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大尺寸 GaSe 单晶生长和光学性能

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摘　要：通过双温区法合成了 GaSe 多晶原料，单次合成量可达 300 g 以上。通过垂直 Bridgman–Stockbarger 法生长了直径 40 mm、长度 130 mm 的 GaSe 单晶体，测定了热学和光学性能。结果显示：吸收系数小于 1 cm^{-1} 的透过波段为 0.64 μm~17.80 μm，吸收系数小于 0.1 cm^{-1} 的透过波段为 0.64 μm~12.82 μm；太赫兹光谱显示有 2 个吸收峰，分别在 0.58 THz 和 1.10 THz 处，吸收系数均小于 5.5 cm^{-1}；GaSe 单晶体的激光损伤阈值为 3.2 J/cm^2。

关键词：硒化镓晶体；中远红外激光；非线性光学材料；太赫兹
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Growth and Optical Properties of Big-sized GaSe Single Crystals

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Abstract: GaSe is one of novel mid, far-IR and THz nonlinear optical materials with the excellent comprehensive performance. GaSe polycrystalline with a mass of 300 g was synthesized by a two-temperature zone method. GaSe single crystals with 40 mm in diameter and 130 mm in length were obtained *via* a vertical Bridgman–Stockbarger (B-S) technique. The thermal and optical properties were investigated. The transparency range is from 0.64 μm to 17.80 μm at the absorption level of 1cm^{-1}. The absorption from 0.64 μm to 12.82 μm is less than 0.1 cm^{-1}. The THz absorption spectra show two absorption peaks at 0.58THz and 1.10THz, and the absorption coefficients both are below 5.5 cm^{-1}. The laser damage threshold of GaSe single crystal is 3.2 J/cm^2.

Keywords: gallium selenide crystal; mid, far-infared laser; nonlinear optical materials; terahertz

Gallium selenide (GaSe) is an excellent material for laser frequency conversion from mid–infrared (IR) to far–IR and further to terahertz regions. This material attracts much attention due to its excellent comprehensive performance in nonlinear applications. It has an extended transparency range from 0.65 μm to 18.00 μm where the optical absorption coefficient does not exceed 1 cm^{-1}[1]. Its nonlinear optical coefficient is d_{22} (10.6 μm) = 86±17 pm/V, which is measured for IR birefringent crystals[2]. GaSe can achieve phase matching in the transmission range due to its adequately large birefringence (Δn = 0.28, at λ = 1.06 μm). Abdullaev, et al reported that the damage threshold for 3 μm wavelength at 100 ps pulses was the energy density of 3 J/cm^2. The observed damage threshold was 30 GW/cm^2[3].

GaSe is formed in hexagonal layers with several modifications designated as β, ε, γ and δ. ε–GaSe is the most promising candidate among the $A^{III}B^{VI}$–type semiconductors crystallized in a layered structure. The

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layered compounds are characterized by highly anisotropic bonding forces. In GaSe, the weak bonding forces along the *c*–axis and the strong bonding forces along the *a*–axis are responsible for an intense anisotropy. The second highly anisotropic characteristic is that the thermal conductivity in the parallel direction (*i.e.*, 16.2 W/(m·K)) to the layers far exceeds the thermal conductivity in the perpendicular direction (*i.e.*, 0.02 W/(m·K)). Each layer of GaSe comprises four covalently bounded sheets in the sequence Se–Ga–Ga–Se per primitive cell. The layers are perpendicular to the crystallographic *c*–axis. The interlayer interactions are weak, predominantly of the van der Waals forces. Cleaving the crystal parallel to the layers is thus easy and it yields excellent optical surfaces without dangling bonds. Most applications and physical property measures were carried out on the smooth cleaved face.

The vertical Bridgman–Stockbarger (B–S) technique was widely used to grow mid–IR nonlinear optical crystals such as $ZnGeP_2$, $AgGaSe_2$, $AgGaS_2$, CdSe, GaSe, etc. because of its ability to maintain low thermal gradient and growth rate independently. In this work, the spontaneous nucleation method combined with the vertical B–S growth technique was applied to grow GaSe single crystals. It is indicated that the PBN crucible with a seed–crystal well could be more suitable for GaSe growth. The big–sized GaSe crystals were obtained, and their optical properties were characterized.

1 Experimental

1.1 Polycrystalline synthesis

In the Ga–Se system, there are two congruent compounds, *i.e.*, GaSe (the melting point (MP) (960 ± 10) ℃) and Ga_2Se_3 (MP (1 020±10) ℃)[4]. An eutectic point between GaSe and Ga_2Se_3 is at an approximate composition of 55% Se at 884 ℃[3]. Terhell[5] and Klemm[6] also reported two further compounds, *i.e.*, Ga_3Se_2 and Ga_2Se, respectively. However, neither of the two compounds could be obtained by direct synthesis of the elements, an effective way to grow them is to use the sublimation method. Since there are several compounds in the Ga–Se system, some factors affect the improvement of GaSe synthesis, such as low impurity content in the reactants, an accurate stoichiometric rate and a proper growth procedure. The elementary components Ga and Se of 99.9999% purity were used. The initial components were weighed and loaded into the PBN boat in a chamber filled by Argon gas due to the readily oxidation of Ga.

GaSe can be synthesized by a horizontal one–temperature zone method and a two–temperature zone method[7–8]. In order to avoid quartz ampoule explosion, caused by a high vapor pressure of the volatile component Se, the two–temperature zone method was adopted. Ga and Se elementary materials were placed in hot and cold zones, respectively. In the first step of synthesis, the temperature in the hot zone and cold zone quickly increased to 970 and 670 ℃, respectively, and then Se material in the cold zone was transported by Se vapor to the hot zone and reacted with Ga. In the second step of synthesis, the temperature in the hot zone and cold zone soaked at 980 and 1 000 ℃, respectively. The temperature in the cold zone is higher than that in the hot zone, leading to the deposition of polycrystalline material in the hot zone. In the two–temperature zone synthesis, a cooling rate of GaSe melting down to 930 ℃was rather slower. The temperature in GaSe melting reduced from 980 to 930 ℃, thus crystallizing the compound and annealing and homogenizing at such a slow cooling rate. The mass of polycrystalline material can reach more than 300 g for one synthesis using the two–temperature zone method. Fig. 1 shows the red, shining as–synthesized ingots of GaSe with the mass of 300 g.



Fig. 1　Two As–synthesized ingots of GaSe

1.2 Single crystal growth

The B–S growth technique was used to grow GaSe crystals in a vertical two–zone furnace. The high and low temperature zones with 20 cm in length were maintained at 966 ℃ and 920 ℃, respectively. The gradient zone was 10 cm length, and a temperature gradient was 4–5 ℃/cm. The moving speed of the crucible loaded with the charges was 1–2 mm/h from the hot zone to the cold one. The spontaneous nucleation technology was applied, the shape of the growth crucible is thus important. The PBN crucible with a thin seed–crystal well of 5 mm in diameter and 25 mm in length was used for the single crystal growth. The seed–crystal well can realize the elimination mechanism of geometric selection during the crystal growth. The PBN crucible was loaded with the polycrystalline materials and inserted into the growth ampoule, then evacuated, sealed off and inserted into the two–temperature zone vertical furnace to begin the crystallization process. Two GaSe crystals with 20 mm in diameter were obtained in the PBN crucible. The first as–grown crystal (see Fig. 2(a)) is red and has a roughened surface. And the second as–grown crystal (see Fig. 2(b)) is gray and has a smooth surface. In Fig. 2(c), the (0001) layers of the crystals are nearly parallel to the growth axis, which is more conducive for cutting and making the device. Layered crystals tend to grow along

the primary thermal gradient. GaSe crystal with 40 mm in diameter and 130 mm in length (see Fig. 3(a)) was also obtained under the same condition. However, the (0001) layers are approximately 45° from the growth direction of crystal (see Fig. 3(b)). Kokh *et al*. reported that GaSe crystals with a sub–orthogonal orientation of the (0001) layers to the growth axis could be obtained in a rotating heat field[9].



(a) As–grown red crystal



(b) As–grown gray crystal

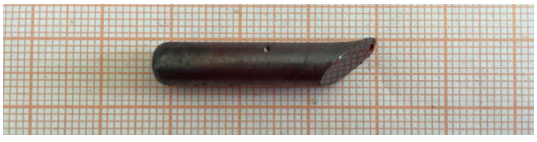


(c) (0001) layers of GaSe crystal

Fig. 2 As–grown single crystal ingots of GaSe with 20 mm in diameter



(a) As–grown gray crystal



(b) (0001) layers of GaSe crystal

Fig. 3 As–grown single crystal ingots of GaSe with 40 mm in diameter

1.3 GaSe device preparation

As a layer crystal, the Mohs hardness of GaSe is almost zero, GaSe crystals are thus readily out of shape during the measurement and application. In order to overcome this disadvantage, GaSe devices were made with aluminum (or copper) and polytetrafluoroethylene (PTFE). The as–grown crystals were cut by a cutting machine along the perpendicular direction of the cleavage plane. A cleavage plane with 10 mm×10 mm area was prepared by gentle cleavage from the cut crystal block. The transparent surfaces did not require further polishing and cleaning treatment because of the natural mirror–like cleavage plane. GaSe crystal blocks with 10 mm×10 mm×8 mm were fixed on an aluminum plate using a hot melt adhesive. The diameters of the finished device and the middle hole were 50 mm and 10 mm, respectively.

1.4 Characterizations

The thermal property of the sample was determined *via* differential scanning calorimetric (DSC) analysis in a model Netzsch STA449–C thermal analyser (Germany). The slice sample of GaSe was placed in an Al_2O_3 crucible and heated from room temperature to 1 100 ℃ at the rate of 10 ℃ /min. Ar gas flowing at the rate of 40 mL/min was used to prevent from the oxidation of GaSe.

An Agilent Cary 5000 UV-Vis-NIR spectrophoto meter (Australia) was used to measure the spectra from 0.2 μm to 3.3 μm and the mid-IR spectra was measured with a Perkin Elmer FT-IR spectrometer (America) in the range of 25 μm to 2.5 μm at room temperature. Two 8 mm–thickness wafers from red and gray crystals without further polishing and cleaning treatment were used for infrared optical measurements using the nonpolarized light in the 2.5–20.0 μm range and the polarized light in the 0.2–2.5 μm range. The absorption coefficient α_o was calculated for both wavelength regions using the o–polarized Sellmeier equation, taken from:[10]

$$n_o^2(\lambda) = 7.443 + 0.3933/\lambda^2 + 0.0186/\lambda^4 + 0.0183/\lambda^6 + 3.1485\lambda^2/(\lambda^2 - 2194)$$

where n_o is the refractive index for the o –ray and the λ is the wavelength, μm.

The major constituents Ga and Se and the atomic ratios of elements were determined by an inductively coupled plasma–atomic emission spectrometer (ICP–AES) (Perkin Elmer, America) with a sensitivity of 0.1–100 ng/L and an accuracy of 1%–3%. The solid state samples were first dissolved layer–by–layer in the aqua regia of HNO_3:HCI (1:3) at the room temperature and then were prepared into the 1–10 mg/L solution.

The terahertz absorption spectra of GaSe was measured by Bruke Vertex 80 V Fourier spectrometer using the liquid Helium bolometer (Germany). A repeating Q–switched 2 091 nm Ho:YAG laser was employed as a pump source to measure the laser damage threshold. The laser power was determined *via* Newport 1918-R optical power meter (America).

2 Results and discussion

2.1 Thermal analysis

Fig. 4 shows the DSC curve of GaSe crystal. The

onset of the melting process is located to be 874 ℃ and an endothermic peak appears at 936 ℃. The melting point data are consistent with the congruent melting point (*i.e.*, 938 ℃) of GaSe in the phase diagram of Ga–Se system by Singh[3], indicating that GaSe crystal is in a nearly stoichiometric ratio. GaSe is a congruently melting compound and has a widely homogeneous range from 42% Se (in mole fraction, above 900 ℃) to 55% Se (above 884 ℃)[3].

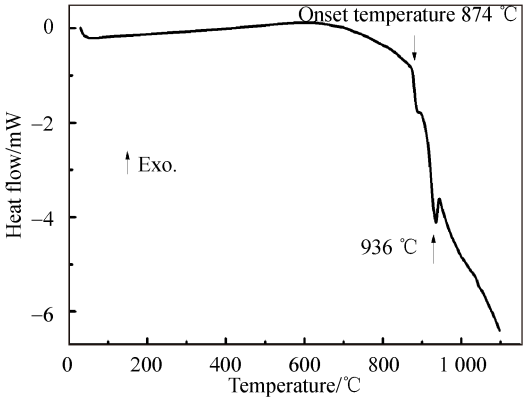


Fig. 4　Differential thermal analysis curve of GaSe crystal

2.2　IR spectra

Fig. 5 shows the IR transmission and absorption spectra of GaSe crystal. Clearly, some absorption peaks from 14 μm to 17 μm are involved in the specific lattice vibrations of GaSe crystals, which are similar to the results in other work[2,11]. The optical absorption of gray crystal is obviously lower than that of red crystal. The optical absorption of gray crystal is less than 0.1 cm^{-1} from 0.64 μm to 12.82 μm, and the absorption curve is flat. The optical absorption of red crystal increases monotonously with the increase of wavelength in the whole transparency range. The absorption distinctions of the two samples might be attributed to the crystal compositions and lattice defects.

According to the relative contents of the elements, the calculated structural formula of red crystal and gray crystal were $GaSe_{1.07}$ and $GaSe_{1.06}$, respectively. The Se contents of the samples both are excessive. The Ga/Se ratio of gray crystal is near stoichiometric, compared to that of red crystal.

The transparency range of GaSe crystals is from 0.64 μm to 17.80 μm at the absorption level of 1cm^{-1}. The shortest wavelength of 0.64 μm and longest wavelength of 17.80 μm are shorter than the references data (*i.e.*, 0.65 μm and 18.00 μm), respectively. The cutoff edge in the short-wave region is related to the band gap, and the types of native point defects lead to the shift of the long-wave cutoff edge. The shifts of two cutoff edges could be attributed to the crystal compositions and crystal colors. The similar cases also occur in another crystal material $LiInSe_2$ [12–14].

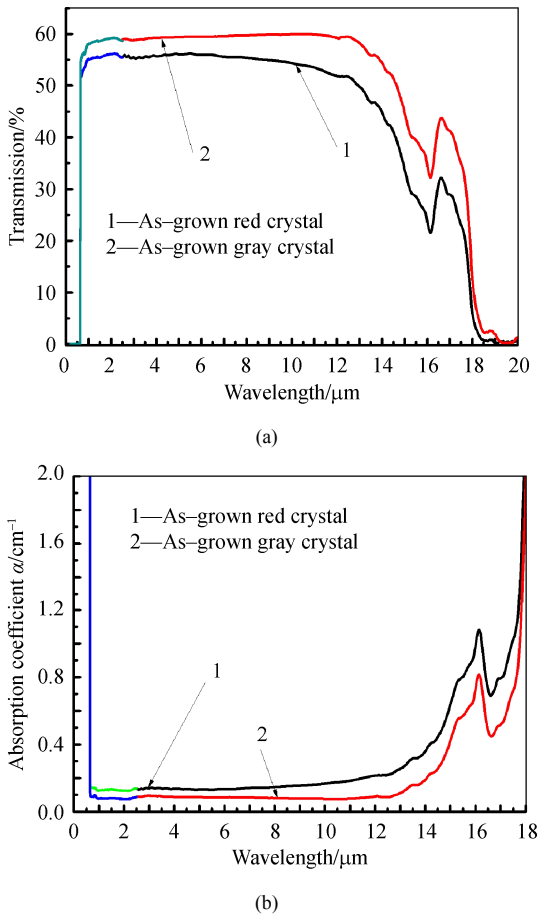


Fig. 5　Transmission spectra (a) and absorption coefficient spectra (b) of GaSe

The possible reasons for the absorption losses could be since a) the Rayleigh scattering (caused by some aggregates) at $\lambda < 5$ μm. which is $\sigma \sim \lambda^{-4} r^{6}(\varepsilon - \varepsilon_0)$, where r is the size of scattering aggregate with $r << \lambda$[15]. The scattering intensity is a maximum value at the short wavelength and decreases as the wavelength increases. The two absorption curves of red and gray crystals are near and flat at $\lambda < 5$ μm, the Rayleigh scattering is thus slight in the crystals; and b) the lattice dislocations and point defects produce a continuous set of energy levels in the forbidden zone[16]. According to the absorption spectra, the major absorption is located at $\lambda > 5$ μm, and the absorption of red crystal increases monotonously with the increase of the wavelength at $\lambda > 5$ μm. The optical absorption of GaSe crystal is probably due to the point defects and dislocations.

2.3　Terahertz absorption spectra

Fig. 6 shows the THz absorption spectra of 8 mm thickness GaSe crystal.The THz absorption of GaSe is mainly determined by the acoustic and optical phonon (*i.e.*, TO and LO) absorption in addition to the free–carrier absorption that is dominant below 1 THz[17]. There exists an acute absorption peak at 0.58 THz and a wide absorption peak at 1.1 THz. The absorption

coefficients, α, are all below 5.5 cm^{-1} at 0–10 THz, but the oscillatory absorption spectra appear above 1.7 THz due to the interference (*i.e.*, etalon effect).

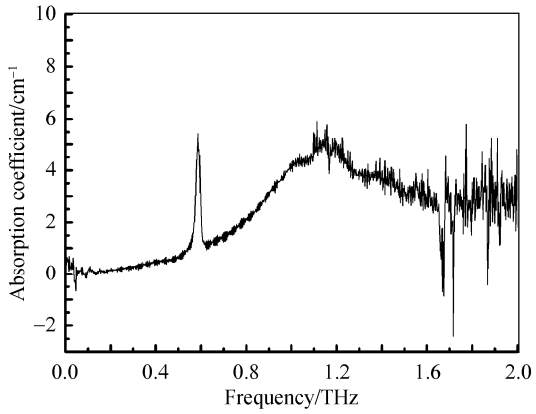


Fig. 6 Terahertz absorption spectrum of GaSe crystal with 8 mm thickness.

2.4 Damage threshold

The pulse frequency and pulse width were 500 Hz and 27 ns, respectively. The $1/e^2$ beam diameter was focused to 0.65 mm on the sample surface, and the beam quality M^2 is 1.2. An energy density of 3.2 J/cm^2 was applied without damage, corresponding to a power density of 118 MW/cm^2.

3 Conclusion

GaSe polycrystalline with mass up to 300 g was synthesized by a two–temperature zone method. GaSe single crystal grew *via* a vertical B–S growth technique in a vertical two–temperature zone furnace. The PBN crucible with seed–crystal well was used to realize the elimination mechanism of geometric selection in the process of spontaneous nucleation crystal growth. GaSe crystal with 40 mm in diameter and 130 mm in length was obtained.

The transparency range of as–grown GaSe was from 0.64 μm to 17.80 μm at the absorption level of 1 cm^{-1}. The optical absorption for the gray crystals was less than 0.1 cm^{-1} from 0.64 μm to 12.82 μm. The optical absorption might mainly come from the lattice dislocations and point defects. Based on the THz absorption spectra, there existed an acute absorption peak at 0.58 THz and a wide absorption peak at 1.1 THz, which were attributed to the acoustic and optical phonon vibrations. At 500 Hz and 27 ns, the damage threshold value of GaSe devices *via* a repeating Q–switched 2 091 nm Ho:YAG laser was 3.2 J/cm^2.

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