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New data on stranskiite from Tsumeb, Southwest Africa

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Abstract

Recently found inclusions of intergrown stranskiite, $Zn_2Cu(AsO_4)_2$, and schultenite, $PbHAsO_4$, in massive tennantite from Tsumeb, Southwest Africa, have been investigated by X-ray diffraction and X-ray fluorescence. Refined unit-cell parameters and indexed powder data are given for analyzed stranskiite, which has a lower Zn:Cu ratio than the original specimen.

Introduction

Stranskiite was described by Strunz (1960) as being a triclinic zinc-copper arsenate, $Zn_2Cu(AsO_4)_2$, from the Tsumeb Mine, Southwest Africa. X-ray powder data have never been published, and there have been no new chemical data since 1960.

In 1976 a specimen of stranskiite was found at Tsumeb (Fig. 1) in the lower oxidation zone at a depth of 950 m below surface, 31st Level, E 9 Pillar. The mineral is found in massive tennantite as mm- to cm-large inclusions, associated with other arsenates such as adamite, olivenite, schultenite, and others. The tennantite also contains small amounts of galena, which presumably supply lead for secondary minerals such as schultenite.

X-ray investigations

The new stranskiite has been examined by X-ray powder technique and single-crystal diffractometry. A 90 mm Bradley camera (vacuum) with Fe radiation and Ni filter gave the values listed in Table 1 (data corrected for film shrinkage). Besides the measured *d*-values, calculated data are also indicated, the latter based on cell parameter determinations given in Table 3. A few correlations seem to be poor, due to the limited resolution of the film technique; close reflections lead to a certain line broadening, in contrast to single-crystal determinations by diffractometry.

The cell parameters were determined with the CAD4F diffractometer system from Enraf Nonius, using Ni filtered Cu$K\alpha$ radiation. They were calculated from the diffractometer angles of 23 automatically centered reflections within a θ range of 15° to 60°. After a least-squares refinement procedure according to Busing and Levy (1967), the following parameters were obtained: Cell 1 $a = 5.073 \pm 0.003$, $b = 6.669 \pm 0.005$, $c = 5.267 \pm 0.004$ A; $\alpha = 109.85$, $\beta = 112.14$, $\gamma = 86.88 \pm 0.05°$; space group $P\bar{1}$.

Discussion

The first cell-parameter calculation using the diffractometer angles of about 15 randomly selected reflections gave the following results: Cell 2 $a = 5.073$, $b = 9.819$, $c = 13.318$, $\alpha = 109.64°$, $\beta = 93.12°$, $\gamma = 96.45°$, space group $P\bar{1}$. Intensity measurements within a θ range of 0° to 30° based on this unit cell showed a special pattern. With a few exceptions only reflections with $h + k$ even and l even were present in this θ range. In order to find the transformation of triclinic cell 2 into triclinic cell 1, the lengths and the angles of the different face and body diagonals in cell 2 and related cells with half the *b*- or half the *c*-axis were calculated with a computer program. From these calculations and the intensity pattern mentioned above, the following transformation matrix to the direct-axis matrix was found: $\bar{1}00/00\frac{1}{2}/\frac{1}{2}\frac{1}{2}0$. This matrix also transforms the indices

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Table 1. X-ray powder data of stranskiite

d(obs)	I/I_o	d(calc)*	h	k	l
6.250	20	6.241	0	1	0
4.690	20	4.682	1	0	0
4.154	30	4.162	1	0	-1
3.911	20	3.907	1	-1	0
		3.921	1	1	-1
3.602	20	3.602	1	1	0
3.134	100	3.135	1	-1	-1
2.841	10	2.843	1	2	-1
2.788	80	2.785	1	0	1
2.696	10	2.704	1	-2	0
2.601	30	2.596	1	1	-2
2.506	60	2.508	2	0	-1
2.460	10	2.460	1	0	-2
2.413	20	2.413	1	-2	1
2.340	10	2.341	2	0	0
		2.338	1	2	-2
2.295	10	2.390	0	0	2
2.252	10	2.252	1	-2	-1
2.202	10	2.201	0	-3	1
2.134	10	2.134	2	1	0
2.081	10	2.080	0	3	0
2.064	10	2.070	1	-1	-2
		2.069	1	3	1
1.964	20	1.964	1	-3	0
1.943	20	1.944	0	1	2
1.851	10	1.852	1	2	1
1.824	10	1.822	2	0	1
1.801	5	1.801	2	2	0
1.702	5	1.705	1	-3	-1
1.688	5	1.688	0	-3	-1
1.663	5	1.662	0	4	1
1.621	5	1.624	2	-3	0
1.596	5	1.601	0	2	2
1.585	5	1.585	2	0	-3
1.572	5	1.570	1	4	-2
1.561	5	1.561	3	0	0
1.543	5	1.543	1	-4	1
1.527	5	1.526	0	0	3
1.500	5	1.500	3	-1	-2

plus 46 additional lines of relative intensity ≤ 5

* based upon data of Table 2

of the reflections with respect to cell 2 into the indices of that reflections with respect to cell 1.

The presence of a few reflections for low θ values which did not fit into the overall intensity pattern (*e.g.* $0\bar{1}2$, $1\bar{2}2$, 021, with respect to cell 2) and which would lead to fractional indices in the transformed cell 1 is best explained by the existence of a supercell in which the extra atoms are arranged at poorly-defined positions.

Chemical investigations

The chemical composition presented in this paper (Table 2) has been determined by X-ray fluorescence

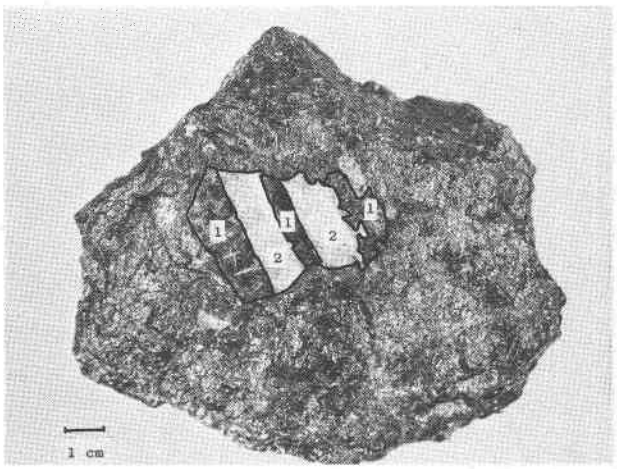

Fig. 1. Massive tennantite with inclusion of stranskiite (1) and schultenite (2) intergrowths.

analysis, using 50 mg hand-picked dried sample, diluted in 750 mg wax (Stern, 1972), pressed (after mixing) into a defined volume. For calibration, a series of "synthetic" stranskiite standards with varying chemical constituents (oxides) was prepared under identical conditions. The results, listed in Table 2, are somewhat different from the ones published by Strunz (1960): the Zu/Cu ratio changes from nearly 2 to 1.3; Mg, Fe, Ca, Si, and Cd seem to be absent.

Conclusions

The combination of powder- and single-crystal diffraction provides indexed *d*-values (Table 1) of stran-

Table 2. Chemical composition of stranskiite (weight percent)

	Calculated after Strunz formula (1960) 1)	Simplified formula 2)	this paper (by x-ray fluorescence) 3)
ZnO	30.4	34.5	28.0
CuO	18.4	16.8	21.1
As_2O_5	47.1	48.7	50.3
FeO	0.8		0.0
MgO	0.8		0.0
CaO	1.2		0.0
SiO_2	1.3		0.0
CdO	n.d.		0.0
Sum	100.0	100.0	99.4

1) $(Zn_{1.73}Fe_{0.05}Mg_{0.09}Ca_{0.10})Cu_{1.07}As_{1.90}Si_{0.10}O_8$

2) $Zn_2Cu(AsO_4)_2$

3) $Zn_{1.69}Cu_{1.28}(AsO_4)_2$ $\quad density_{calc}$ 5.1

$\quad density_{exp}$ 5.3

Table 3. Crystallographic data of stranskiite

	Strunz	Plieth + Sänger	this paper
a (Å)	5.07	5.094	5.073 ± 0.003
b	6.77	6.752	6.669 0.005
c	5.28	5.304	5.267 0.004
α (°)	111°	111.0	109.85 0.05
β	113.5	112.5	112.14 0.05
γ	86	86.0	86.88 0.05
V(Å^3)	154.6	156.9	154.69

skiite. The values of Plieth and Sänger (1967) are probably based upon determination of synthetic crystals of $Zn_2Cu(AsO_4)_2$, and may therefore differ somewhat from data of natural stranskiite. Chemical investigations show that the idealized Zn/Cu ratio of stranskiite can be at least as low as 1.3 in case of natural crystals. Thus, the mineral formula $(Zu,Cu)_3(AsO_4)_2$ seems preferable.

Acknowledgment

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