

scope with an accelerating voltage of 650 kV (Hitachi 650) to take a diffraction pattern with the incident beam parallel to a hexagonal plate. A pattern with streaks along the c^* direction about the 002 reciprocal lattice point could be obtained. The results obtained with the 100 kV electron microscope were confirmed.

It was also shown by the X-ray powder method that the pyrrhotite is dimensionally hexagonal with $a = 2A = 6.90 \text{ \AA}$ and $c = C = 5.76 \text{ \AA}$. $d(102)$ is 2.072 \AA , showing an iron composition of 47.75% (Arnold & Reichen, 1962).

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A monoclinic modification of germanium disulfide, GeS_2 . By M. RUBENSTEIN and G. ROLAND, *Westinghouse Research Laboratories, Pittsburgh, Pennsylvania 15235, U.S.A.*

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Crystals of the high-temperature modification of GeS_2 were grown by solidification of GeS_2 melts and by vapor transport. The crystals are monoclinic ($P2_1/a$) with $a = 11.46 \pm 0.05$, $b = 16.1 \pm 0.5$, $c = 6.69 \pm 0.08 \text{ \AA}$, $\beta = 90^\circ 48' \pm 9'$, $Z = 16$. A possible structural relation between GeS_2 and CdI_2 is discussed.

Introduction

In a recent paper dealing with phase relations in the Ge-S system, Viaene & Moh (1970) reported that germanium disulfide, GeS_2 has both high-temperature and low-temperature structural modifications. We have grown crystals of the high-temperature modification ($\alpha\text{-GeS}_2$) and find that it is monoclinic. Orthorhombic modifications of GeS_2 have previously been reported by Zachariasen (1936) and Ch'ün-hua, Pashinkin & Novoselova (1963) and a tetragonal form with a three-dimensional network structure has been synthesized at high pressure (Prewitt & Young, 1965). The crystal growth and symmetry determination of monoclinic GeS_2 are described in this note.

Crystal synthesis

Crystals were prepared using both melt and sealed tube vapor transport methods. The sulfur used was purity 99.999+ wt.% (ASARCO) and the germanium was undoped material having a resistivity $> 40 \Omega \cdot \text{cm}$ (Allegheny Electronics Chemical Co.). In preparation from the melt, powdered Ge and S ($\text{GeS}_{1.1}$ composition) were reacted in a sealed, evacuated quartz tube by raising temperature slowly and stepwise to 875°C (above the congruent melting point). The Ge:S ratio was increased stepwise to the final composition, GeS_2 , by repeatedly quenching the charge, adding more sulfur, and remelting. Several days heating of the final composition were necessary to obtain homogeneous GeS_2 liquid. Plate-like crystals covered the surface of the slowly cooled melt. Crystals were also prepared by thermally transporting GeS_2 through a temperature gradient of 800°C (source) to 600°C (deposit) in initially-evacuated, quartz tubes. The close comparison of the X-ray powder patterns of ground crystals with the data for $\alpha\text{-GeS}_2$ reported by Viaene & Moh (1970), and the identity of the patterns with those we obtain from microscopically pure synthetic GeS_2 powder, serves to demonstrate that the crystals are in fact crystals of $\alpha\text{-GeS}_2$ and not of some other phase in the Ge-S system.

Both methods of synthesis yielded plate-like GeS_2 crystals commonly two to three mm on an edge and occasionally as thick as 0.3 mm. Individual plates are colorless, but aggregates and powders have a distinctly yellowish tint. The plates are highly birefringent under polarized light. Twins were not observed. Crystals deformed readily by translation gliding in the plane of the plates and bending about any axis lying in that plane - features characteristic of a layer structure.

Crystal symmetry

With the help of a petrographic microscope, we were able to isolate a few platelets of $\alpha\text{-GeS}_2$ that could be studied using a Buerger precession camera. The area of the plates was larger than the X-ray beam and edge effects could be minimized by carefully positioning them such that the beam did not encounter obvious distortion. Zero, first, and second level precession photographs were taken using Mo $K\alpha$ radiation with the beam normal and parallel the large face of the plates. The crystals are monoclinic (class $2/m$) with the unique twofold axis lying in the plane of the prominent face, which is (100) in second setting. Because of the plate-like morphology, $0kl$ reflections were broadened and $h0l$ reflections were streaked so that the precession photographs were not well suited for measurements of the cell dimensions. Averaged measurements from several zero level photographs yielded the values $a = 11.46 \pm 0.05$, $b = 16.1 \pm 0.5$, $c = 6.69 \pm 0.08 \text{ \AA}$, $\beta = 90^\circ 48' \pm 9'$. There are numerous structural absences in the reciprocal lattice but $0k0$ absent when k is odd and $h0l$ absent when h is odd were the only systematic absences. These uniquely define the space group as $P2_1/a$. The density measured using pycnometer is $2.88 \text{ g}\cdot\text{cm}^{-3}$ which gives $Z = 16$ ($D_{\text{calc}} = 2.94 \text{ g}\cdot\text{cm}^{-3}$).

Ch'ün-hua *et al.* (1963) deduced from powder X-ray data that the structure of GeS_2 is a highly deformed modification of the cadmium iodide (CdI_2) eight-layer structure and related their orthorhombic cell to hexagonal CdI_2 by $a = \sqrt{3}a_{\text{CdI}_2}$, $b = 3a_{\text{CdI}_2}$, and $c = 3c_{\text{CdI}_2}$. In this context, an interesting feature of the monoclinic GeS_2 lattice found in this

study is the almost pseudohexagonal dimensionality of a and $c - a = 1.71 c$ (ideally the ratio is 1.732). Were one to relate monoclinic GeS_2 and CdI_2 knowing only the cell dimensions of each (say based on powder data) one would likely choose (010) of our cell as the basal plane, (001), of the hexagonal CdI_2 subcell. This would position the pronounced layers of the two structures almost at right angles. Clearly one must be careful in relating these structures solely on the basis of cell dimensions. Knowing the orientation of the monoclinic cell relative to the pronounced layering, we can relate monoclinic GeS_2 to CdI_2 by $a = 2c_{\text{cat}_2}$, $b = 4a_{\text{cat}_2}$, and $c = \sqrt{3}a_{\text{cat}_2}$. This gives approximate values for the CdI_2 subcell dimensions of $a = 3.94$, $c = 5.73$, $c/a = 1.45$. In known CdI_2 -like structures c/a lies between 1.40 and 1.50 (Wyckoff, 1963). A number of disulfides do have CdI_2 -like structures, e.g. PtS_2 , SnS_2 , but in

GeS_2 the CdI_2 -type substructure would have to be considerably distorted to account for the many structural absences in the precession photographs, and we hesitate to conclude a relation between the two until complete structural data become available.

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Notes and News

Announcements and other items of crystallographic interest will be published under this heading at the discretion of the Editorial Board. The notes (in duplicate) should be sent to the Executive Secretary of the International Union of Crystallography (J. N. King, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England).

Fedorov's Symmetry of Crystals

An English version of the 1890 Russian Classic, *Symmetry of Crystals* by E. S. Fedorov, has been prepared under the joint sponsorship of the American Crystallographic Association and the National Science Foundation. Translated by David and Katherine Harker, it encompasses the five monographs which together contain Fedorov's development of the principles of crystalline symmetry and his derivation of the 230 space groups. This work also embodies his complete theory of the division of three-dimensional periodic space into stereohedra, a subject not well known to scholars unable to read Russian. Many of Fedorov's analytical and mathematical methods are original and, the translators note, could be used profitably by modern workers and teachers. Published in 1971 as ACA Monograph 7, the ~325 page hard cover book is available at \$25 from the ACA, c/o Polycrystal Book Service, P.O. Box 11567, Pittsburgh, Pennsylvania 15238, U.S.A. Additional information may be obtained from the ACA Secretary, Dr Walter Roth, General Electric Research and Development Center, P.O. Box 8, Schenectady, New York 12301.

Denver conference on applications of X-ray analysis

The 20th annual Denver Conference on Applications of X-ray Analysis will be held on 11, 12, and 13 August 1971, at the Albany Hotel, Denver, Colorado. Technical papers on subjects related to X-rays and their applications will be presented during the three-day conference. The emphasis this year will be on instrumentation as applied to diffraction, fluorescence, microprobe, and other related techniques; this will include developments in automation. Also, as in the past, general papers concerning any aspect of X-ray analysis will be welcomed. Proceedings of the conference will be published as a bound volume entitled, *Advances in X-Ray Analysis*, Volume 15.

Abstracts of papers for presentation at the conference are now invited. Three copies of titles and abstracts (about 300 words) should be sent before 15 April 1971, to Dr C. O. Ruud, Conference Co-chairman, Department of Metallurgy and Materials Science, University of Denver, Denver, Colorado 80210, U.S.A. Final manuscripts are due by 16 July 1971.