

Optical Transmittance Range of High-Temperature Stable Phase Germanium Dichalcogenide (GeS₂) Single Crystal Grown by the Bridgman Method

Masaru Nakamura¹, Yoshitaka Matsushita¹*

National Institute of Materials Science (NIMS), 1-1 Namiki, Tukuba, Inaraki 305044,
Japan

Corresponding Author

*Masaru Nakamura, E-mail address: nakamura.masaru@nims.go.jp.

ABSTRACT

A high-temperature (HT) stable phase germanium dichalcogenide (GeS_2) was grown in an evacuated quartz ampoule to investigate its transparency range. First, as a starting material for the crystal growth of HT- GeS_2 , GeS_2 glass containing HT- GeS_2 crystals was synthesized using our previously improved process for synthesizing polycrystalline sulfide compounds in a conventional horizontal furnace. The HT- GeS_2 crystal was grown using the Bridgman method under a temperature gradient of 20–30 °C/cm. The grown HT- GeS_2 single crystal was easily cleaved along the growth direction, and this cleaved surface was identified as the (001) face using X-ray diffraction (XRD). Single-crystal XRD analysis confirmed the growth of an HT- GeS_2 single crystal with a monoclinic structure (space group $P2_1/c$) and lattice parameters of $a = 6.7061(4)$ Å, $b = 16.0877(13)$ Å, and $c = 11.4242(11)$ Å, and $\beta = 91.069(8)^\circ$. The optical transmittance spectra of the HT- GeS_2 single crystal were measured in the visible and infrared (IR) regions, revealing a transparency range of 0.36–22.5 μm . Differential thermal analysis revealed the melting point of HT- GeS_2 as 841 ± 1 °C. The HT- GeS_2 single crystal is expected to be a new candidate for IR optical crystal.

Keywords: A2. Bridgman technique, Growth from melt, Single crystal growth, B1. Sulfides, B3. Infrared devices

1. Introduction

The demand for infrared (IR) light sources (wavelength: 2.5 to 25 μm) is surging in various fields such as medicine, environmental measurement, materials processing, and optical communications. Materials capable of transmitting in the far-IR region above 10 μm are mainly limited to halogenated (nonfluoride) and chalcogenated materials. A zinc telluride (ZnTe), zinc selenide (ZnSe), and zinc sulfide (ZnS) crystals are promising candidate crystals in this region (transparency region: 0.59–25 μm (ZnTe) [1], 0.47–19 μm (ZnSe) [1], and 0.35–23 μm (ZnS) [1]). However, these materials do not melt at ambient pressure, making the growth of crystals from the melt difficult. High-pressure and high-temperature (HT) growth conditions are required to grow these crystals from melts [2].

Se and Te are present in small amounts in the environment, whereas S is abundant. Therefore, we focused on the sulfide crystals, particularly GeS_2 crystals. GeS_2 has been studied for many years. In 1886, Winkler successfully synthesized GeS_2 for the first time [3]. Phase diagrams of the Ge–S system have been published [4–7]. Based on these phase diagrams, GeS_2 is found to melt congruently at 821 $^{\circ}\text{C}$ [6] and 840 $^{\circ}\text{C}$ [4] at ambient pressure. In addition, GeS_2 has been found to occur in the phase transition at 600 $^{\circ}\text{C}$ [4,6] from the HT to the low-temperature (LT) stable phase. However, there are

few studies on the physical properties of GeS₂ crystals, although there are many studies on glasses in the Ge–S system. In addition, fewer studies have been conducted on HT-GeS₂ crystals were fewer compared to LT-GeS₂ crystals.

Transparency range is one of the most important parameters in IR applications. However, data on the transparency range of HT-GeS₂ crystal have not been published. Although these two papers described the crystal growth of the HT-GeS₂ single crystal using the Bridgman method, transmittance data near the IR region of the HT-GeS₂ crystal have not been reported. In these two studies, the optical transmittance of the HT-GeS₂ single crystals was measured in the range near the absorption edge, owing to the bandgap [8,9].

Therefore, in this study, we investigated the transmittance range of an HT-GeS₂ single crystal. First, as a starting material for the crystal growth of HT-GeS₂, GeS₂ glass containing HT-GeS₂ crystals was synthesized using our previously improved process for the synthesis of polycrystalline sulfide compounds in a conventional horizontal furnace. A single crystal of HT-GeS₂ was grown in an evacuated quartz ampoule using the Bridgman method. The optical transmittance spectra of the HT-GeS₂ single crystal were measured in the visible and IR regions.

2. Experimental Procedure

2.1. Preparation of Starting Material for Crystal Growth of HT-GeS₂

First, we synthesized a GeS₂ glass, containing GeS₂ crystals, as the starting material for the crystal growth of HT-GeS₂. This process is similar to our previously improved method for synthesizing sulfide polycrystals [10,11]. The raw materials used for this process were commercially available Ge metal of (99.999%) 5N equivalent purity (resistivity > 50 $\Omega \cdot \text{cm}$, Mitsubishi Materials Electronic Chemicals Co. Ltd. Akita, Japan) and purified S powder. A commercially available S powder (reagent-grade S powder; Kanto Chemical Co. Inc. Tokyo, Japan) was purified by a three-cycle distillation process developed in-house [12]. The compositional ratio of the preparation was Ge:S = 33.3 mol% : 66.7 mol% (stoichiometric composition), for a total of 5.0 g. The raw materials were placed in a quartz ampoule with an outer diameter of 13 mm, evacuated to approximately 10^{-3} Pa using a diffusion pump, and vacuum-sealed. The vacuum-sealed quartz ampoule was approximately 170 mm long and more than half the length of the furnace.

Figure 1 shows the schematic of the equipment used to prepare the starting material for the crystal growth of HT-GeS₂. These materials in the ampoule were pulled to one side of the ampoule and this part was placed in a single-zone horizontal furnace at

approximately 1080 °C in the center. Immediately after insertion, the sulfur evaporated, and its vapor moved in the opposite direction of the ampoule, which was outside the furnace; thus, the section was water-cooled to reduce its vapor pressure. The reaction between Ge and S started after approximately 1 h. The content of sulfur vapor decreased as the reaction between Ge and S progressed; thus, the ampoule was gradually inserted deeper into the furnace. When the reaction was complete, the entire ampoule was placed in a furnace, and water cooling was completed. The reaction between Ge and S completed after approximately 1 h from its initiation. Notably, the quartz ampoule did not crack during this water-cooling process. The temperature was then lowered to about 1000 °C and held for about 12 h, after which the ampoule was removed from the furnace and quenched to room temperature. The sample synthesized by this process was characterized using powder X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2.2. Growth of HT-GeS₂ Single Crystal

Once the identification of the samples synthesized by the above method was complete, the quartz ampoule with the pointed tip for crystal growth (outer diameter 13 mm ϕ) was used to synthesize the above samples. Then, the ampoule was shortened as

much as possible and used for crystal growth after the sample synthesis to eliminate the need to transfer the synthesized sample from the synthesis ampoule to the growth ampoule.

The HT-GeS₂ single crystals were grown using the vertical Bridgman method. The growth temperature was based on the reported melting point of the phase diagrams (821 °C [6] and 840 °C [4]). The ampoule was set at the center of the furnace at room temperature. The furnace temperature was elevated to approximately 935 °C and held for approximately 4 h to achieve a homogeneous melt. The temperature was lowered to 900 °C before crystal growth began. Based on these reported melting points, the temperature gradient for the growth furnace was determined to be 20–30 °C/cm. The growth conditions were a pull-down speed of 0.5–1.0 mm/h, no rotation, and no seed crystal. At the end of the crystal-growth process, the furnace temperature was maintained, and the ampoule was removed from the furnace to room temperature to suppress the phase transition from an HT stable phase to an LT stable phase.

2.3. Characterization

Powder XRD was used to identify the synthesized sample as the starting material for crystal growth. The diffractogram was recorded on a MiniFlex (Rigaku, Tokyo, Japan) X-ray diffractometer, using Cu K α radiation at 40 kV and 15 mA, in the 2 θ scan range of

5°–90° at a scan rate of 2°/min and scan step of 0.02°. This diffractometer was also used to perform an XRD analysis of a platelet crystal with a cleaved surface to identify the face of the cleaved surface.

SEM (JSM-6500F, JEOL Ltd., Tokyo, Japan) and SEM-energy-dispersive X-ray spectrometry (SEM-EDX; JED-2300, JEOL) analyses were performed to identify the starting material for crystal growth.

Single-crystal XRD was performed to precisely analyze the crystal structures of the grown crystals. Data collection for crystal structure analysis was performed at 296 K using a RIGAKU Synergy Custom DW diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å). Cell refinement and data reduction were performed using the d*trek package of the CrystalClear software suite [13]. Preliminary structures were solved using SHELXT [14] and refined by full-matrix least-squares on F^2 using SHELXL-2016 [15] in the WinGX program package [16].

The optical transmission spectra of the grown single crystal were measured at room temperature using an ultraviolet (UV)–visible–near-IR spectrophotometer (Lambda 900, PerkinElmer, USA) and a Fourier transform IR spectrometer (FT/IR-6800, JASCO, Tokyo, Japan). A 0.1-mm-thick sample with cleaved surfaces on both sides was used for these measurements.

Finally, the melting point of HT-GeS₂ was confirmed using a grown HT single crystal by differential thermal analysis (DTA). The melting point is the most important information regarding crystal growth. Next, 0.3405 g of the grown HT-GeS₂ single crystal was vacuum-sealed in a quartz ampoule with an outer diameter of 8.0 mm in the same manner as described for the synthesis process. The heating rate for the DTA measurement was 10 °C/min up to 1000 °C, and an empty quartz ampoule was used as a reference. The details of the in-house apparatus used for DTA measurements are described in our previous paper [11].

3. Results and Discussion

The synthesized sample used as the starting material for the crystal growth of HT-GeS₂ is shown in Figure 2. The overall color was transparent yellow, with brown dots scattered throughout.

The powder XRD patterns of the sample are shown in Figure 3. The XRD pattern without the brown dots (red line) shows no diffraction peaks, indicating an amorphous (glass) phase. In contrast, the XRD pattern with brown dots shows a diffraction peak (black line), indicating the crystalline phase and the peak position is consistent with the 002 reflection from the HT-GeS₂ phase. In Figure 3, the observed powder XRD pattern

differs from the ideal powder XRD pattern. This phenomenon is probably due to the strong preferential orientation during powdering. Because the GeS₂ crystal has a layered structure, this phenomenon seems plausible. Therefore, GeS₂ has attracted considerable attention as a two-dimensional (2D) material [17–19].

In addition, SEM observations were conducted to investigate this sample; an SEM image of the sample is shown in Figure 4, in which the dendritic shape is considered as a brown dot. To determine the compositional difference between the dendritic shape and the locations not included in the dendritic shape, SEM-EDX analysis was performed. The composition of the dendritic shape was found to be the same as that of the locations not included in the dendritic shape, indicating that the dendritic shape represented an HT-GeS₂ dendritic crystal. These results indicate that the GeS₂ glass containing the HT-GeS₂ crystals was the synthesized sample used as the starting material for the crystal growth of HT-GeS₂. No oxide phase was detected within the accuracy of the powder XRD measurements. By contrast, the presence of oxygen in the sample not be precisely estimated using SEM-EDX because the sample could not be placed in the SEM-EDX apparatus without exposing it to the atmosphere.

The grown HT-GeS₂ crystal cleaved along the growth direction is shown in Figure 5. The grown crystals were brown and transparent. Because a photograph of HT-

GeS₂ crystals has not yet been reported, we cannot compare the features of the HT-GeS₂ crystal. No cracks were observed in the crystal despite quenching from a temperature close to the growth temperature to room temperature to suppress the transition from the HT phase to the LT phase. The grown crystals were easily cleaved. This phenomenon may be natural because GeS₂ has attracted considerable interest as a 2D material [17–19]. In addition, the grown crystals could be easily removed from the quartz ampoule, even though no carbon-coated quartz ampoule was used. The cleavage plane extends from the early stage of crystal growth to the end of crystal growth, suggesting that the crystal is a single crystal. The XRD pattern of the cleaved surface is shown in Figure 6. Since only 001 peaks were observed, the cleavage plane was determined to be the (001) plane. This result shows that HT-GeS₂ single crystals can be grown without using seed crystals and that the growth direction is parallel to the (001) plane. Although the temperature gradient of 20–30 °C/cm in this growth condition was gentler than those reported in previous studies (180 [8] and 45 °C/cm [9]), the HT-GeS₂ single crystal could be grown without a seed crystal. This feature is advantageous for growing large crystals.

The details of the crystal data, data collection, and structure refinement from the single-crystal XRD analysis are summarized in Table 1. The fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$) and geometric

parameters ($\text{\AA}$, $^\circ$) are given in Tables 2 and 3, respectively. These results indicate that the grown crystal is the HT-GeS₂ single crystal with the monoclinic structure (space group $P2_1/c$) and lattice parameters of $a = 6.7061(4) \text{ \AA}$, $b = 16.0877(13) \text{ \AA}$, $c = 11.4242(11) \text{ \AA}$ and $\beta = 91.069(8)^\circ$, which are almost identical to those of a previously reported structure [20,21].

The optical transmittance spectra of the HT-GeS₂ single crystal in the visible and IR regions are shown in Figure 7(a) and (b), respectively. From these data, the transmittance range of the HT-GeS₂ single crystal is found to be 0.358–22.5 μm , except for the absorption near 12.5 μm . This transparency range of the HT-GeS₂ is found to be comparable to those of ZnTe (0.59–25 μm), ZnSe (0.47–19 μm), and ZnS (0.35–23 μm) [1]. In addition, the results of the crystal structure analysis show that the space group of this crystal is not centrosymmetric; therefore, it is expected to have nonlinear optical effects in the IR region. From Figure 7(a), the band gap of GeS₂ was estimated to be $E_g = 3.46 \text{ eV}$ as determined by UV absorption (358 nm) (thickness: 100 μm). This value of the band gap is slightly larger than those previously reported ($E_g = 3.2 \text{ eV}$ (thickness: 14 μm) [8] and $E_g = 3.092, 3.245 \text{ eV}$ (thickness: 50 μm) [9]); this difference may be attributed to the purity of the samples. Golubkov et al. [8] described a moderate degree of amorphization of the sample, whereas Wu et al. [9] demonstrated the growth of HT-

GeS₂ and LT-GeS₂ crystals. These data therefore suggest that the HT-GeS₂ single crystal is a promising new optical single-crystal candidate for use in the IR region. The cause of this absorption is yet to be elucidated.

Finally, the DTA thermogram obtained using the HT-GeS₂ single crystal is shown in Figure 8. In this figure, only one endothermic peak is observed. This peak is thought to be associated with the melting of the HT-GeS₂ single crystal. The melting point of HT-GeS₂ is determined to be 841 ± 1 °C; Ge–S diagrams of two melting point datasets were published in 1990 (840 °C) [4] and 1963 (821 °C) [6]. This value is in good agreement with the Ge–S diagram data reported by Okamoto [4]. The precise melting point data of HT-GeS₂ will be useful for the crystal growth of HT-GeS₂.

4. Conclusion

To investigate the transparency range of HT-GeS₂, an HT-GeS₂ single crystal was grown in an evacuated quartz ampoule. First, the GeS₂ glass contained in the HT-GeS₂ crystals was synthesized as the starting material for crystal growth using our previously improved process for synthesizing sulfide polycrystals. The single crystal of HT-GeS₂ was grown by the Bridgman method under a temperature gradient of 20–30 °C/cm. The grown HT-GeS₂ single crystal was easily cleaved along the growth

direction, and this cleaved surface was identified as the (001) face using XRD. Single-crystal XRD was carried out to precisely determine the crystal structure, revealing that the grown crystal was the HT-GeS₂ single crystal with the monoclinic structure (space group $P2_1/c$) and lattice parameters of $a = 6.7061(4)$ Å, $b = 16.0877(13)$ Å, and $c = 11.4242(11)$ Å, and $\beta = 91.069(8)^\circ$. The optical transmittance spectra of the HT-GeS₂ single crystal were measured in the visible and IR regions, revealing a transparency range of 0.36–22.5 µm. The HT-GeS₂ single crystal is expected to be a new candidate for optical crystals in the IR region. DTA confirmed that the melting point of the as-grown HT-GeS₂ single crystal was determined to be 841 ± 1 °C. In the near future, we would like to clarify the cause of the absorption near the 12.5 µm in the optical spectra of the HT-GeS₂ single crystal, eliminate this absorption, and investigate nonlinear optical effects.

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References

- [1] F. Charra, G. Gurzadyan, In *Nonlinear Dielectric Susceptibilities*; Landolt-Börnstein, Group III Condensed Matter, Vol. 30B; Nelson, D. F., Eds.; SpringerMaterials, Springer-Verlag, Berlin, Heidelberg, 2000. DOI: https://doi.org/10.1007/10134958_42
- [2] T. Hattori, Y. Homma, A. Mitsuishi, M. Tacke, Indices of Refraction of ZnS, ZnSe, ZnTe, CdS, and CdTe in the Far Infrared. *Opt. Comm.* **1973**, 7, 229–232. DOI: [https://doi.org/10.1016/0030-4018\(73\)90015-1](https://doi.org/10.1016/0030-4018(73)90015-1)
- [3] C. Winkler, Mittheilungen über das Germanium, *J. für Praktische Chem.* **1886**, 34, 177–229. DOI: <https://doi.org/10.1002/prac.18860340122>
- [4] H. Okamoto, Ge–S (Germanium–Sulfur) Binary Alloy Phase Diagrams. In *ASM Handbook Alloy Phase Diagrams*, Vol. 12; Materials Park, OH, USA, 1990; pp. 3528–3531, ASM International, ASM Alloy Phase Diagrams Database. <https://matdata.asminternational.org/apd/>, 2023
- [5] W. Viaene, G. H. Moh, Das Binäre System Germanium-Schwefel und p-T-Relationen im Druckbereich bis 5 kba r. *Neues Jahrb. Mineral. Abh.* **1973**, 119, 113–144, ASM International, ASM Alloy Phase Diagrams Database. <https://matdata.asminternational.org/apd/>, 2023

- [6] C. H. Liu, A. S. Pashinkin, Novoselova, A. V. An Investigation of the Germanium-Sulphur System, *Dokl. Akad. Nauk SSSR* **1963**, 151, 1335–1338, ASM International, ASM Alloy Phase Diagrams Database. <https://matdata.asminternational.org/apd/>, 2023
- [7] H. Okamoto, Ge–S (Germanium–Sulfur) *J. Phase Equilib.* **2002**, 23, 194, ASM International, ASM Alloy Phase Diagrams Database. <https://matdata.asminternational.org/apd/>, 2023
- [8] A. V. Golubkov, G. B. Dubrovski, A. I. Shelykh, Preparation and Properties of GeS₂ Single Crystals. *Semiconductors* **1998**, 32, 734–735.
- [9] C. C. Wu, C. H. Ho, J. Y. Wu, S. L. Lin, Y. S. Huang, Characterization of Ge(Se_{1-x}S_x)₂ Series Layered Crystals Grown by Vertical Bridgman Method. *J. Cryst. Growth* **2005**, 281, 377–383. DOI: 10.1016/j.jcrysgro.2005.04.001
- [10] M. Nakamura, H. Nakamura, Y. Matsushita, K. Shimamura, N. Ohashi, Growth of Germanium Monosulfide (GeS) Single Crystal by Vapor Transport From Molten GeS Source Using a Two-Zone Horizontal Furnace. *J. Cryst. Growth* **2020**, 547, 125813. DOI: <https://doi.org/10.1016/j.jcrysgro.2020.125813>
- [11] M. Nakamura, H. Nakamura, K. Shimamura, N. Ohashi, Growth and Characterization of a Gallium Monosulfide (GaS) Single Crystal Using the Bridgman

Method. *J. Cryst. Growth* **2021**, *573*, 126303. DOI:

<https://doi.org/10.1016/j.jcrysgro.2021.126303>

[12] M. Nakamura, H. Nakamura, M. Imura, S. Otani, K. Shimamura, N. Ohashi, SnS Crystal Grown Using Horizontal Gradient Freeze Method and its Electrical Properties. *J. Alloy Compd.* **2014**, *591*, 326–328. DOI: <https://doi.org/10.1016/j.jallcom.2013.12.230>

[13] *CrystalClear*, Rigaku Corporation, Tokyo, Japan (2005).

[14] G. M. Sheldrick, SHELXT–Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr. A: Found. Adv.* **2015**, *71* (1), 3–8. DOI: <https://doi.org/10.1107/S2053273314026370>

[15] G. M. Sheldrick, Crystal Structure Refinement With SHELXL. *Acta Crystallogr. C: Struct. Chem.* **2015**, *71* (1), 3–8. DOI: <https://doi.org/10.1107/S2053229614024218>

[16] L. J. Farrugia, WinGX Suite for Small-Molecule Single-Crystal Crystallography. *J. Appl. Crystallogr.* **1999**, *32* (4), 837–838. DOI: <https://doi.org/10.1107/S0021889899006020>

[17] J. C. Yong, S. I. Hyung, M. Yoon, H. K. Chang, S. K. Han, H. B. Seung, R. L. Young, S. J. Chan, M. J. Dong, P. Jeunghye, H. C. Eun, H. C. Sung, S. S. Min, I. C. Won,

Germanium Sulfide (II and IV) Nanoparticles for Enhanced Performance of Lithium-Ion

Batteries. *Chem. Commun.* **2013**, 49, 4661. DOI: 10.1039/c3cc41853g

[18] W. Qifan, K. Shi-Zhao, L. Xiangqing, Y. Ying-Wei, Q. Lixia, M. Jin, A Facile Preparation of Crystalline GeS₂ Nanoplates and Their Photocatalytic Activity. *J. Alloys Compd.* **2015**, 631, 21–25. DOI: <http://dx.doi.org/10.1016/j.jallcom.2014.12.259>

[19] W. Jiangjing, R. Ider, Z. Ling, L. Lu, L. D. Volker, Z. Baiyu, T. Lin, D. Hongchu, J. Chunlin, Q. Xiaofeng, W. Matthias, M. Riccardo, Z. Wei, Unconventional Two-Dimensional Germanium Dichalcogenides. *Nanoscale* **2018**, 10, 7363. DOI: 10.1039/c8nr01747f

[20] M. Rubenstein, G. Roland, A Monoclinic Modification of Germanium Disulfide, GeS₂. *Acta Crystallogr. B: Struct. Crystallogr. Cryst. Chem.* **1971**, 27 (2), 505–506. DOI: <https://doi.org/10.1107/S0567740871002450>

[21] Von G. Dittmar, H. Schäfer, Die Kristallstruktur von HT-GeS₂. *Acta Crystallogr. B: Struct. Crystallogr. Cryst. Chem.* **1975**, 31 (8), 2060–2064. DOI: <https://doi.org/10.1107/S0567740875006851>

Figure Captions

Figure 1. Schematic of the equipment used to prepare the starting material for the HT-GeS₂ crystal growth.

Figure 2. Synthesized sample used as the starting material for the crystal growth of HT-GeS₂.

Figure 3. Powder XRD patterns of the sample used as the starting material for the crystal growth of HT-GeS₂; XRD pattern without brown dots and that with brown dots (black line).

Figure 4. SEM image of the sample used as the starting material for the crystal growth of HT-GeS₂.

Figure 5. Grown HT-GeS₂ crystal cleaved along the growth direction.

Figure 6. XRD pattern measured from the cleaved surface of the grown HT-GeS₂ crystal.

Figure 7. Optical transmittance spectra of the HT-GeS₂ single crystal in the visible (a) and IR regions (b).

Figure 8. DTA thermogram of the HT-GeS₂ single crystal.

Table 1. Crystal data, collected data, and structure refinement details.

Crystal data	
Chemical formula	GeS ₂
M_r	136.71
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	296
a, b, c (Å)	6.7061 (4), 16.0877 (13), 11.4242 (11)
β (°)	91.069 (8)
V (Å ³)	1232.29 (17)
Z	16
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	10.96
Crystal size (mm)	0.49 × 0.17 × 0.07
Data collection	
No. of reflections	2510
No. of parameters	109
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.090, 0.263, 1.04
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ⁻³)	2.59, -1.50

Table 2. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ge3	0.67153 (18)	0.34855 (9)	0.28012 (14)	0.0356 (5)
Ge2	0.17398 (19)	0.30746 (8)	0.27810 (15)	0.0350 (5)
Ge4	0.3400 (2)	0.49735 (9)	0.20585 (15)	0.0377 (5)
Ge1	-0.1568 (2)	0.15315 (8)	0.22174 (15)	0.0373 (5)
S4	0.4212 (5)	0.3314 (2)	0.4016 (4)	0.0408 (9)
S6	0.9280 (5)	0.3320 (2)	0.3999 (4)	0.0411 (9)
S5	0.6728 (5)	0.2567 (2)	0.1377 (4)	0.0430 (9)
S3	0.1773 (5)	0.3906 (2)	0.1239 (4)	0.0445 (9)
S1	-0.2218 (6)	0.0372 (2)	0.1228 (4)	0.0439 (10)
S7	0.6651 (5)	0.4743 (2)	0.2013 (4)	0.0475 (11)
S2	0.1677 (5)	0.1772 (2)	0.2151 (5)	0.0471 (11)
S8	0.2711 (6)	0.6127 (2)	0.1060 (4)	0.0462 (10)

Table 3. Geometric parameters (Å, °).

Ge3—S6	2.194 (4)	Ge4—S1 ⁱⁱ	2.220 (4)
Ge3—S5	2.198 (4)	Ge4—S8	2.222 (4)
Ge3—S7	2.215 (4)	Ge4—S3	2.231 (4)
Ge3—S4	2.215 (4)	Ge4—Ge1 ⁱⁱ	2.918 (2)
Ge2—S4	2.191 (4)	Ge1—S2	2.213 (4)
Ge2—S3	2.212 (4)	Ge1—S1	2.220 (4)
Ge2—S6 ⁱ	2.213 (4)	Ge1—S8 ⁱⁱⁱ	2.222 (4)
Ge2—S2	2.216 (4)	Ge1—S5 ⁱ	2.228 (4)
Ge4—S7	2.213 (4)		
S6—Ge3—S5	111.47 (15)	S8—Ge4—Ge1 ⁱⁱ	48.98 (11)
S6—Ge3—S7	111.95 (15)	S3—Ge4—Ge1 ⁱⁱ	125.11 (12)
S5—Ge3—S7	108.27 (18)	S2—Ge1—S1	108.28 (15)
S6—Ge3—S4	100.86 (16)	S2—Ge1—S8 ⁱⁱⁱ	115.93 (18)
S5—Ge3—S4	113.17 (15)	S1—Ge1—S8 ⁱⁱⁱ	97.86 (15)
S7—Ge3—S4	111.05 (15)	S2—Ge1—S5 ⁱ	110.57 (15)
S4—Ge2—S3	112.81 (15)	S1—Ge1—S5 ⁱ	108.34 (16)
S4—Ge2—S6 ⁱ	97.35 (16)	S8 ⁱⁱⁱ —Ge1—S5 ⁱ	114.71 (16)
S3—Ge2—S6 ⁱ	114.31 (15)	S2—Ge1—Ge4 ⁱⁱⁱ	125.41 (12)
S4—Ge2—S2	112.65 (15)	S1—Ge1—Ge4 ⁱⁱⁱ	48.92 (11)
S3—Ge2—S2	108.27 (18)	S8 ⁱⁱⁱ —Ge1—Ge4 ⁱⁱⁱ	48.95 (10)
S6 ⁱ —Ge2—S2	111.26 (15)	S5 ⁱ —Ge1—Ge4 ⁱⁱⁱ	123.32 (11)
S7—Ge4—S1 ⁱⁱ	115.91 (18)	Ge2—S4—Ge3	101.05 (18)
S7—Ge4—S8	108.86 (16)	Ge3—S6—Ge2 ^{iv}	102.39 (18)
S1 ⁱⁱ —Ge4—S8	97.89 (15)	Ge3—S5—Ge1 ^{iv}	101.11 (17)
S7—Ge4—S3	109.59 (15)	Ge2—S3—Ge4	98.24 (17)

S1 ⁱⁱ —Ge4—S3	114.38 (16)	Ge4 ⁱⁱⁱ —S1—Ge1	82.17 (15)
S8—Ge4—S3	109.40 (16)	Ge4—S7—Ge3	98.93 (15)
S7—Ge4—Ge1 ⁱⁱ	124.80 (12)	Ge1—S2—Ge2	99.63 (15)
S1 ⁱⁱ —Ge4—Ge1 ⁱⁱ	48.92 (10)	Ge4—S8—Ge1 ⁱⁱ	82.07 (15)

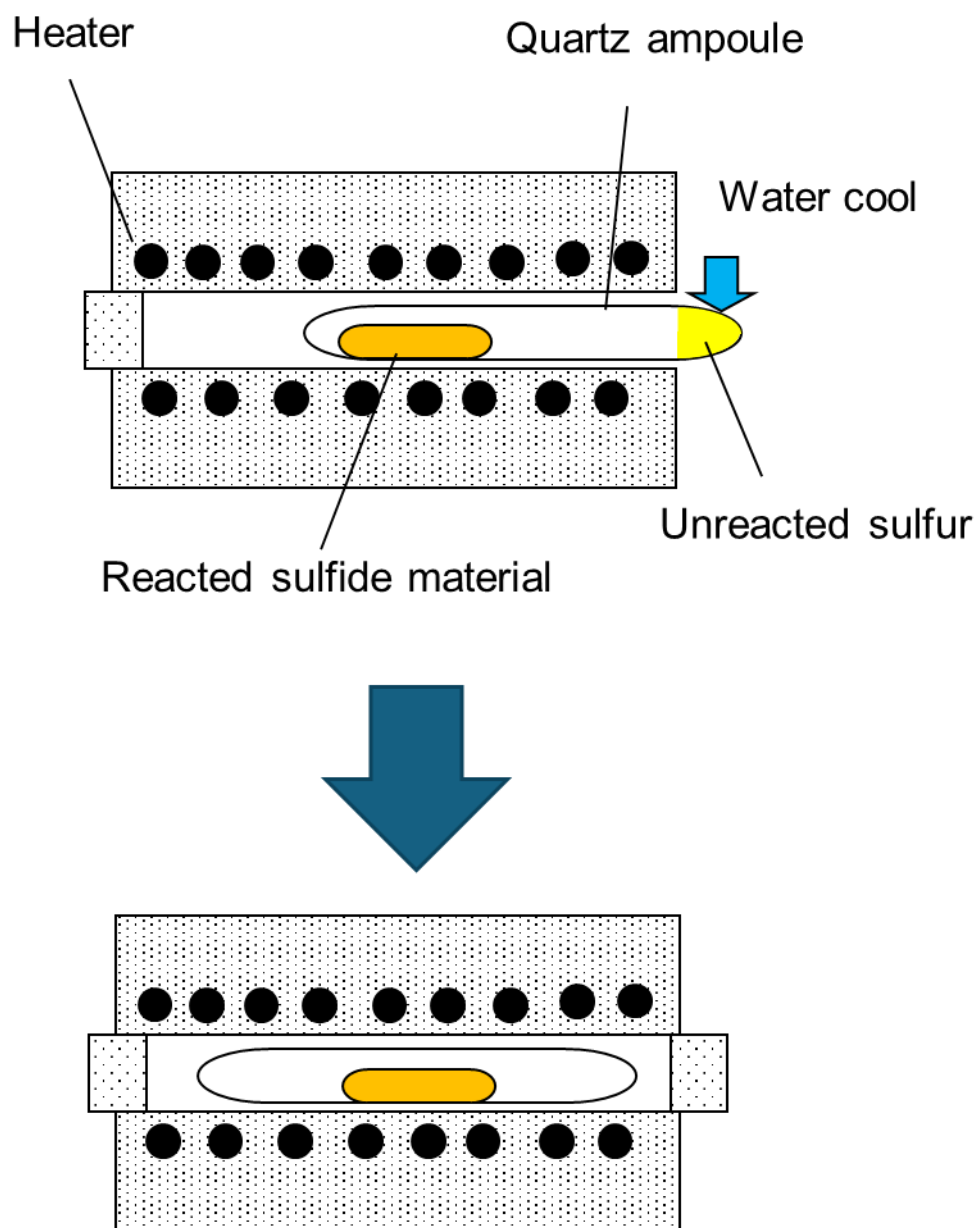


Figure 1. Schematics of the equipment used to prepare the starting material for the crystal growth of HT-GeS₂.



Figure 2. Synthesized sample used as the starting material for the crystal growth of HT-GeS₂.

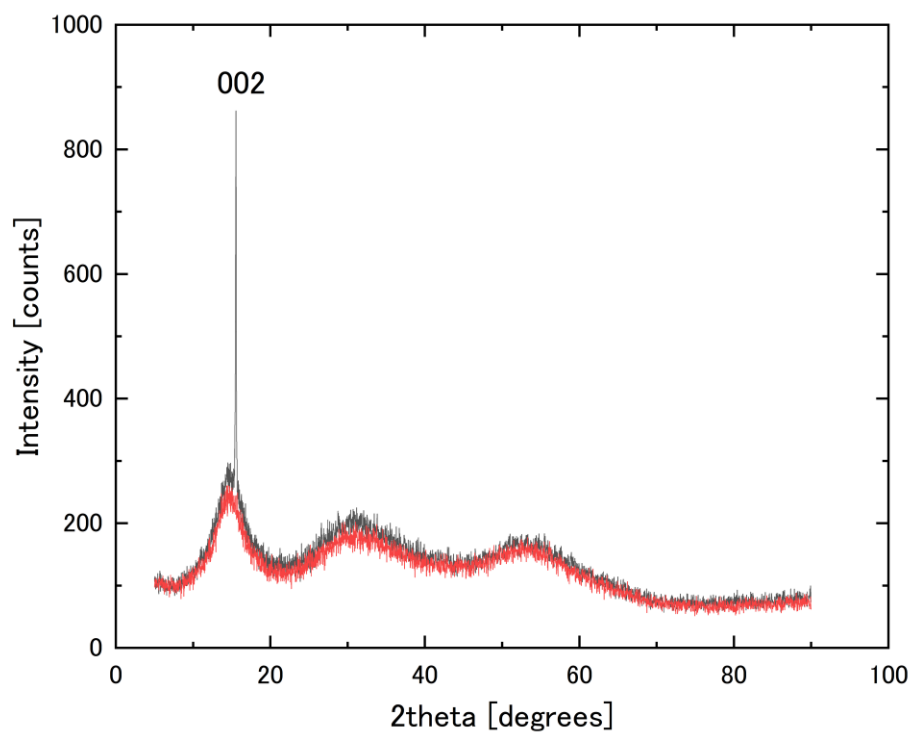


Figure 3. Powder XRD patterns of the sample used as the starting material for the crystal growth of HT-GeS₂; XRD pattern without brown dots and that with brown dots (black line).

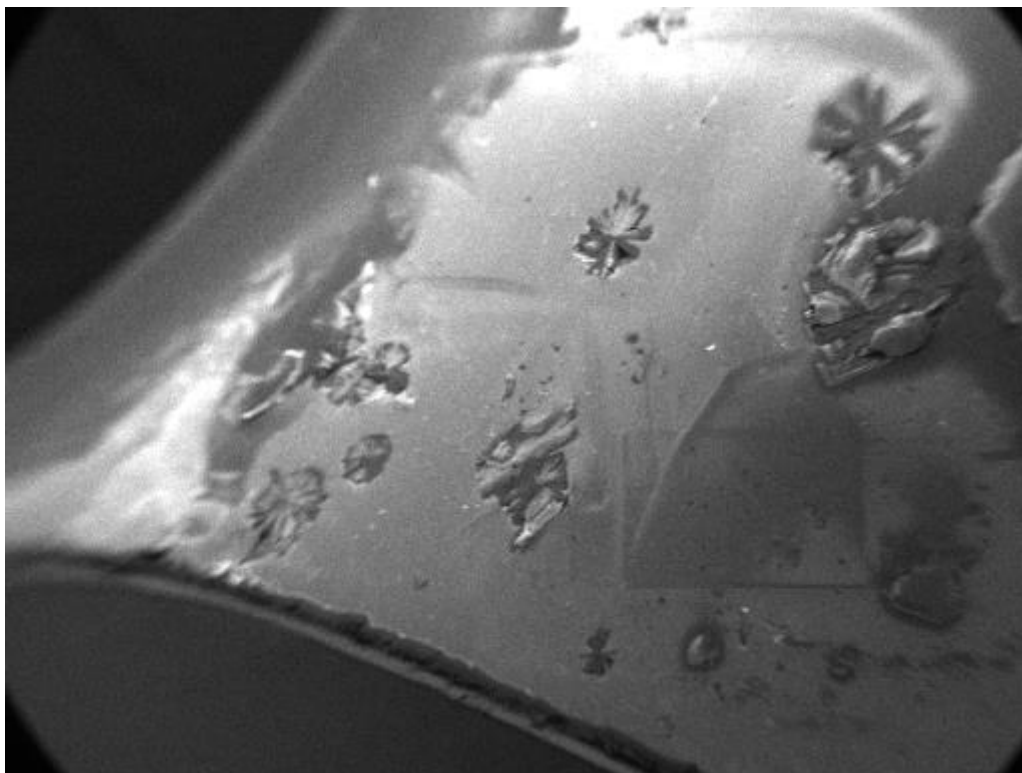


Figure 4. SEM image of the sample used as the starting material for the crystal growth of HT-GeS₂.



Figure 5. Grown HT-GeS₂ crystal cleaved along the growth direction.

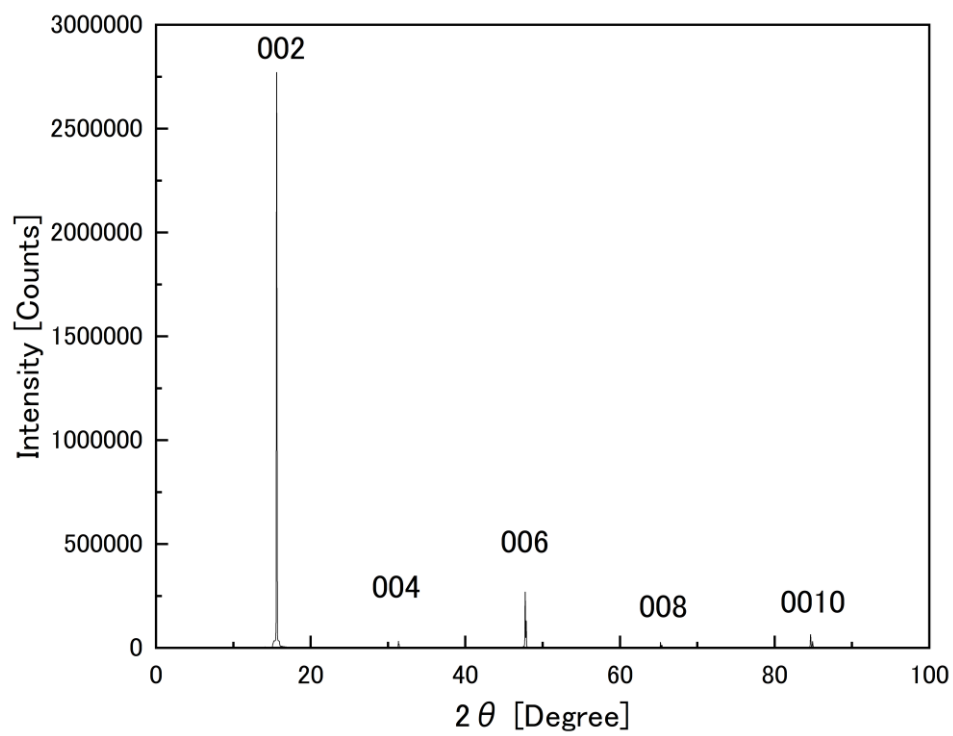


Figure 6. XRD pattern measured from the cleaved surface of the grown HT-GeS₂ crystal.

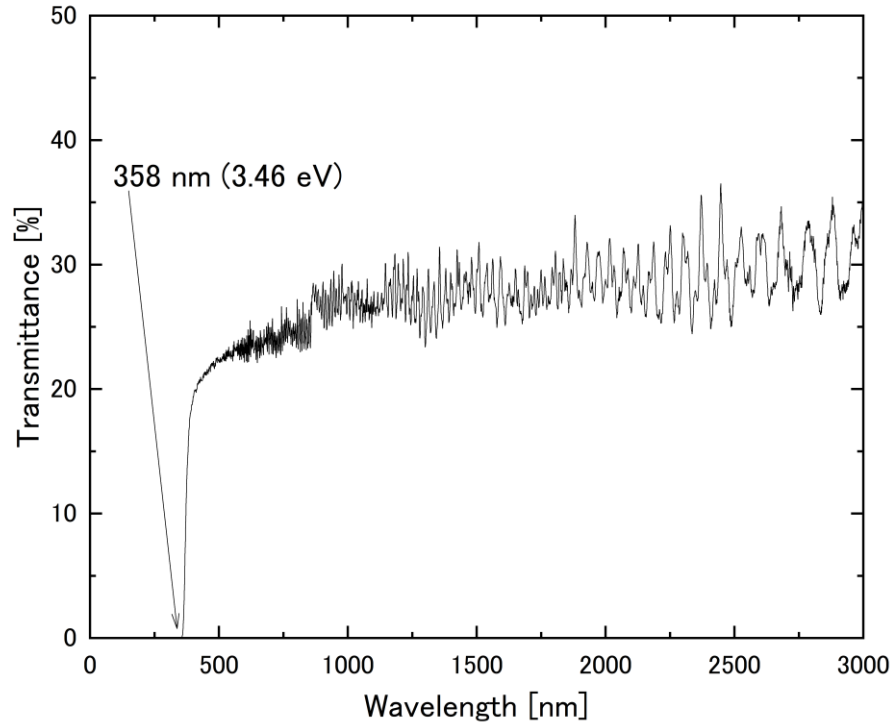


Fig. 7(a)

Figure 7. Optical transmittance spectra of the HT-GeS₂ single crystal in the visible (a) and IR regions (b).

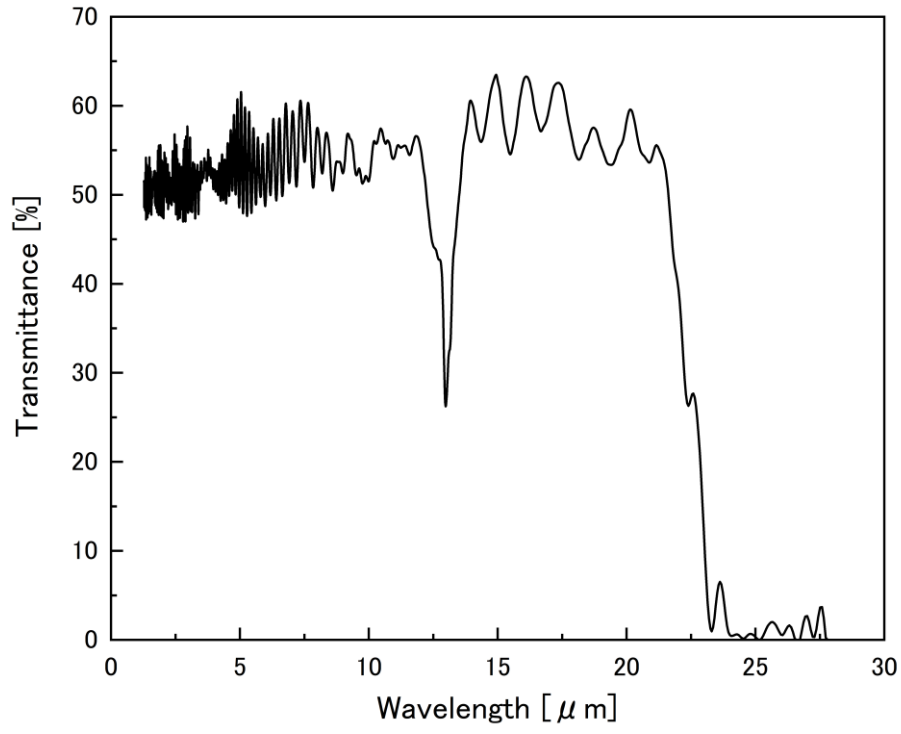


Fig. 7(b)

Figure 7. Optical transmittance spectra of the HT-GeS₂ single crystal in the visible (a) and IR regions (b).

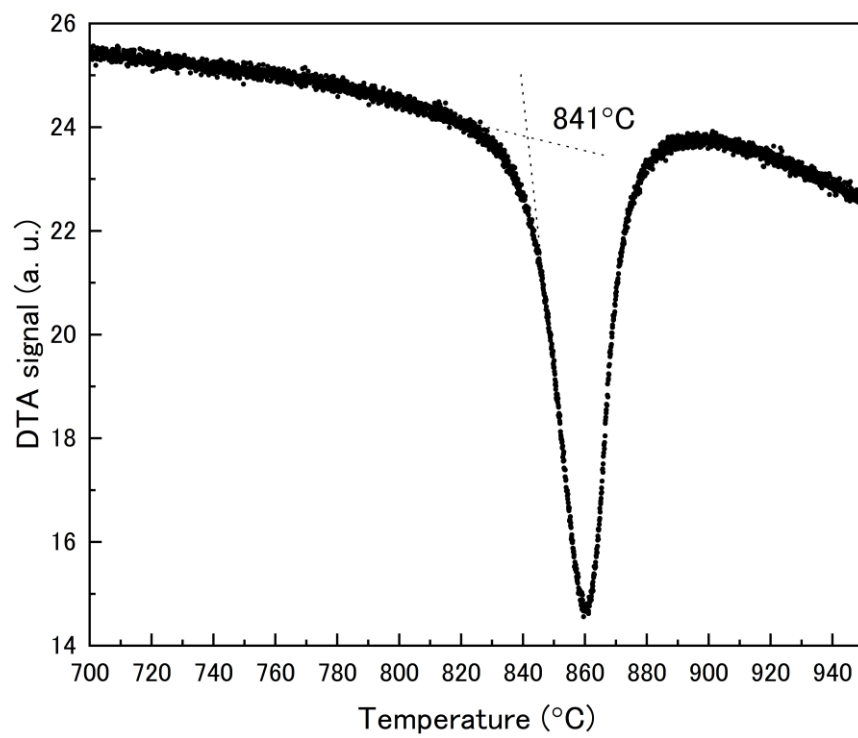


Figure 8. DTA thermogram of the HT-GeS₂ single crystal.