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Growth and quality of gallium selenide (GaSe) crystals

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ABSTRACT

High quality nonlinear infrared crystal material GaSe was grown using a seed aided Bridgman–Stockbarger method having a size of 24–26 mm in diameter and 55–70 mm in length. The crystals were characterized using X-ray diffraction, electron energy scattering, transmission spectrophotometry and infrared microscopy. The transmission spectrum showed that the infrared transmission is about 67% in an 8 mm thick sample cleaved along (001) face, and mean absorption 0.01–0.08 cm^{-1} in the range 0.9–15 μm. It may be suitable for the fabrication of infrared nonlinear optical devices, photoelectric analyzers of polarized light and so on. Crystals grown by this method with the described procedures may also be useful for other similar layered compounds.

1. Introduction

GaSe crystal is an excellent material for NLO applications, especially in the 8–15 μm middle–far infrared wavelength range. The crystal has some unique advantages [1,2], including extremely low optical losses (<0.1 cm^{-1}, 1–15 μm), a broad transparency range (0.65–18 μm), large nonlinear optical coefficient (d_{22}≈70–80 pm/v), high surface damage threshold (121 MW, 9.55 μm, and 30 ns) and excellent thermal conductivity (0.162 W/cm K). It is very suitable for long wave tunablity with high power at $\lambda > 8$ μm without multi-phonon absorption, although the crystal's mechanical softness properties make it generally difficult to cut and polish along some arbitrarily chosen directions.

Up to now, various methods have been used for the growth of GaSe crystals, such as, the vertical Bridgman–Stockbarger method [3,4], high-pressure vertical zone melting [5], liquid-phase medium [6], vapor deposition [7], and molecular beam epitaxy techniques [8].

These are all important growth methods. Yet, the high equilibrium partial pressures of Se (g) in the liquid state, stoichiometric variation, second-phase precipitates, high dislocation density, twins and cleaving have resulted in GaSe crystal study being almost abandoned [9]. Furthermore, the crystal's weak mechanical machining behavior is also an encumbrance for real applications.

Therefore, it is not readily feasible to optimize the reproducible growth of high quality GaSe crystals.

However, using long time periods for crystal growth and experience as guiding principles, we investigated a seed aided Bridgman–Stockbarger method for the growth of large, high quality single GaSe crystal under carefully controlled thermal conditions. Also, according to reference [10], some small samples were cut and polished containing c axis with simply chosen directions. Certain properties, especially transmittance and absorption, were measured parallel and perpendicular to the c axis respectively. The structure and component proportions of crystals grown using this method have also been tested in detail.

2. Experimental procedure

2.1. Preparation of polycrystals

GaSe polymaterials were synthesized in a 2 temperature zone horizontal furnace. High purity elements Ga, and Se (EMei Semiconductor Co. Ltd., Sichuan, China) with 5–9′s and 6–9′s grade were used as starting materials. The appropriate Ga, Se mixture was sealed in a transparent fused quartz ampoule with 30 mm diameter and 400 mm length. According to the detailed operation reviewed in [3,11], using a high temperature (970–980 °C), 200–300 g GaSe polycrystals could be obtained in 1 run (Fig. 1).

2.2. Crystal growth of GaSe

The GaSe crystal growth was carried out in a 3-zone tube furnace using a vertical Bridgman method.

A slice of GaSe single crystal (obtained by spontaneous nucleation before this experiment) with (100) seed orientation was put into a carbon-coated growth quartz crucible with a cone-shaped bottom. Then the as-prepared GaSe polycrystals were filled up to

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Fig. 1. The photograph of about 200–300 g as synthesized GaSe polycrystals.

Fig. 2. Photograph of as-grown GaSe boule 26 mm in diameter.

an inner diameter 26 mm. The quartz crucible was then evacuated and sealed. An S-type thermocouple was attached to the bottom of the ampoule in order to control the processes of melting and growth. Until the set temperature profile was attained, the melt was stirred and homogenized with the help of the furnace's rotation system. But under these conditions the position of the seed crystal was arranged for the temperature to be limited strictly at about 5–10 K lower than the melting point to avoid the seed fusing. Here, a visible observation port had been built intentionally to better control the real situation inside the furnace.

A growth run was carried out at rate of 0.5–1.2 mm/h, with a temperature gradient of 30 °C/cm typically at the interface. It was established that the optical homogeneity depends on the growth rate. The growth process was finished 2 weeks later. Then the ampoule was cooled slowly to room temperature. After careful extraction from the container, a GaSe single crystal 26 mm in diameter and 55 mm in length with black-red color cleaved along (001) plane was successfully obtained. A typical photograph of as-grown crystal is displayed in Fig. 2.

Some samples of GaSe crystals cleaved along (001), 10–30 mm long, and 5–9 mm thick were fabricated. Also, some centimeter sized samples (5–10 mm in square and 2–3 mm thick) were prepared at an arbitrary angle to the *c*-axis. By careful cutting, and polishing, the surfaces of the samples allowed examination of the primary properties structure, thermal study, optics and so on. To better preserve the planarity of the certain angled samples prepared, they were mounted on some specially prepared metal aluminum plates. Two types of typical GaSe crystals named *G*-1 (size: 30 mm × 14 mm × 8 mm) and *G*-2 (size: 6 mm × 6 mm × 3 mm) are shown in (Fig. 3a and b.)

The phase properties and crystallography of the products were characterized using X-ray diffraction (XRD), which was recorded by using a Shimadzu XRD-6000 X-ray diffractometer equipped with CuKα radiation ($\lambda=0.15406$ nm). The scanning rate of $0.05^\circ\ s^{-1}$ was applied to record the pattern in the 2θ range of 5–65°.

The elemental composition of as-prepared products was analyzed using an energy dispersive spectrometer (EDS) attached to a scanning electron microscope (SEM; FEI Sirion 200, 15 kV).

Transmittance spectra were measured on a Hitachi 270–30 spectrophotometer in the range of 0.6–20 μm at room temperature. The visual transmittance morphologies of the sample were observed with glaring flashlight and a low multiples infrared microscope HG-2 at room-temperature.

3. Results and discussion

3.1. XRD analysis

A little thin slice of single-crystal sample was ground into powder and its XRD pattern was recorded as Fig. 4, which shows the presence of reflections characteristic of hexagonal phase GaSe. The XRD pattern indicates that the as-prepared products have high crystallinity. The cell parameter is calculated to be $a=b=0.376\pm0.002$ nm, $c=1.595\pm0.005$ nm, which is also in agreement with the values $a=b=0.375$ nm, $c=1.591$ nm reported [JCPDS 37-931].

In order to further confirm the crystallinity of the as-grown GaSe crystal, sample *G*-1 has been tested. The XRD spectrum is shown in Fig. 5(a) and no peaks except {002} are observed. Fig. 5 (b) is a typical XRD rocking curve of the as-prepared sample. It can be seen that the intensity of the diffraction peak is high and the shape of the peak has good symmetry with no signs of peak splitting. The full width at half maximum (FWHM) of the (002) diffraction peak is about 0.07°. All the above characterizations demonstrate that the crystal has good crystallinity.

3.2. Composition examination

A piece of single-crystal 2 mm thick obtained from the middle-part of a boule was used for composition test with 9 independent points spreading over an area above 1 cm^2. Fig. 6 is a typical EDX spectrum of the as-prepared sample. No peaks of other elements except Ga and Se are observed in the spectrum, indicating the fine purity of the product. The weight ratio of gallium to selenium is about 0.46:0.51, corresponding to the atomic proportion 50.59:49.41. In all, the composition of Ga and Se varied from 50.42: 49.58 to 50.86:49.14, which indicates that the average chemical formula is about $GaSe_{0.976}$ and approaching the ideal one. The tiny composition deviation probably resulted from the loss of Se during synthesis and growth procession because of its higher vapor pressure.

3.3. Visible to mid–far IR transmission tests

The short cut-off wavelength of GaSe crystal is about 0.62 μm; therefore, the crystal's internal quality could be checked by naked eyes roughly. Fig. 3a, c, and d exhibits the images of sample *G*-1 under table lamp light, natural light, and glaring flashlight, respectively. *G*-2 sample was tested on a 920 nm infrared microscope (Fig. 3e). The two samples are free of cracks, precipitates, voids, twins, or micro-bubbles. These preliminarily results showed that the optical quality was fine in visible to near infrared wavelength.

The spectrophotometer was employed to verify the crystal's optical property in the whole transmission range. *G*-1 and *G*-2 without any coating were still used for testing. Fig. 7a shows the transmittance spectra. Both of them have the transparent range in the region from 0.6 to 20 μm (16700–500 cm^{-1}); the energy band-

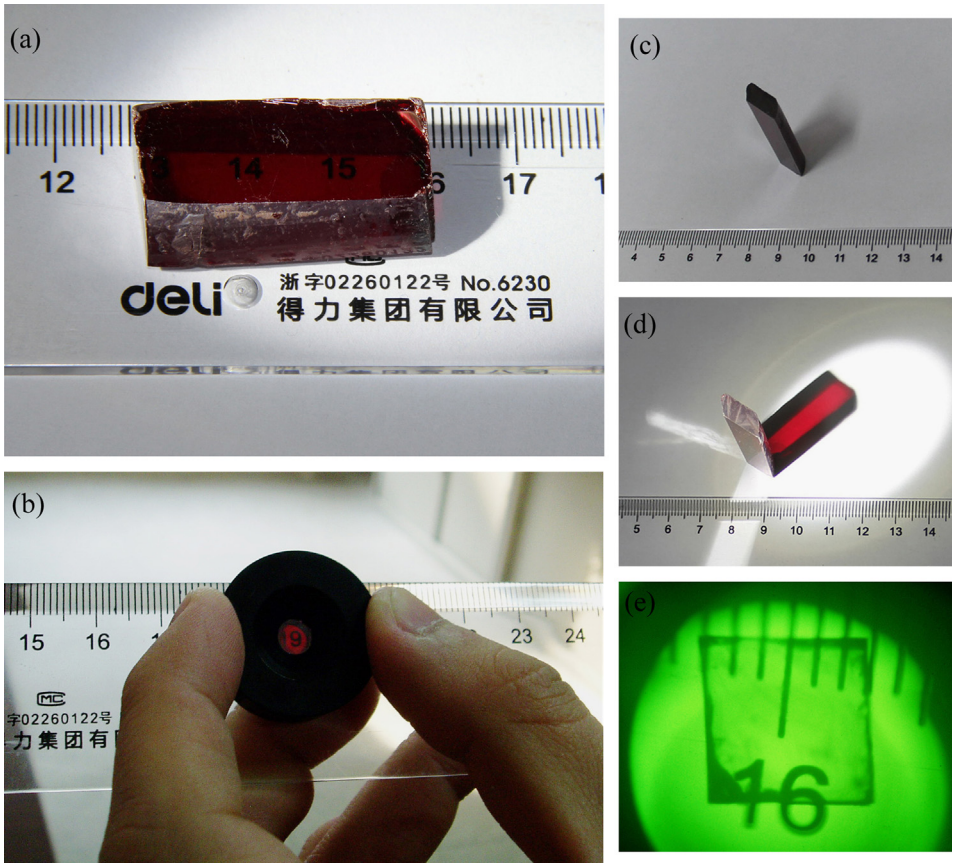

Fig. 3. Two types of typical GaSe crystals: (a) cleaved along (001) named *G*-1 with size $30 \times 14 \times 8$ mm^3; (b) prepared at an arbitrary angle to the *c*-axis with metal aluminum plates and named *G*-2, size $6 \times 6 \times 3$ mm^3; (c) *G*-1 under naked eyes; (d) *G*-1 under glaring flashlight and (e) *G*-2 under 920 nm infrared microscope.

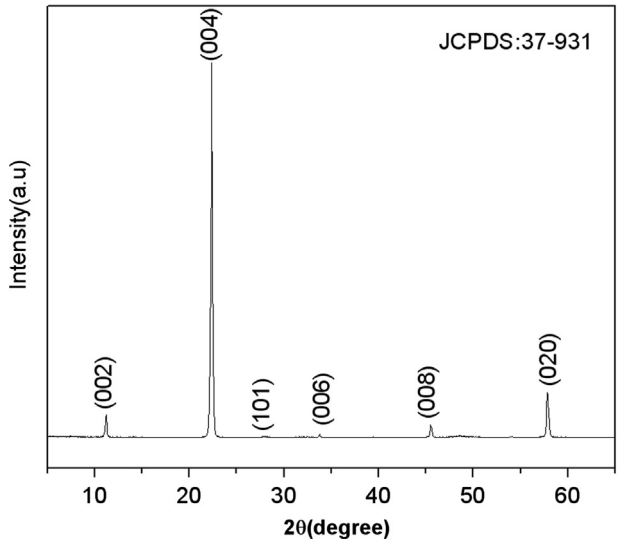

Fig. 4. The XRD pattern of as-grown GaSe crystal, which agreed well with the JCPDS 37-931 card for GaSe.

gap 2.01 eV corresponds to a fundamental absorption edge of 618 nm (inset), and these parameters are very similar to those of the reference [12]. To our surprise, sample *G*-1's transmittance was about 6–7% higher than that of *G*-2.

Here we want to emphasize that *G*-1 is about 2.67 times thicker than *G*-2. Probably the results can be explained by the behavior of GaSe's characters. Low Mohr's hardness GaSe crystals have the tendency to cause plastic deformation, and cleavage along (001) is relatively easier than other directions. Though *G*-2 sample cutting, and polishing was very careful under the preparation procedure, a tiny mistake may induce the crystal's internal structural change. This inference was confirmed by the XRD rocking curve; the *G*-2's FWHM's value was large and the peaks indicated cracking, and asymmetry. In addition, according to reference [10], probably the anisotropy free carrier absorption due to scattering by longitudinal acoustic vibrations can also affect *G*-2's transmission.

The transmittance absorption coefficients can be calculated utilizing the equation [13]

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

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. 7b) clearly exhibit absorption coefficients for the crystal in the range 0.9–15 μm (*G*-1 about $0.01-0.08$ cm^{-1}, *G*-2 about 0.2–0.3 cm^{-1}), indicating that the crystal that is cleaved along (001) has fine optical quality, but in other directions the quality is poor. Now, one still needs to pay much attention in the preparation of arbitrary angle samples in order to avoid crystal deformation.

4. Summary

In summary, 200–300 g large batches of stoichiometric mixture GaSe were synthesized by a two-zone method. With the use of a

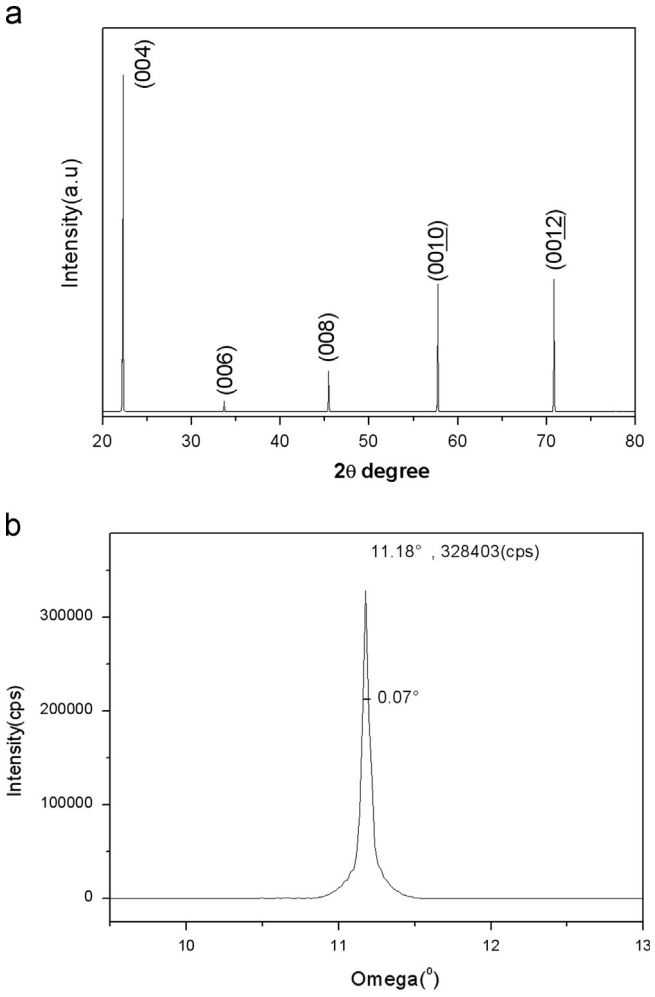

Fig. 5. (a) The XRD patterns of the {002} faces; and (b) the rocking curve of the (002) face.

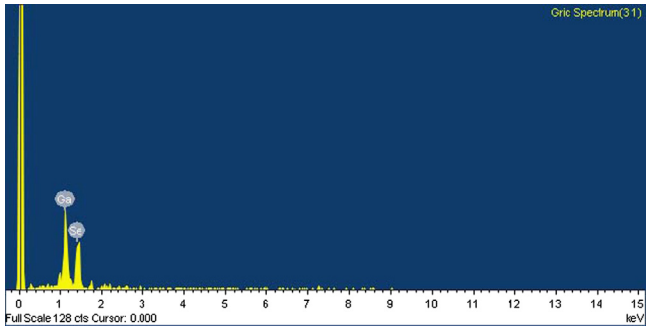

Fig. 6. EDX spectrum of GaSe revealing its chemical composition of Ga:Se = 50.59: 49.41.

seed aided Bridgman technique, 24–26 mm in diameter and 55–70 mm in length GaSe crystals boules could be grown. Preliminary results showed that crystals cleaved along (001) have high crystallinity, uniform composition and fine optical qualities with low absorption. They are suitable for the fabrication of infrared nonlinear optical devices for laser application, photoelectric analyzers of polarized light and so on. The crystals grown by this method with the described procedures may also be useful for other similar layered compounds. But preparing arbitrary angle, high quality devices is still a big challenge.

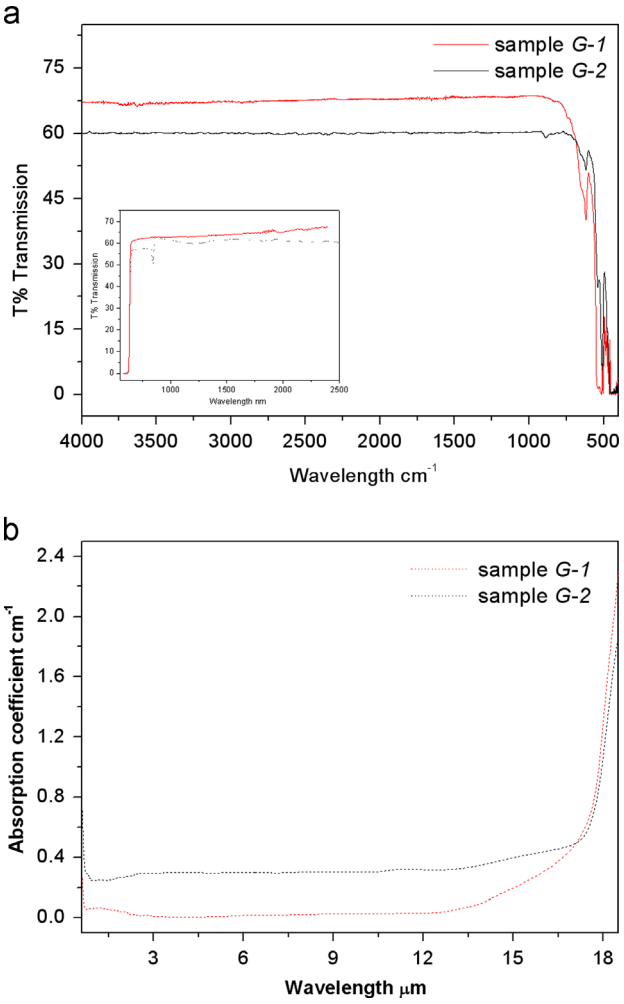

Fig. 7. (a)Transparency measured with unpolaried light of *G*-1, *G*-2 GaSe samples in the range 2.5–20 μm (inset: 0.6–2.5 μm) and (b) optical absorption spectra in the region of 0.8–20 μm by calculation.

Acknowledgments

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