

Monoclinic high-pressure phase of AgGaS₂

Hiroki Kitahara and Nobuo Ishizawa

Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226, Japan

Fumiyuki Marumo

Department of Geosciences, Nihon University, 3-25-40 Sakurajosui, Setagaya-ku, Tokyo 156, Japan

Yasutoshi Noda

Department of Materials Science, Faculty of Engineering, Tohoku University, Aramaki, Aoba-ku, Sendai 980-77, Japan

(Received 12 August 1996)

Single-crystal x-ray diffraction study under high pressure has been carried out on AgGaS₂ to obtain crystallographic information on the stable phase in the pressure range between 4.2 and 11.6 GPa. The high-pressure phase has monoclinic symmetry with space group Cc , $a=8.065(4)$ Å, $b=8.039(1)$ Å, $c=6.226(3)$ Å, and $\beta=128.50(3)^\circ$ at 5.6 GPa. The monoclinic cell can be approximated as a pseudotetragonal cell of $a_{pt}=b_{pt}=5.694$ Å, $c_{pt}=9.750$ Å, $\alpha_{pt}=\beta_{pt}=88.70^\circ$, and $\gamma_{pt}=89.82^\circ$ on the basis of the conventional chalcopyrite-type unit cell. The high-pressure phase is assumed to have a distorted chalcopyrite-type structure. The phase transition is reversible. A transformation twinning was observed in the high-pressure phase. The four possible twin components are related by the twofold axes present in the symmetry of the ambient-pressure phase. [S0163-1829(97)06105-5]

I. INTRODUCTION

Carlone *et al.* carried out a Raman spectroscopic study on AgGaS₂ under high pressure, and observed two pressure-induced phase transitions at 4.2 and 11.6 GPa.¹ Werner, Hochheimer, and Jayaraman carried out a powder x-ray diffraction study on AgGaS₂ at pressures up to about 25 GPa.² They reported that AgGaS₂ undergoes three phase transitions: (1) from chalcopyrite-type tetragonal lattice to a hexagonal lattice near 5 GPa, (2) from tetragonal and hexagonal to α -NaFeO₂-type near 12 GPa, and (3) to the NaCl type at pressures above 15 GPa. These authors carried out a single-crystal x-ray diffraction study under pressures up to 5 GPa using a precession camera, and reported that the diamond-glide planes parallel to $\{110\}$ in the ambient-pressure phase disappeared above 4.2 GPa.³

No further work has been done on the high-pressure phase of AgGaS₂ above 4.2 GPa. In the present paper, we report more detailed crystallographic data on the phase transition of AgGaS₂ taking place at 4.2 GPa, employing the single-crystal diffraction technique combined with a miniature diamond-anvil high-pressure cell.

II. EXPERIMENTS

Single crystals were grown in an evacuated silica-glass ampoule by the Bridgman technique using the binary compounds Ag₂S and Ga₂S₃, which were synthesized by direct reaction of 4N-grade constituent elements. Crystals were cut into rectangular pieces with dimensions of about 100–150 μm in length and width and 50–80 μm in thickness. A piece of the crystal was mounted in a diamond-anvil cell designed by Miyake *et al.*⁴

The diamond-anvil cell was mounted on a four-circle diffractometer (Rigaku AFC-5), and the measurements were

carried out with graphite- or LiF-monochromated Ag $K\alpha$. The bisecting mode was employed to set the crystal in the diffraction condition. A precession camera was also used to obtain information in a two-dimensional area in reciprocal space. The pressure range surveyed was from ambient to about 6 GPa, and all diffraction studies were carried out at room temperature.

III. RESULTS AND DISCUSSION

A. General features of the changes in diffraction patterns associated with the phase transition

Precession photographs taken at pressures above 4.2 GPa showed that the size and the orientation of the reduced cell of the high-pressure phase are approximately the same as those of the ambient one. Above the transition point, most diffraction spots split into several fragments around the original ambient-pressure phase spots.

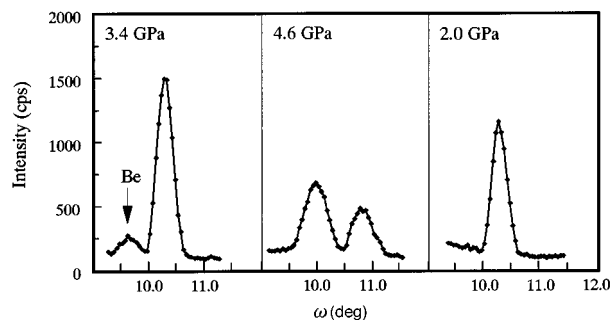


FIG. 1. Changes of the profile of $2\bar{2}4$ reflection at 3.4 and 4.6 GPa with increasing pressure, and at 2.0 GPa with decreasing pressure. Data were obtained with a four-circle diffractometer using the 2θ - ω scan technique.

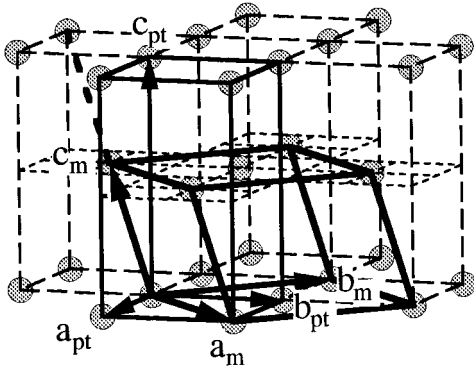


FIG. 2. Relation between the pseudotetragonal cell defined by a_{pt} , b_{pt} , and c_{pt} , and the monoclinic cell defined by a_m , b_m , and c_m . Circles show the body-centered pseudotetragonal lattice points.

The changes in the diffraction profile with pressure are shown in Fig. 1 for the 224 reflection. The deviation from tetragonal symmetry was obvious in the high-pressure phase, because respective fragmental spots related to the same original spot had different d spacings. The intensity ratio of the fragments differed from one sample to another, suggesting a variation in the amount of twin components. The fragmental spots combined again into a single spot on releasing pressure, as shown in Fig. 1. In addition, the reflection condition $2h+l=4n$ for hhl in the ambient-pressure phase changed reversibly to $2h+l=2n$ in the high-pressure phase. The reversible nature of the transition and the slight distortion of the lattice accompanied by the formation of twins above transition point suggest that the phase transition is of a displacive type with small displacements of constituent atoms.

B. Unit cell of the high-pressure phase

Twinning seemed to be inevitable in the high-pressure modification for the transition of AgGaS_2 at 4.2 GPa. After an intensive examination of the crystals, the authors found a specimen which was mainly composed of one twin component, though it contained small fractions of two additional components with different orientations, and used it for detailed crystallographic studies. Using 24 reflections measured in the $\sin\theta/\lambda$ range between 0.294 and 0.446 \AA^{-1} , the cell dimensions at 5.6 GPa were determined as $a=5.690(5) \text{ \AA}$, $b=5.693(1) \text{ \AA}$, $c=9.751(1) \text{ \AA}$, $\alpha=88.69(2)^\circ$, $\beta=88.66(4)^\circ$, and $\gamma=89.86(5)^\circ$ without placing any constraints on the parameters.

Assuming that $a=b$ and $\alpha=\beta$, the pseudotetragonal cell can be reduced into a monoclinic one by taking the b_m axis unique as follows:

$$\begin{pmatrix} a_m \\ b_m \\ c_m \end{pmatrix} = \begin{pmatrix} 1 & 1 & 0 \\ -1 & 1 & 0 \\ -0.5 & -0.5 & 0.5 \end{pmatrix} \begin{pmatrix} a_{pt} \\ b_{pt} \\ c_{pt} \end{pmatrix}, \quad (1)$$

where subscripts m and pt indicate the monoclinic and pseudotetragonal cells, respectively. The geometrical relation between the monoclinic and pseudotetragonal unit cells is shown in Fig. 2. The monoclinic c corresponds to the vector from the origin to the body center of the pseudotetragonal cell. The cell dimensions were determined as $a_m=8.065(4)$

TABLE I. Crystal data for the ambient and high-pressure phase of AgGaS_2 .

	Ambient-pressure	High-pressure (at 5.6 GPa)	
Crystal system	Tetragonal	Pseudotetragonal	Monoclinic
Space group	$I42d$		Cc
Z	4	4	4
Cell dimensions			
a (\AA)	5.7626(5)	5.694	8.065(4)
b (\AA)	5.7626(5)	5.694	8.039(1)
c (\AA)	10.3128(9)	9.750	6.226(3)
α (deg)	90	88.70	90
β (deg)	90	88.70	128.50(3)
γ (deg)	90	89.82	90
Cell volume (\AA^3)	342.47(7)		315.9(2)
Density (g cm^{-3})	4.69		5.08
Temperature (K)	298		298

\AA , $b_m=8.039(1) \text{ \AA}$, $c_m=6.226(3) \text{ \AA}$, and $\beta_m=128.50(3)^\circ$ using the same 24 reflections with monoclinic indices. The backward calculation from the monoclinic cell to the pseudotetragonal cell gives $a_{pt}=b_{pt}=5.694 \text{ \AA}$, $c_{pt}=9.750 \text{ \AA}$, $\alpha_{pt}=\beta_{pt}=88.70^\circ$, and $\gamma_{pt}=89.82^\circ$. Crystal data for the

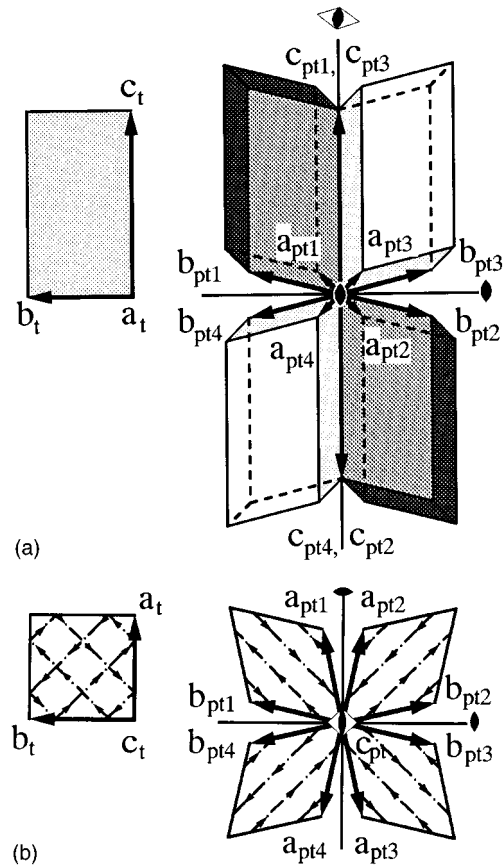


FIG. 3. The geometrical relation among the four twin components formed above the transition point and the orientation of the ambient-pressure phase viewed along (a) a_t and (b) c_t . The subscripts pt and t indicate pseudotetragonal and tetragonal cells, respectively. The deformation of the high-pressure cell is exaggerated.

high-pressure phase are given in Table I with those at ambient-pressure for comparison. For convenience, the index hkl for a reflection in the high-pressure phase is expressed based on the pseudotetragonal cell throughout this paper. It can be transformed into the monoclinic index using the transformation matrix in Eq. (1).

C. Possible space group for the high-pressure phase

In tetragonal $I\bar{4}2d$, diamond-glide planes parallel to $\{110\}$ provide a reflection condition $2h+l=4n$ for hhl and equivalent reflections. It is obvious that the diamond-glide planes parallel to (110) provide $2h+l=4n$ for hhl and equivalents with h and k having the same sign, and those parallel to $(\bar{1}10)$ provide $2h+l=4n$ for hhl and equivalents with h and k having the opposite sign. The diffraction experiments revealed that the hhl reflections such as 110 , 222 , 114 , 226 , 118 , 442 , 446 , 338 , 4410 , and 3312 had intensities in the high-pressure phase, while hhl reflections such as 002 , 006 , 114 , 118 , 118 , 226 , and 338 did not. This means that the set of diamond-glide planes parallel to (110) is lost in the high-pressure phase while the set of diamond-glide planes parallel to $(\bar{1}10)$ is preserved. With this symmetry reduction, the 4 axes and all the rotation and screw diads disappear automatically in the high-pressure phase.

The diamond-glide planes parallel to $(\bar{1}10)$ have glide vectors one quarter of the body diagonal of the tetragonal cell, which corresponds to half of the centering vector. Successive glide planes have glide vectors $\frac{1}{4}a_t + \frac{1}{4}b_t + \frac{1}{4}c_t$ and $-\frac{1}{4}a_t - \frac{1}{4}b_t + \frac{1}{4}c_t$, in turn, where the subscript t indicates the tetragonal $I\bar{4}2d$ cell. The former operation corresponds to the n glide plane perpendicular to the b_m axis with a glide vector of $\frac{1}{2}a_m + \frac{1}{2}c_m$ and the latter corresponds to the c glide plane perpendicular to the b_m axis with a glide vector of $\frac{1}{2}c_m$. Therefore it is plausible that the high-pressure phase has the space group Cc , which is a *translationengleiche* subgroup of $I\bar{4}2d$.

D. Orientation of twin components in the high-pressure phase

The orientation relation of the twin components is schematically shown in Fig. 3. The twin components are quadruplets related by the twofold axes parallel to a_t , b_t , and c_t of the tetragonal $I\bar{4}2d$ cell. They can also be related to each other by the 4 axis of $I\bar{4}2d$. Each component has c_{pt} parallel or antiparallel to the c_t axis. The glide planes in each component are originally part of the diamond-glide planes in $I\bar{4}2d$. The presence of such twin components also confirms the derivation of the symmetry of the high-pressure phase described in Sec. III C.

E. Reinterpretation of previous study

In the high-pressure phase of AgGaS_2 , Werner, Hochheimer, and Jayaraman² reported that an extra powder line appeared apart from those expected from the ambient-pressure phase. The extra line had a d spacing slightly smaller than that of the strongest 112 line and was interpreted based on a hexagonal lattice. The pseudotetragonal cell at 5.6 GPa in the present study has d spacings of $d_{112}=3.16$ Å, $d_{\bar{1}12}=d_{1\bar{1}2}=3.10$ Å, and $d_{11\bar{2}}=3.06$ Å. Therefore, the extra hexagonal line may correspond to $11\bar{2}$ of the pseudotetragonal high-pressure phase.

IV. CONCLUSIONS

The symmetry of the high-pressure phase of AgGaS_2 has been determined in this study using the single-crystal x-ray diffraction technique. The crystal has monoclinic symmetry with space group Cc , $a=8.065(4)$ Å, $b=8.039(1)$ Å, $c=6.226(3)$ Å, and $\beta=128.50(3)^\circ$ at about 5.6 GPa. The high-pressure phase is assumed to have a distorted chalcopyrite-type structure. The transition leads to twinning of the specimen above the transition point. Four possible twin components are related by the twofold axes of $I\bar{4}2d$. The phase transition was reversible and the transformation twin formed above the transition point disappeared when the pressure was released.

¹C. Carlone, D. Olego, A. Jayaraman, and M. Cardona, Phys. Rev. B **22**, 3877 (1980).

²A. Werner, H. D. Hochheimer, and A. Jayaraman, Phys. Rev. B **23**, 3836 (1981).

³N. Ishizawa, H. Kitahara, T. Komori, Y. Noda, and F. Marumo,

Proceedings of the 9th International Conference on Ternary and Multinary Compounds, Yokohama, 1993 [Jpn. J. Appl. Phys. **32**, Suppl. 32-3, 171 (1993)].

⁴M. Miyake, T. Fujii, H. Ishii, and F. Marumo, Rep. RLEM, Tokyo Inst. Tech. **7**, 1 (1982).