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Crystallography of dimorphites*

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Auszug

Die Untersuchung von Dimorphit-Einzelkristallen auf Grund von Röntgenstrahl-Interferenzen bestätigte die Existenz zweier Modifikationen, der Dimorphite I und II. Dimorphit I erwies sich als identisch mit dem synthetischen As_4S_3 WHITFIELDS und YUS. Dimorphit II hat als Raumgruppe *Pnma* oder $Pn2_1a$ und die Gitterkonstanten $a = 11{,}24 \pm 0{,}02$, $b = 9{,}90 \pm 0{,}03$, $c = 6{,}56 \pm 0{,}02$ Å. Viele Dimorphite sind scheinbar einheitliche Kristalle, die meisten erweisen sich jedoch als kristalline Aggregate. Unter den Kristallen mit einem identifizierbaren Gitter waren die meisten Dimorphit II, einer Dimorphit I und ein weiterer einwandfrei ein nach Dimorphit I pseudomorpher Dimorphit II.

Abstract

Single-crystal x-ray diffraction studies on natural, Vesuvian dimorphites confirmed the existence of two phases: dimorphite I and II. The former was found to be identical with the synthetic As_4S_3 of WHITFIELD (1970) and of YU (1971). Dimorphite II has the space group of *Pnma* or $Pn2_1a$ and the unit-cell dimensions of $a = 11.24 \pm 0.02$, $b = 9.90 \pm 0.03$, $c = 6.56 \pm 0.02$ Å. Much of the dimorphite occurred in apparent single crystals. However, most were found to be polycrystalline. Of the crystals having an identifiable lattice most were dimorphite II, one was dimorphite I and one was clearly a dimorphite II pseudomorphic after dimorphite I.

Introduction

Dimorphite was first described by SCACCHI (1850), who discovered the new mineral in the Phlegraean Fields, near Naples and Mount Vesuvius. He described dimorphite as a yellow-orange, transparent or translucent mineral having adamantine luster, lacking distinct cleavage, and occuring in tiny orthorhombic crystals. Among the crystals he

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found two distinct morphologies and axial ratios, on the basis of which he distinguished between the two phases: dimorphite I (sometimes referred to as A or α) had an axial ratio of 1: 1.287:1.153 and dimorphite II (sometimes referred to as B or β) of 1: 1.658:1.508 for $a:b:c$. SCACCHI reported only a probable chemical formula because of the small quantity of material used in the analysis and because the method used involved quantitative analysis only for sulfur.

Over the last hundred years there has been considerable disagreement concerning whether dimorphite is indeed a distinct mineral or is a morphologically unusual orpiment which was not recognized by SCACCHI (KENNGOTT, 1870; DANA, 1920; PALACHE *et al.*, 1944). Work on synthetic As_4S_3 has demonstrated the existence of the synthetic counterparts of one or two dimorphites (SCHULLER, 1894; KRENNER, 1907; WHITFIELD, 1970; YU, 1971). However, with the exception of a single x-ray powder pattern (NEUMANN and HEIER, 1955) there have been no crystallographic or x-ray diffraction studies reported on natural dimorphites.

X-ray powder diffraction

A sample of Vesuvian dimorphites, weighing a fraction of a gram and containing about 100 crystals was obtained through the courtesy of the Swedish Natural History Museum, Stockholm. Practically all crystals were fragmented and all exhibited similar morphology. There were, however, two distinct color phases present, one being yellow and the other orange. First it was assumed that the two colors represent the two phases of dimorphite. It was soon learned, however, that there is no relationship between the colors and the two dimorphites. Most crystals gave a powder pattern which was later identified as dimorphite II, some gave the patterns of both dimorphites and only one crystal gave the powder pattern of dimorphite I. The powder pattern published by NEUMANN and HEIER (1955) can be analysed as a mixture of the two dimorphites.

The powder patterns of dimorphite I and II are given in Table 1. The former was calculated from the lattice parameters and structure factors published by WHITFIELD (1970). The latter was obtained from a single crystal of dimorphite II.

Single crystal x-ray diffraction

The precession photographs obtained from a single crystal of dimorphite I gave the symmetry reported by WHITFIELD (1970) and

YU (1971) for synthetic As_4S_3; that is, the space group of *Pnma* (or $Pn2_1a$). The unit-cell dimensions are also comparable:

WHITFIELD	$a = 9.12$,	$b = 7.99$,	$c = 10.10$ Å
YU	$a = 9.13$,	$b = 8.00$,	$c = 10.18$ Å
Present study	$a = 9.07$,	$b = 8.01$,	$c = 10.30$ Å .

Several dimorphite-II crystals have been investigated on a precession camera and zero and higher level photographs were taken on the *hk*0, 0*kl* and *h*0*l* reciprocal-lattice planes. The symmetry and space group obtained is the same as that of dimorphite I: *Pnma* (or $Pn2_1a$). The unit-cell dimensions obtained from the precession photographs were: $a = 11.22$, $b = 9.90$ and $c = 6.61$ Å [1]. These parameters were

Table 1. *X-ray powder patterns of dimorphites*

Dimorphite I			Dimorphite II		
d	*I*	*hkl*	*d*	*I*	*hkl*
6.77	15	101	5.64	30	101, 200
6.27	50	011	5.48	20	011
5.16	100	111	4.89	100	111, 210, 020
4.16	40	201	4.24	5	201
4.00	7	020	3.91	40	211
3.87	25	112	3.72	20	121, 220
3.44	17	121	3.27	15	301, 002
3.38	5	202	3.23	20	221
3.16	7	103	3.15	10	102
3.13	25	022	3.07	25	311
3.12	62	212	2.94	25	031
3.10	10	013	2.84	25	131, 202, 400
3.00	5	220	2.72	15	212, 410
2.96	50	122	2.67	14	122
2.91	30	301	2.57	14	401
2.71	25	203	2.47	13	302, 040
2.57	20	213	2.27	12	141, 240
2.43	10	104	2.14	50	241, 430
2.35	10	321	2.08	5	511, 412
2.33	5	114	2.05	5	203, 431
2.30	15	230	1.973	10	123

[1] This unconventional labelling of the unit translations was elected in order to illustrate the identical symmetry of the two dimorphites.

Table 1. *(Continued)*

Dimorphite I			Dimorphite II		
d	*I*	*hkl*	*d*	*I*	*hkl*
2.28	10	400	1.957	5	142, 422, 521
2.26	12	303	1.893	7	223, 051
2.24	24	223, 231	1.861	10	242, 151, 313, 440
2.22	5	401	1.820	5	033, 512
2.09	5	232	1.789	10	441, 531
2.08	10	402, 124	1.770	10	611, 323
2.04	5	133	1.734	10	233, 403, 522
1.86	15	042	1.673	2	152, 351, 621
1.84	20	413	1.650	5	060, 004, 333
1.77	5	125	1.620	50	143, 541, 423
1.75	10	511	1.542	5	024, 214, 513
1.71	15	431	1.491	5	314 etc.
1.70	5	234	1.472	5	361 etc.
1.68	10	305	1.450	5	641 etc.
1.65	5	341	1.400	6	414 etc.
1.62	6	116	1.372	3	362 etc.
			1.358	6	144 etc.
			1.308	3	561 etc.
			1.290	3	115 etc.

refined from precision Weissenberg and powder pattern data. The a and c unit translations were refined by using the 12 0 0 and 008 reflections in the precision Weissenberg film. The b unit translation was refined from the 020, 040 and 060 lines in the powder pattern. The refined unit translations are: $a = 11.24 \pm 0.02$, $b = 9.90 \pm 0.03$ and $c = 6.56 \pm 0.02$ Å. Using these parameters the powder pattern of dimorphite II was indexed as given in Table 1.

Attempts were made to confirm the chemical composition of the two dimorphites by electron-microbe analysis for arsenic and sulfur, and by a colorimetric analysis for arsenic. Unfortunately, neither method gave conclusive values, although both methods indicate the validity of the As_4S_3 formula as obtained by SCACCHI (1850), SCHULLER (1894) and KRENNER (1907).

The As_4S_3 chemical formula, the above unit-cell parameters and the symmetry required $Z=4$ define the specific gravity of dimorphite II as 3.60 g/cm^3. This value is in reasonable agreement with 3.58 of SCACCHI (1850), 3.60 of SCHULLER (1894) and of 3.58 obtained in this study.

Pseudomorphism

Among the dozen crystals examined, one exhibited good dimorphite-I morphology but in its precession photographs the lattices of both dimorphites were present. The dimorphite-I lattice was consistent with the morphology of the crystal while the dimorphite-II lattice was in a seemingly irrational orientation with respect to the morphology. Figure 1 is an idealized sketch of this crystal showing the approximate relative positions of the dimorphite-I and -II lattices.

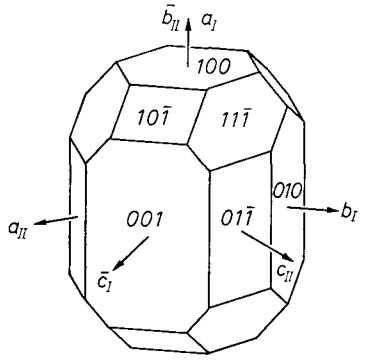

Fig. 1. Idealized diagram of a dimorphite crystal containing both dimorphite I and II

The existence of dimorphite-II crystals pseudomorphous after dimorphite I suggests that dimorphite I is unstable under conditions to which it was exposed after crystallization, and inverts to dimorphite II. This tendency for inversion can explain both the prevalence of polycrystalline diffraction effects from crystals which appear single morphologically, and the presence of both dimorphites in the powder patterns obtained from morphologically single crystals.

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