Growth and Raman spectroscopic characterization of

As$_4$S$_4$ (II) single crystals

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ABSTRACT

As described by Kutoglu (1976), single crystals of As_4S_4 (II) phase have been grown using a new two-step synthesis that drastically increases the reproducibility that is attainable in synthetic experiments. First, through photoinduced phase transformation, pararealgar powder is prepared as a precursor instead of AsS melt. Then it is dissolved and recrystallized from CS_2 solvent. Results show that single crystals of the As_4S_4 (II) phase were obtained reproducibly through the dissolution–recrystallization process. Single crystals of As_4S_4 (II) obtained using the method were translucent and showed a uniform yellow–orange color. The crystal exhibits a platelet-like shape as a thin film with well-developed faces (0 1 0) and (0 -1 0). The grown crystals are as large as $0.50 \times 0.50 \times 0.01$ mm. They were characterized using powder and single crystal X-ray diffraction techniques to confirm the phase identification and the lattice parameters. The As_4S_4 (II) phase crystallizes in monoclinic system with cell parameters $a = 11.202(4)$ Å, $b = 9.954(4)$ Å, $c = 7.142(4)$ Å, $\beta = 92.81(4)°$, $V = 795.4(6)$ Å^3, which shows good agreement with the former value. Raman spectroscopic studies elucidated the behavior of the substance and the relation among phases of tetraarsenic tetrasulfide.

1. Introduction

Investigations of photochemical sensitivity in arsenic chalcogenides are important for fundamental sciences and for their practical applications in optical memories, optical switches, optical memories, and fiber lasers. Tetraarsenic tetrasulfide, As_4S_4, exists in four crystalline modifications. Many studies have been made of their crystal structures, spectroscopic properties, phase transitions, and stability fields of the As_4S_4 polymorphs: realgar (α-As_4S_4) [1–6]; the high-temperature phase (β-As_4S_4) based on the same realgar-type molecule with different molecular packing [7–13]; pararealgar obtained by photo-induced phase transformation of both the realgar and the high-temperature phases [14,15]; and As_4S_4 (II) phase, composed of the pararealgar-type molecule with different molecular arrangements [16]. The summary of crystal structural information is shown in Table 1. Because of the unique effect induced by photoexcitation, which is analogous to a domino effect [17], numerous studies have been made to date of the photoinduced phase transition from realgar-type molecule to pararealgar molecule [18–27].

Although many studies have examined α-As_4S_4, β-As_4S_4, and pararealgar, very little information about the As_4S_4 (II) phase is available. Single crystals of the As_4S_4 (II) phase are synthesized by recrystallizing a quenched AsS melt from 500–600°C [16]. To date, this is the only report describing the crystallization and structural characterization by X-ray diffraction analysis of this phase. Although Kutoglu [16] documented conditions under which As_4S_4 (II) phase single crystals have been grown,

we have never obtained the crystals using this method. During thirty years, no reported study has examined the structure and optical properties of the As_4S_4 (II) phase.

This study is intended to reveal an appropriate crystal growth method of the As_4S_4 (II) phase. This paper reports the growth of As_4S_4 (II) single crystals by recrystallization of the pararealgar from CS_2 solution. The crystals were subsequently characterized using powder and single-crystal X-ray diffraction analyses. For this study, the Raman spectra of the As_4S_4 (II) phase were first measured on the flat surface of the single crystal under ambient conditions.

2. Experimental and Results

According to Kutoglu [16], single crystals of As_4S_4 (II) phase were obtained from a quenched AsS melt as a starting substance. The method documented in the previous study [16] was attempted to synthesize As_4S_4 (II) single crystals, but the crystals were never obtained. The structure of As_4S_4 (II) phase comprises pararealgar-type molecules held together by van der Waals forces, which suggests that the pararealgar possessing the same molecular configuration is more effective as a precursor than AsS melt is. Therefore, the single crystals of As_4S_4 (II) phase were synthesized in two steps. First, pararealgar powder was prepared as a precursor through photoinduced phase transformation from pure realgar. The pure realgar crystals were synthesized using the sublimation method with arsenic and sulfur powder as evaporation sources [28]. The realgar, ground into fine powder using an agate mortar,

was exposed to irradiation with visible light for 14 days. Through the photo-induced phase transformation, the realgar powder was altered completely into a fine yellowish powder of pararealgar.

In the second step, 10 mg of pararealgar powder was placed into a beaker containing 100 ml of CS_2 solvent. The solution was stirred for 10 min at room temperature on a magnetic stirrer plate. Then, the clear supernatant liquid was transferred carefully to a Petri dish and kept overnight in a laboratory hood. Finally, yellow-orange thin platy single crystals were grown on the Petri dish.

Figure 1 presents a photograph of the single crystals obtained by recrystallizing pararealgar powder from CS_2 solvent. The grown crystals were as large as 1 mm $\times$ 1 mm $\times$ 0.02 mm. The obtained crystals with average size of 0.5 mm $\times$ 0.5 mm $\times$ 0.01 mm were light yellow–orange and translucent, which indicates that the recrystallization technique using pararealgar can be considered as a most appropriate crystal growth method concerning the As_4S_4 (II) phase. The crystal exhibits a platelet-like shape with well-developed faces (0 1 0) and (0 -1 0) (Fig. 2). According to Kutoglu [16], As_4S_4 (II) crystals have a yellow–orange color with very thin platy morphology. The characteristics are entirely consistent with those obtained using this method.

Phase identification of the grown crystals was conducted through powder and single-crystal X-ray diffraction analyses using graphite monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å). Powder X-ray diffraction data were collected on a two-dimensional imaging plate area detector (RAXIS-RAPID; Rigaku Corp. Japan). The observed intensities on the imaging plate were integrated as a function of 2θ

to give conventional one-dimensional diffraction profile. The typical uncertainty of the angular resolution of the integrated diffraction pattern was about 0.02°. The powder X-ray diffraction pattern was analyzed using a peak-fitting program (JADE 9; Materials Data Inc., USA). A simulated X-ray diffraction pattern was generated using a software package (CrystalDiffract; CrystalMaker Software Ltd., UK) to compare them with the experimental X-ray diffraction pattern.

Figure 3 depicts the experimental and simulated powder X-ray diffraction patterns. The observed diffraction peaks are very broad because of both the radiation source with short wavelength and the many overlapping peaks in the region. The resolution is, however, sufficient to identify the materials present in the compound. No impurity phase such as α-As_4S_4, β-As_4S_4, or pararealgar was detected from the powder X-ray diffraction pattern. All powder X-ray diffraction peaks that were observed can be indexed perfectly to the As_4S_4 (II) phase, which implies that the crystals prepared in the method are single-phase and compositionally homogeneous. Single-crystal X-ray diffraction data were obtained using a four-circle diffractometer (424/511.1; Huber Diffraktiontechnik GmbH & Co. KG, Germany). Unit cell parameters were refined from 20 well-centered reflections in the region 10° < 2θ <30° using least-squares calculations. The unit cell parameters refined with monoclinic system are as follows: $a =$ 11.202(4) Å, b = 9.954(4) Å, c = 7.142(4) Å, β = 92.81(4)°, V = 795.4(6) Å^3. These values are consistent with those of As_4S_4 (II) that was previously synthesized [16].

Raman spectroscopy measurements were conducted at room temperature in ambient atmosphere.

The Raman system comprised an imaging spectrometer equipped with a thermoelectrically cooled CCD detector. Two holographic super notch filters were used to reject the Rayleigh line. The 514.5 nm line of an Ar^+ laser was used as the excitation source. The laser beam was focused on the sample down to about a 5 μm spot through a microscope objective (20×) that was also used to collect the backscattered Raman light. The laser power density was kept low to avoid laser damage to the sample surface. The Raman spectra were obtained with an integration time of 600 s per measurement. The laser beam produced no visible damage on the surface of the sample in the measurements. Band positions were determined using the least-squares fitting software PeakFit (AISN Software Inc., USA) with Lorentzian-shaped functions.

Figure 4 shows the Raman spectrum of As_4S_4 (II) obtained using the measurements, which represents the first reported Raman spectrum of this phase. The Raman spectrum of As_4S_4 (II) phase is characterized by a pair of strong peaks near 230 cm^{-1} and by a grouping of four distinguishable peaks centered at about 340 cm^{-1}. The Raman spectrum of pararealgar has already been reported by several groups [19–21], which exhibits similar features to that of As_4S_4 (II) with the same molecular configuration as pararealgar.

3. Summary

Single crystals of As_4S_4 (II) phase were grown using dissolution–recrystallization method. No

impurity phase was formed using this crystal growth method. Crystals obtained using this method

exhibit a platelet-like form with well-developed faces (0 1 0) and (0 -1 0) with size of several hundred

micrometers square. The largest crystals were approximately 1 mm × 1 mm × 0.02 mm. As determined

from X-ray diffraction analyses, these single crystals prepared in this study are highly homogeneous.

This simple method is expected to be readily applicable for the preparation of As_4S_4 (II) phase.

Acknowledgments

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and theoretical powder X-ray diffraction patterns for (b) As_4S_4 (II) phase and for (c)

pararealgar calculated using CrystalDiffract software.

Figure 4   Raman spectrum of As_4S_4 (II) single crystals.

5. Table(s)

Table 1 Summary of crystal structure information for the polymorphs of As_4S_4.

Phase	Molecular structure	S.G.	a (Å)	b (Å)	c (Å)	β (°)	Volume (Å^3)	References
Realgar	Realgar-type	$P2_1/n$	9.325	13.571	6.587	106.38	787.7	[4]
β-As_4S_4	Realgar-type	$C2/c$	9.957	9.335	8.890	102.48	807.4	[9]
Pararealgar	Pararealgar-type	$P2_1/c$	9.909	9.655	8.502	97.29	807.0	[15]
As_4S_4(II)	Pararealgar-type	$P2_1/n$	11.193	9.994	7.153	92.80	799.2	[16]

Figure 1

500 μm

Figure 2

Figure 3

Figure 4