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SYNTHETIC TRECHMANNITE

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ABSTRACT

A phase of $AgAsS_2$ composition prepared by crystallizing $AgAsS_2$ glass at 290°C for 315 hours is identical to the rare sulfosalt mineral trechmannite. The synthetic material is hexagonal (rhombohedral) and least-squares refinement of X-ray powder-diffraction data yields $a_{HEX} = 13.967 \pm 0.002$ Å, $c_{HEX} = 9.135 \pm 0.002$ Å ($a_{RH} = 8.619 \pm 0.002$ Å, $\alpha_{RH} = 108°14' \pm 4'$), $c_{HEX}/a_{HEX} = 0.6540 \pm 0.0002$ in agreement with values reported in thr literature for natural trechmannite. X-ray powder-diffraction data for synthetic trechmannite are reported and the optical properties of both synthetic smithite and trechmannite in polished section are described.

INTRODUCTION

Occurrences of the sulfosalt mineral trechmannite ($AgAsS_2$) have so far been confined to the classic Pb-Cu-Ag-Tl-As-sulfosalt assemblages found near Binnatal, Canton of Valais, Switzerland. Trechmannite in minute amounts has been identified in only a few specimens and the indexed X-ray diffraction data and optical properties of this mineral in polished section have not previously been reported. The opportunity to collect these data was presented when synthetic trechmannite was prepared during a study of phase relations in the system Ag-As-S and the purpose of this paper is to describe the synthesis, report the X-ray powder data, and present some observations of optical properties in polished section. This information should aid the identification of trechmannite at other localities where it may previously have been overlooked or misidentified.

Trechmannite was described as a rhombohedral mineral of uncertain composition by Solly (1905). Qualitative chemical tests by Smith and Prior (1907) indicated the presence of Ag and As as major-element constituents and these authors therefore correctly assumed that trechmannite is a sulfarsenite of silver. Evidence that trechmannite might be a low-temperature polymorph of smithite ($AgAsS_2$) was found by Larsen (1921), who noted that it changed on heating to a biaxial form, probably smithite. Nowacki and Bahezre (1963) analyzed both smithite and trechmannite with an electron microprobe and confirmed that both have $AgAsS_2$ composition (within the limits of the analytical technique). A natural crystal of trechmannite from Binnatal was studied by Nowacki and Kunz (1961) using single-crystal techniques; they confirmed the re-

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ported rhombohedral symmetry and determined the cell dimensions (see below). Unindexed X-ray powder-diffraction data for trechmannite were reported by Graeser (1965).

PREVIOUS EXPERIMENTAL DATA

Although several previous investigators have synthesized phases of $AgAsS_2$ composition, only in two instances have X-ray diffraction methods been used to characterize the products. Single crystals precipitated by Béland (1948) from aqueous alkali-sulfide solutions were examined by Peacock (1946), who used single-crystal techniques, and showed them to be identical to natural smithite. Attempts by Béland to precipitate trechmannite failed. Hall (1966), who used silica-tube quenching techniques, reported synthesis of three crystalline modifications of $AgAsS_2$: a high-temperature cubic modification (α-$AgAsS_2$), stable only between about 415° and 421° (the melting point of $AgAsS_2$); smithite (β-$AgAsS_2$), stable between $320 \pm 5°$ and 415°C; and a low-temperature form of undetermined symmetry (γ-$AgAsS_2$) stable below $320 \pm 5°$C.

EXPERIMENTAL PROCEDURES

The silica-tube quenching technique was used for trechmannite synthesis in the present study. A one-gram charge of $AgAsS_2$ composition was prepared from the elements,[2] heated in a sealed, evacuated, silica glass tube (with minimum vapor volume as described by Kullerud and Yoder, 1959) at 550°C for one week, and rapidly chilled to room temperature in water. The resulting homogeneous product was glassy in appearance and only a broad maximum at low 2θ angles (Cu radiation)—characteristic of amorphous material—was observed in X-ray powder-diffraction patterns. Portions of this glass weighing about 100 mg were finely ground (to promote crystallization) and reheated in silica-tube reaction vessels at various temperatures below the melting point of $AgAsS_2$ ($421 \pm 2°$C) for various lengths of time. After chilling in water to room temperature, the solid phases produced by crystallization of glass were examined by means of X-ray and polished-section techniques.

The various computations on X-ray powder data were performed on the GE-225 computer at Lehigh University. The least-squares refinement program for cell dimensions was written by the author in WIZ language and operates on the 2θ values of previously indexed reflections. Each reflection is accorded a weighing factor using the method described by Burnham (1962).

SYNTHESIS OF TRECHMANNITE

Charges of $AgAsS_2$ composition annealed at temperatures between 320° and 421°C rapidly crystallized (in less than 24 hours) to smithite, which was identified by comparison of the X-ray powder pattern with

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[2] Spectrographically analyzed Ag, As, and S were obtained from the American Smelting and Refining Company. The spectrographic analyses show the purity of the elements used to exceed 99.999 weight percent.

the powder data reported for smithite by Berry and Thompson (1962). X-ray patterns of the products of charges annealed for similarly short periods of time below 320°C show additional reflections which are not compatible with smithite but which can be indexed on the basis of a rhombohedral cell close to that reported for natural trechmannite by Nowacki and Kunz (1961). Traces of the successive powder patterns obtained after crystallizing $AgAsS_2$ glass at 290°C for increasing periods of time are compared with a smithite powder-diffraction pattern (Fig. 1). It appears that smithite initially crystallizes from the glass at 290°C but slowly changes to trechmannite on further heating—an illustration of Ostwald's Step Rule. The strongest reflection of smithite ($d=2.82$ Å) has a relative intensity of about 3 (the most intense reflection being assigned intensity 10) in a powder pattern of the product annealed for 315 hours.

X-RAY DIFFRACTION DATA AND CELL REFINEMENT

The powder-diffraction pattern obtained after annealing glass at 290°C for 315 hours was indexed on a hexagonal cell by comparing computed d values for possible reflections (calculated from the cell dimensions reported by Nowacki and Kunz, 1961) with observed d values. The indexed diffraction data are compared with the data for trechmannite (Graeser, 1965) in Table 1. All observed reflections obey the rhombohedral criterion $-h+k+l=3n$ and no general extinctions are evident which would preclude either $R3$ or $R\bar{3}$, the possible space groups of trechmannite according to Nowacki and Kunz.

The cell dimensions of synthetic trechmannite were refined by precise measurement of the angular positions of thirteen unambiguously indexed reflections found between about 25° and 50°2θ (Cu radiation), using synthetic PbS ($a=5.9358\pm0.0002$ Å, Bethke and Barton, 1961) as an internal standard. Measurement data were processed by least-squares computer program to yield best fits of the cell dimensions and minimum standard deviations. The results of the refinement are compared (Table 2) with the data reported for natural trechmannite by Nowacki and Kunz (1961). The agreement between the two sets of data shows that the $AgAsS_2$ phase synthesized at 290°C is identical to trechmannite.

The diffraction data for synthetic trechmannite (Table 1) are similar but not identical to data reported by Hall (1966) for γ-$AgAsS_2$ synthesized at 313°C. Several additional reflections observed by Hall cannot be indexed on the basis of either smithite or trechmannite. Possibly these are due to the existence of metastable crystalline products formed during the crystallization of $AgAsS_2$ glass to trechmannite. All reflections observed during this study, however, could be indexed either as smithite or as trechmannite.

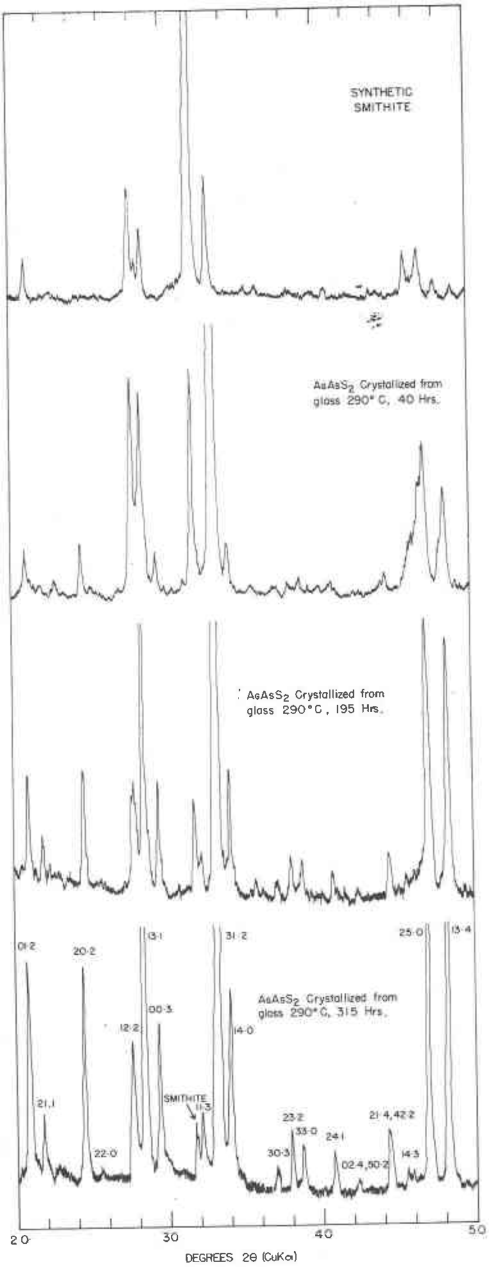

FIG. 1. Traces of X-ray powder-diffraction patterns obtained after heating $AgAsS_2$ glass at 290°C for various lengths of time. The top pattern, shown for comparison, is that of smithite.

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR SYNTHETIC AND NATURAL TRECHMANNITE.

Synthetic trechmannite (This study)				Natural trechmannite (Graeser, 1965)	
hk'l	d_{calc}	d_{obs}	I_{rel}	d_{obs}	I_{rel}
11.0	6.983	6.959	5	7.12	40
02.1	5.043	5.028	1	5.12	20
01.2	4.273	4.268	7	4.31	50
21.1	4.088	4.086	3	4.15	30
20.2	3.645	3.641	7	3.67	50
22.0	3.492	3.485	½	n.o.	
12.2	3.231	3.232	6	3.26	30
13.1	3.149	3.147	9	3.17	90
00.3	3.045	3.042	6	3.07	40
11.3	2.791	2.791	3	2.80	10
31.2	2.704	2.703	10	2.72	100
14.0	2.640	2.635	7	2.66	50
04.2	2.521	2.519	½	n.o.	
30.3	2.430	2.427	½	n.o.	
23.2	2.372	2.372	3	n.o.	
33.0	2.328	2.328	3	n.o.	
24.1	2.217	2.215	2	n.o.	
02.4 50.2	2.136 2.138	2.136	½	n.o.	
21.4 42.2	2.043 2.044	2.042	3	2.05	20
14.3	1.994	1.992	½	n.o.	
25.0	1.937	1.937	8	1.944	80
13.4	1.887	1.888	9	1.889	70
33.3	1.849	1.848	½	n.o.	
40.4	1.822	1.824	3	1.827	20

Calculated d values were obtained for a hexagonal cell with $a = 13.967$ Å, $c = 9.135$ Å, derived by least-squares refinement from the powder data. Relative intensities (visual estimation) are reported. Ni-filtered CuK_α radiation ($\lambda K_\alpha = 1.5418$ Å). n.o. = not observed.

Many unindexed reflections with smaller d values occur.

PHYSICAL AND OPTICAL PROPERTIES

Synthetic trechmannite has a distinctive scarlet-vermillion color and is easily distinguished macroscopically from the more reddish-brown smithite. The synthetic material is a very fine-grained powder and no macroscopic observations of cleavage or crystal habit were possible. No cleavage was observed in polished section. Synthetic trechmannite is nearly indistinguishable from smithite in polished section. Both readily take a polish, although it is difficult to obtain scratch-free surfaces. The

TABLE 2. CELL DIMENSIONS OF SYNTHETIC TRECHMANNITE COMPARED WITH THOSE OF NATURAL TRECHMANNITE.

	Synthetic trechmannite (This study)	Natural trechmannite (Nowacki and Kunz, 1961)
a_{HEX}	13.967±0.002 Å	14.02±0.01 Å[a]
c_{HEX}	9.135±0.002 Å	9.15±0.01 Å
$c_{\text{HEX}}/a_{\text{HEX}}$	0.6540±0.0002	0.653±0.001
a_{RH}	8.619±0.002 Å	8.65±0.01 Å
α_{RH}	108°14′±4′	108°17′±17′

[a] The uncertainties applied by Nowacki and Kunz to their measured rhombohedral cell dimensions have been extended to their equivalent hexagonal cell dimensions and calculated c/a ratio.

polished hardness of either is less than that of proustite. Smithite and trechmannite in polished section are both white (in air); both have a slightly bluish tint when oil immersion is used, but appear distinctly less bluish than proustite. Both are moderately bireflecting (observed under oil) with colors ranging from bluish-white to bluish-gray. Internal reflections in trechmannite are orange-red in color, more orange than the reddish internal reflections of proustite and more red than the bright orange of smithite. Anisotropic effects in both smithite and trechmannite are moderate but difficult to observe (especially under oil) because of the internal reflections. Smithite and trechmannite could readily be confused in polished section with miargyrite ($AgSbS_2$) and with several Pb-As-S sulfosalt minerals and positive identification of these minerals should thus be based on X-ray diffraction data.

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