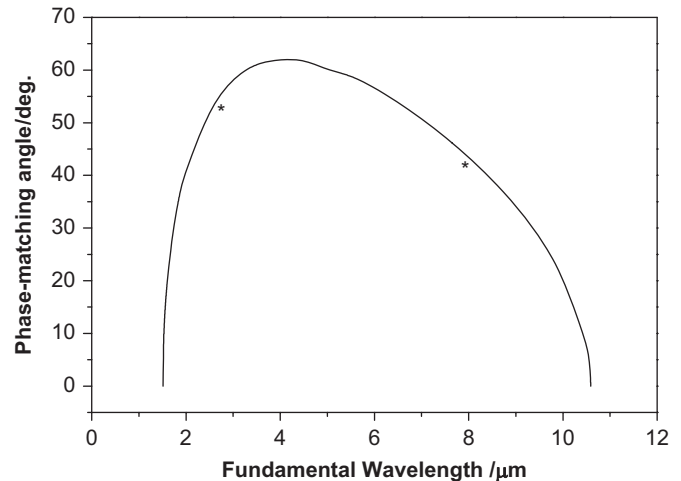

Fig. 4. Angular tuning characteristics for type I phase-matching SHG-tunable laser radiation in AgGaGeS$_4$ crystal (* are our experimental data).

light can still be been found. All these gave us the confidence that AGGS crystal grown by this method had high-frequency conversion ability.

4. Conclusions

Under the reaction of AgGaS$_2$ and GeS$_2$ with the ratio of about 1:1, high-quality nonlinear infrared crystal material AGGS was synthesized using the modified Bridgman–Stockbarger spontaneous nucleation method. This method is easy to maintain and control. It may be useful in the synthesis of the other high-quality Ag$_x$Ga$_x$Ge$_{1-x}$S$_2$ composite materials.

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