

## A new phase of chalcopyrite-type AgGaS<sub>2</sub> under high pressures

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Single-crystal X-ray diffraction study under high pressures has been carried out on AgGaS<sub>2</sub> to obtain crystallographic information of the phase newly found in the pressure range between 4.2 and 11.6 GPa. The high-pressure phase has a monoclinic symmetry with the 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  $a_{pt} = 5.690(5)$  Å,  $b_{pt} = 5.693(1)$  Å,  $c_{pt} = 9.751(1)$  Å,  $\alpha_{pt} = 88.69(2)^\circ$ ,  $\beta_{pt} = 88.66(4)^\circ$  and  $\gamma_{pt} = 89.86(5)^\circ$ , which are similar to those for the ambient-pressure phase. The phase transition was reversible and supposed to be a displacive type. All the lattice points observed at the ambient-pressure phase were essentially maintained even in the high-pressure phase though the symmetry was lowered due to a slight distortion of the unit cell. The transformation twin associated with the high-pressure phase transition was observed in most experimental runs with twin variants having the common *c* directions of their pseudotetragonal cells.

### 1. INTRODUCTION

Chalcopyrite-type structure is related to a one-dimensional superstructure of zincblende-type one with an ordered disposition of two kinds of metal elements. The optical property of chalcopyrite-type structure has therefore uniaxial anisotropy. Crystals of silver thiogallate, AgGaS<sub>2</sub>, are transparent for rays with the wavelengths from 0.45 to 13 μm and have a potential for the secondary harmonic generation device in the range of wavelength between 1.8 and 11 μm [1].

In a recent Raman scattering study on zone-center phonons, the crystal of AgGaS<sub>2</sub> has been reported to show the first phase transition at about 4.2 GPa and the second at about 11.6 GPa [2]. The authors reported that the diamond glide planes parallel to {110} present in the ambient-pressure phase disappear in the newly found high-pressure phase in the range between 4.2 and 11.6 GPa [3]. The present study deals with the determination of the symmetry and cell parameters of the high-pressure phase at about 5.6 GPa by the single-crystal X-ray diffraction technique utilizing a miniature diamond-anvil high-pressure cell.

## 2. EXPERIMENTS

Single crystals were grown in an evacuated quartz ampoule by the Bridgman technique using the binary compounds  $\text{Ag}_2\text{S}$  and  $\text{Ga}_2\text{S}_3$ , which were synthesized by direct reaction of 4N-grade constituent elements. A piece of the crystal was cut into a rectangular prism with dimensions of about  $120 \times 110 \times 50 \mu\text{m}^3$  and 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) with  $\text{Ag K}\alpha$ . Precession camera was also used to check the crystallinity of the sample under high pressures. Cell dimensions and the orientation matrix were determined at 5.6 GPa at room temperature using the four-circle diffractometer. The cell dimensions were calculated by the least-square procedure from  $2\theta$  values of 24 strong reflections measured with  $\text{Ag K}\alpha$  radiation.

## 3. RESULTS AND DISCUSSION

At ambient pressure the crystal of  $\text{AgGaS}_2$  has a tetragonal symmetry with the space group  $I4_2d$  and the cell dimensions  $a = 5.7626(5) \text{ \AA}$  and  $c = 10.3128(9) \text{ \AA}$ . The reflections which break the systematic condition  $h + k + l = 2n$  for the body-centred lattice were not observed under high pressures, indicating that all the lattice points obtained in the ambient-pressure phase were apparently maintained in the high pressure phase. However, several weak reflections were found to be added in the high pressure phase. They were, for example,  $\overline{110}$ ,  $\overline{222}$ ,  $\overline{114}$ ,  $\overline{226}$ ,  $\overline{118}$ ,  $\overline{442}$ ,  $\overline{446}$ ,  $\overline{338}$ ,  $\overline{4410}$  and  $\overline{3312}$ . In addition, most diffraction spots became split in the high pressure phase, suggesting that the transformation twin was formed with the phase transition. Since the split

spots of  $hkl$  had slightly different  $d$  spacings with each other, the true symmetry was supposed to be monoclinic or triclinic. The intensity ratio of the split pairs, triplets or quadruplets differed from one specimen to the other, indicating a variation in the amount of the twin variants in the crystal. Fortunately, one specimen was found to be composed of a single variant in most part, the pseudotetragonal cell dimensions were determined as  $a_{pt} = 5.690(5) \text{ \AA}$ ,  $b_{pt} = 5.693(1) \text{ \AA}$ ,  $c_{pt} = 9.751(1) \text{ \AA}$ ,  $\alpha_{pt} = 88.69(2)^\circ$ ,  $\beta_{pt} = 88.66(4)^\circ$  and  $\gamma_{pt} = 89.86(5)^\circ$ . The unit cell was reduced into a monoclinic one by taking the  $b$  axis unique as:

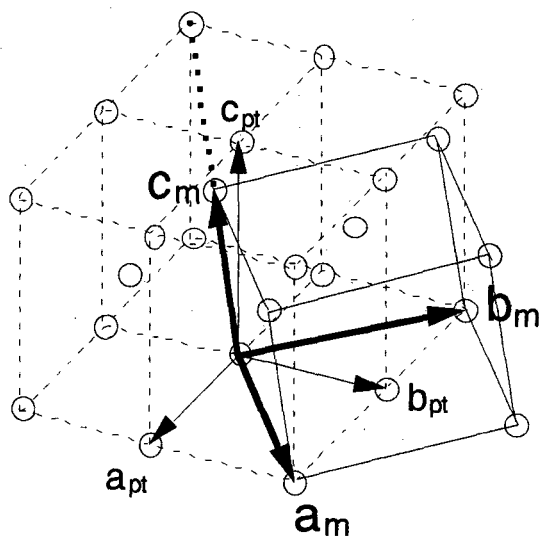


Fig. 1. Relation between the pseudotetragonal cell defined by  $a_{pt}$ ,  $b_{pt}$  and  $c_{pt}$ , and the monoclinic cell defined by  $a_m$ ,  $b_m$  and  $c_m$ . Circles show the body-centred pseudotetragonal lattice points.

Table 1

Crystal data for the ambient and high-pressure phase of AgGaS<sub>2</sub>

	Ambient-pressure	High-pressure (at 5.6 GPa)	
		Pseudotetragonal	Monoclinic
Crystal system	Tetragonal	Pseudotetragonal	Monoclinic
Space group	I $\bar{4}2d$		Cc
Z	4	4	4
Cell dimensions			
a (Å)	5.7626(5)	5.690(5)	8.065(4)
b (Å)	5.7626(5)	5.693(1)	8.039(1)
c (Å)	10.3128(9)	9.751(1)	6.226(3)
α (°)	90.0	88.69(2)	90.0
β (°)	90.0	88.66(4)	90.0
γ (°)	90.0	89.86(5)	128.50(3)
Cell volume (Å <sup>3</sup> )	342.47(7)		315.9(2)
Density (g cm <sup>-3</sup> )	4.69		5.08
Temperature (K)	298		298

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

The geometrical relation between the monoclinic and pseudotetragonal unit cells is shown in the Fig. 1. The monoclinic *c* axis corresponds to the vector from the origin to the body centre of the pseudotetragonal lattice. Crystal data for the high pressure phase are given in Table 1 with those at ambient pressure for comparison. All the split spots were interpreted assuming the presence of possible four monoclinic variants which have the *c<sub>pt</sub>* axes in the same direction.

In the tetragonal I $\bar{4}2d$ , a set of (110) diamond glide planes perpendicular to the direction [110] gives a systematic extinction rule

of  $2h + l = 4n$  for the reflections  $\bar{h}h\bar{l}$ ,  $h\bar{h}l$ ,  $\bar{h}h\bar{l}$  and  $h\bar{h}l$ . Similarly, a set of (1 $\bar{1}$ 0) diamond glide planes perpendicular to the [1 $\bar{1}$ 0] direction gives a systematic extinction rule of  $2h + l = 4n$  for the reflections  $hh\bar{l}$ ,  $h\bar{h}l$ ,  $\bar{h}h\bar{l}$ , and  $\bar{h}h\bar{l}$ . It was confirmed from the experiment using the four-circle diffractometer and the precession camera that the former extinction rule was broken in the high pressure phase. On the other hand, it was not confirmed whether the latter extinction rule held effective or not. The reason was due to the restriction aperture angle of the diamond anvil cell and the crystal orientation. If the latter rule holds effective, the crystal system becomes monoclinic Cc which is a subgroup of I $\bar{4}2d$ . On the other hand, if the latter rule were to be broken, there is no appropriate space group which consists of a subset of the symmetry elements of I $\bar{4}2d$ .

Therefore it was concluded that the space group Cc is plausible for the high pressure phase.

The structural change associated with the phase transition at 4.2 GPa seems to be a displacive type. A slight deformation of the tetragonal cell removes a set of diamond glide planes running perpendicular to [110] direction above the transition point, while not the remaining set of the diamond glide planes perpendicular to  $[1\bar{1}0]$ . A detailed study on the structure of the high-pressure phase is being in progress.

#### 4. CONCLUSION

The symmetry of the high-pressure phase of AgGaS<sub>2</sub> has been first determined in this study using a single-crystal X-ray diffraction technique. The crystal has a monoclinic symmetry with the 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. Since the lattice

points observed at the ambient pressure phase were essentially maintained even in the high pressure phase, the structure of the high pressure phase is considered to be a slightly distorted chalcopyrite-type. The transition brought the twinning of the sample in the high-pressure phase in most experimental runs. Four variants having the pseudotetragonal  $c$  axes along the same direction were easy to occur. The transformation twin disappeared when the pressure was released.

#### REFERENCES

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