Synthesis and study of diaboleïte

By R. E. Winchell[1] and H. E. Wenden

Department of Mineralogy, Ohio State University, Columbus, Ohio

[Taken as read 7 November 1968]

Summary. Diaboleïte has been synthesized between 25 and 100° C at atmospheric pressure and approximate water vapour partial pressures of 14·7 lb/in^2. Under similar conditions at 170° C cumengéite appears to be the stable phase produced from a diaboleïte composition. Synthetic diaboleïte is much simpler morphologically than the natural mineral but the hemimorphic symmetry is more clearly demonstrated morphologically in the artificial specimens. A comparison of X-ray powder data for natural and synthetic diaboleïte shows almost exact detailed correspondence in line position and intensity between 0 and 180° 2θ. The cell dimensions obtained from X-ray powder data are a $5{\cdot}869 \pm 0{\cdot}002$ Å and c $5{\cdot}495 \pm 0{\cdot}003$ Å.

DIABOLEÏTE, $Pb_2CuCl_2(OH)_4$, originally described incompletely by Spencer and Mountain (1923), has been described in detail by Palache (1941) who has given crystallographic, optical, X-ray single crystal, and chemical data for the species. Byström and Wilhelmi (1950) have proposed a structure for the species and have given data from which a calculated powder pattern has been compiled (A.S.T.M. 5–0220). No complete powder pattern obtained from powder diffraction methods is to be found in the literature. No synthesis, and very little information on the stability of diaboleïte, have been reported in the literature.

Synthesis. Diaboleïte has been synthesized at two different temperatures from solutions of $CuCl_2.2H_2O$ and $Pb(OH)_2$ in stoichiometric proportions according to the formula given by Palache (1941). Slow diffusion, evaporation, and hydrothermal techniques were used in the synthesis experiments.

The slow diffusion technique employed was that described by Friedel (1892). In the present study, a solution of $CuCl_2.2H_2O$ was allowed to diffuse through the wall of a cracked test tube into a hydrous bath of $Pb(OH)_2$ until reaction appeared complete. In the evaporation

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[1] Present address: Department of Geology, California State College at Long Beach, Long Beach, California.

experiment the components were mixed with excess distilled water and placed in a drying oven at 100° C until evaporation was complete. Sealed Pyrex tubes were used for hydrothermal synthesis at 100 and 170° C. A sealed pot bomb with a Teflon liner was used for the hydrothermal experiment above 170° C. Table I summarizes the experimental conditions and the results obtained from the synthesis experiments.

TABLE I. Summary of synthesis experiments for diaboleïte.

Method	*Temp.*	*Time (days)*	*Phases obtained*
Slow diffusion	25° C	339	Diaboleïte
Evaporation	100° C	2	Diaboleïte, chloroxiphite (?), unidentified phase
Pyrex tube	100° C	55	Diaboleïte, unidentified phase
	170° C	16	Cumengéite, cotunnite, unidentified phase
Pot bomb	270° C	9	Murdochite, unidentified phase

Although the evaporation method yielded only microcrystalline to cryptocrystalline powder, the slow diffusion experiment and the hydrothermal experiment at 100° C produced small diaboleïte single crystals, the largest of which were 0·07 mm parallel to the *c*-axis and 0·18 mm parallel to the *a*-axis.

The synthesis experiments indicate that diaboleïte is a low-temperature phase whose upper stability limit under hydrothermal conditions is between 100 and 170° C. Further, cumengéite appears to be the stable Pb–Cu phase formed immediately above the stability limit of diaboleïte under hydrothermal conditions approximating those used in this study. A study of the association and occurrence of diaboleïte at Mammoth mine, Tiger, Arizona, by one of the authors (H. E. W.) led him to the conclusion that diaboleïte and the associated species were formed at low temperatures consistent with those established during this study.

Morphology and optics. Synthetic diaboleïte is much simpler morphologically than the natural crystals described by Palache (1941). Although the dominant forms present on the synthetic crystals gave excellent reflections, the crystals were too small to allow accurate measurement on the large two circle goniometer available, but did show that the dominant forms developed on all the crystals are $\bar{c}\{00\bar{1}\}$, $a\{010\}$ and $e\{011\}$. In addition to the faces of the dominant forms, smaller faces belonging to other forms were observed and the synthetic crystals may be divided into two groups on the basis of the presence or absence of these subordinate forms (fig. 1): The first, to which most of the crystals obtained belong, is characterized by a combination of the dominant forms in approximately equal development. The second is characterized by a combination of the equally developed dominant forms with the forms $\bar{e}\{01\bar{1}\}$ and $\bar{s}\{02\bar{1}\}$. Development of $\{01\bar{1}\}$, {010}, and {011} on the synthetic crystals is such as to lengthen the crystal in the direction of the *c*-axis and results in a decidedly more hemimorphic appearance than is exhibited by natural crystals and lend added weight to the morphological evidence in support of the hemimorphism of diaboleïte already given by Palache *et al.* (1941).

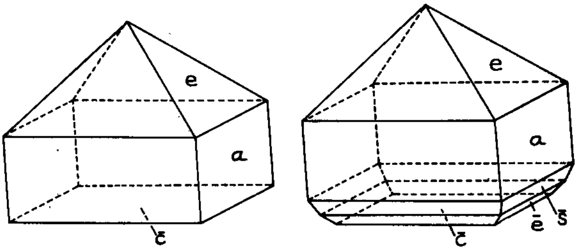

FIG. 1. Morphology of synthetic diaboleïte.

Synthetic diaboleïte is a transparent pale blue and yields a uniaxial negative interference figure under conoscopic conditions; no evidence of the distortion of the interference figure reported by Palache (1941) was observed in the synthetic material examined.

X-ray investigation. Three specimens of natural material and several specimens of synthetic diaboleïte were subjected to X-ray powder diffraction examination. All the natural specimens were from Mammoth mine, Tiger, Arizona, and were obtained from the Harvard Collection (H.N. 104521), the Royal Ontario Museum (R.O.M. M24959), and the United States National Museum (U.S.N.M. 114577). Both the *d*-spacings and the line intensities of the natural and synthetic specimens are identical within the limit of error of the measurements. X-ray powder data for one of the natural and one of the synthetic specimens studies are tabulated and compared with the calculated data taken from the work of Byström and Wilhelmi (1950) (A.S.T.M. 5–0220) in table II. These data as well as the powder photographs from which they were obtained (fig. 2) show a remarkably close agreement in line position and intensity over nearly the whole interval from 0 to 180° 2θ. In addition the weak lines obtained during this study further establish the lack of systematic omissions and confirm the space group *P4mm*

Table II. X-ray powder data for: (3) natural diaboleïte from Mammoth mine, Tiger, Arizona (U.S.N.M. 114577), and (4) synthetic diaboleïte from slow diffusion compared with: (1) indexed, calculated spacings using *a* 5·870±0·003, *c* 5·494±0·003 Å., *P4mm* (Byström and Wilhelmi, 1950) and (2) single crystal data (Byström and Wilhelmi, 1950 and A.S.T.M. 5–0220). 11·46 cm diameter camera, Cu-$K\alpha$ radiation.

	1	2		3		4	
hkl	$d_{\text{calc.}}$	*I*	*d*	*I*	*d*	*I*	*d*
100	5·870	—	—	3	5·799	3	5·770
001	5·494	100	5·507	10	5·507	10	5·496
110	4·151	60	4·156	7	4·143	7	4·084
101	4·011	40	4·008	3	3·991	3	3·967
111	3·312	100	3·314	9	3·305	9	3·282
200	2·935	80	2·930	8	2·929	8	2·910
002	2·747	40	2·740	5	2·737	5	2·724
210	2·625	—	—	1	2·615	1	2·609
201	2·589	80	2·587	9	2·580	9	2·572
102	2·488	40	2·487	3	2·477	3	2·466
211	2·369	—	—	2	2·358	1	2·351
112	2·291	100	2·292	10	2·283	10	2·279
220	2·075	80	2·074	8	2·070	8	2·063
202	2·006	60	2·008	7	2·001	7	1·996
300	1·957	—	—	≪1	1·970	≪1	1·969
221	1·942	—	—	7	1·936	7	1·931
212	1·898	40	1·897	2	1·893	2	1·892
310	1·856	60	1·854	4	1·853	4	1·850
301	1·843						
003	1·831	60	1·831	6	1·829	6	1·823
311	1·759	100	1·758	9	1·755	9	1·749
103	1·748						
113	1·675	60	1·675	6	1·674	6	1·671
222	1·656	40	1·662	4	1·653	4	1·652
320	1·628	—	—	<1	1·627	<1	1·623
302	1·594	—	—	<1	1·590	<1	1·590
321	1·561	—	—	—	—	—	—
203	1·554	80	1·554	7	1·554	7	1·550
312	1·538	80	1·537	9	1·537	9	1·534
213	1·502	—	—	—	—	—	—
400	1·468	60	1·467	6	1·466	6	1·466
410	1·424	—	—	—	—	—	—
401	1·416	60	1·417	5	1·417	5	1·414
322	1·401	—	—	<1	1·398	<1	1·399
330	1·383	—	—	1	1·382	1	1·380
411	1·378						
004	1·374	80	1·373	7	1·372	7	1·370
223	1·373						
331	1·342	60	1·341	5	1·341	5	1·338
104	1·337						
303	1·337						
420	1·313	60	1·315	5	1·312	5	1·312
114	1·304	80	1·303	7	1·303	7	1·302
313	1·304						
402	1·294	—	—	1	1·293	1	1·291
421	1·277	60	1·276	5	1·274	5	1·275
412	1·264	—	—	<1	1·265	<1	1·263
204	1·244	60	1·245	5	1·244	5	1·242
332	1·236	60	1·235	5	1·235	5	1·234
214	1·217	—	—	1	1·217	1	1·215
323	1·217						

TABLE II (*cont.*)

	1	2		3		4	
hkl	$d_{\text{calc.}}$	*I*	*d*	*I*	*d*	*I*	*d*
422	1·184	60	1·182	5	1·184	5	1·183
500	1·174	—	—	—	—	—	—
430							
510	1·151	10	1·151	2	1·150	2	1·150
501	1·148	—	—	2	1·147	2	1·147
431							
224	1·145	60	1·145	3	1·145	3	1·144
403	1·145						
511	1·127	60	1·126	4	1·126	4	1·126
304	1·124						
413	1·124						
314	1·104	60	1·103	4	1·103	4	1·103
333	1·104						
005	1·099	—	—	—	—	—	—
520	1·090	—	—	—	—	—	—
105	1·080	—	—	<1	1·079	<1	1·077
502	1·079						
432							
521	1·069	60	1·066	5	1·067	5	1·065
423	1·067						
115	1·062	70	1·061	6	1·062	6	1·061
512	1·062						
324	1·050	—	—	1	1·051	1	1·049
440	1·038	—	—	3	1·037	3	1·037
205	1·029	—	—	3	1·029	3	1·028
441	1·020	—	—	3	1·019	3	1·019
215	1·013	—	—	—	—	—	—
522	1·013						
530	1·007			1	1·006	1	1·006
404	1·003			2	1·003	2	1·003
531	0·9903			4	0·9899	4	0·9899
414	0·9885			—	—	—	—
503	0·9884			—	—	—	—
433							
600	0·9784			1	0·9779	1	0·9776
334	0·9748			2	0·9747	2	0·9741
513	0·9746						
225	0·9711			2	0·9711	2	0·9710
442	0·9708						
610	0·9651			—	—	—	—
601	0·9632			2	0·9268	2	0·9623
305	0·9581			—	—	—	—
611	0·9505			—	—	—	—
424	0·9489			3	0·9487	3	0·9483
315	0·9456			—	—	—	—
532	0·9453			4	0·9451	4	0·9448
523	0·9367			—	—	—	—
620	0·9281			—	—	—	—
602	0·9216			2	0·9214	2	0·9213
540	0·9158			—	—	—	—
006	0·9157			—	—	—	—
621	0·9152			4	0·9150	4	0·9157

TABLE II (*cont.*)

	1	2		3		4	
hkl	$d_{\text{calc.}}$	*I*	*d*	*I*	*d*	*I*	*d*
325	0·9108			—	—	—	—
612	0·9105			—	—	—	—
106	0·9047			—	—	—	—
541	0·9043			—	—	—	—
443	0·9028			3	0·9025	3	0·9025
116	0·8942			3	0·8941	3	0·8936
504	0·8924			—	—	—	—
434							
514	0·8823			6	0·8818	6	0·8818
533	0·8822						
405	0·8796			6	0·8794	6	0·8794
622	0·8793						
630	0·8751			—	—	—	—
206	0·8741			3	0·8741	3	0·8741
415	0·8699			—	—	—	—
542	0·8696			—	—	—	—
216	0·8646			—	—	—	—
631	0·8642			—	—	—	—
603	0·8630			2	0·8628	2	0·8625
335	0·8605			3	0·8604	3	0·8602
524	0·8538			—	—	—	—
613	0·8538						
425	0·8426			4	0·8425	4	0·8425
700	0·8386			—	—	—	—
226	0·8377			3	0·8378	3	0·8376
632	0·8338			—	—	—	—
710	0·8302			3	0·8299	3	0·8298
550							
306	0·8293			—	—	—	—
701	0·8290			—	—	—	—
444	0·8280			8	0·8277	8	0·8278
623	0·8279						
316	0·8212			—	—	—	—
711	0·8209			8	0·8208	9	0·8207
551							
543	0·8198			—	—	—	—
640	0·8141			2	0·8137	2	0·8138
534	0·8120			2	0·8116	2	0·8117
720	0·8064			—	—	—	—
641	0·8052			5	0·8050	5	0·8049
505	0·8023			—	—	—	—
435							
702	0·8021			—	—	—	—
326	0·7981			—	—	—	—
721	0·7978			—	—	—	—
604	0·7969			1	0·7968	1	0·7966
515	0·7949			10	0·7946	10	0·7945
712	0·7947						
552							
614	0·7896			1	0·7893	1	0·7897
633	0·7896						
007	0·7849			2	0·7849	2	0·7848
642	0·7805			4	0·7804	4	0·7801
107	0·7780			—	—	—	—
406	0·7769			3	0·7768	3	0·7766

given for diaboleïte by Palache *et al.* (1941) and Byström and Wilhelmi (1950).

The Cu-$K\alpha$ doublets for six relatively sharp reflections known from the indexing to be single lines and having 2θ values greater than 146° 2θ were used to obtain precise values for a and c. The results, a 5·869±0·002 Å, c 5·495±0·003 Å, are in reasonable agreement with Palache *et al.* (1941; a 5·83±0·02 Å, c 5·46±0·02 Å), and in excellent agreement with Byström and Wilhelmi (1950; a 5·870±0·003 Å, c 5·494±0·003 Å).

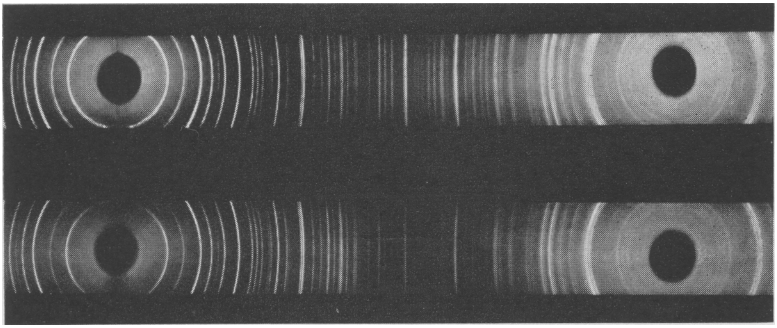

Fig. 2. X-ray powder diffraction photographs for natural diaboleïte (U.S.N.M. 114577) (above) and synthetic diaboleïte (below) prepared the slow diffusion method.

Acknowledgements. The authors wish to express their gratitude to Professor C. S. Hurlbut of Harvard University, Dr. J. A. Mandarino of the Royal Ontario Museum and Dr. Paul E. Desautels of the United States National Museum for providing the specimens of natural diaboleïte used in this study.

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[*Manuscript received 19 February 1968*]