

## New data on hungchaoite, the second world occurrence, Death Valley region, California

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### Abstract

Hungchaoite occurs with ginorite, mcallisterite, sborgite, sassolite, nobleite, ulexite, and, where gypsum and ulexite are abundant, with kurnakovite, inderite, and mcallisterite in surficial matrix as products from weathered colemanite and priceite veins in late Tertiary rocks.

Hungchaoite is triclinic, space group  $P\bar{1}$ ;  $a = 8.811(1)$ ,  $b = 10.644(2)$ ,  $c = 7.888(1)\text{Å}$ ;  $\alpha = 103^\circ 23(1)'$ ,  $\beta = 108^\circ 35(1)'$ ,  $\gamma = 97^\circ 09(1)'$  unit-cell volume  $666.2(1)\text{Å}^3$ ;  $Z = 2[\text{MgO} \cdot 4\text{B}_2\text{O}_3 \cdot 9\text{H}_2\text{O}]$ . Euhedral, tabular {100} to equant, colorless, untwinned crystals, up to 0.5 mm, show 17 forms. The strongest lines in the X-ray powder pattern are, in Å: 6.71(100), 3.356(92), 5.36(85), 4.093(78), 4.079(64), and 7.14(59).

Hungchaoite is optically (-):  $\alpha = 1.445(2)$ ,  $\beta = 1.485(2)$ ,  $\gamma = 1.490(2)$  (Na light);  $2V_\alpha = 15(4)^\circ$ ;  $r < v$ , distinct;  $X \Delta a = +28^\circ$ ,  $Z \Delta b = +37^\circ$ ,  $Y \Delta c = -66^\circ$ . Good  $\{\bar{1}11\}$  and  $\{\bar{1}\bar{1}1\}$  and imperfect {010} cleavages. Hardness  $2\frac{1}{2}$ .  $G$  (meas) 1.706(5),  $\rho$  (calc)  $1.705 \text{ g cm}^{-3}$ .

Hungchaoite is metastable with respect to inderite and mcallisterite in solution. Dehydration data are given.

### Introduction

Hungchaoite,  $\text{MgO} \cdot 2\text{B}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ , was first described by Chu *et al.* (1964a,b) from saline lacustrine sediments at an unspecified locality in China where it reportedly occurs as fine-grained material associated with ulexite, hydroboracite, and szaibelyite in gypsiferous sediments. It is identical in its chemical composition and physical properties with the compound  $\text{MgO} \cdot 2\text{B}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ , first synthesized by Nikolaev and Chelishcheva (1940).

We present data here for the second world occurrence of this mineral discovered by McAllister in the Death Valley region, California (1970). The larger size of the crystals in the California occurrence has enabled us to characterize more completely this mineral and has permitted the determination of its crystal structure (Wan and Ghose, 1977).

### Occurrence (J.F.M.)

In the Furnace Creek borate area hungchaoite has been found at three places in the northeastern foothills of the Black Mountains. The localities are on old patented mining claims of the U.S. Borax & Chemical Corporation, which are now within the boundary

of Death Valley National Monument. The first locality is about 50 m southwest of the road in Twenty Mule Team Canyon, 2,140 m N25°W of U.S. mineral monument 40 on Monte Blanco (McAllister, 1970), and is in the southeastern part of the Meridian claim. The second locality is about 550 m S30°E from the first and is on the South Meridian claim. The third is on the Hard Scramble claim (Erd *et al.*, 1959, Fig. 1), about 10 km southeast of the first locality and 3 km N72°W of Ryan.

The hungchaoite occurs in a surficial sponge formed by weathering of fragmental basalt around veins of priceite and colemanite. The basalt unit is in lacustrine deposits in the lower part of the Furnace Creek Formation that was assigned somewhat inconclusively to the early Pliocene (Clarendonian) by K. E. Lohman (in McAllister, 1970, p. 6) on the basis of diatoms. The formation, which reaches a thickness of about 2,100 m, extends upward into clearly the middle Pliocene (Hemphillian), according to Lohman. In a stratigraphic sequence measured (McAllister, 1976) from the underlying Artist Drive Formation across Twenty Mule Team Canyon southeast of the Meridian localities, this basalt unit is about 300 m above the base of the Furnace Creek Formation and

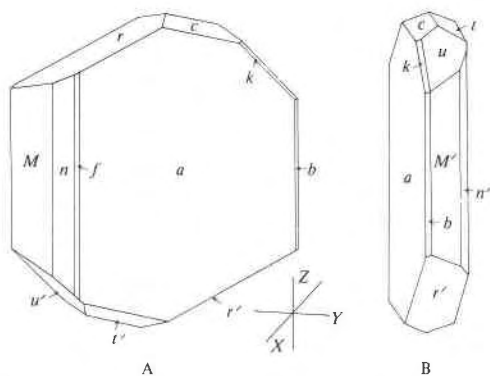


Fig. 1. Tabular hungchaoite crystal in isometric perspective: (A) Standard orientation (with axial cross); (B) Viewed along Y. Computer drawing by K. L. Keester using the computer program of Keester and Giddings (1971).

about 100 m above the colemanite–ulexite–probertite ore zone.

Although the rocks enclosing the priceite and colemanite veins are of late Tertiary age, the hungchaoite and associated minerals around the veins are Holocene and still form in the present desert environment, as shown by the fragile, ephemeral nature of puffed ground in which the hungchaoite occurs and by encrustations of some of the minerals on man-made surfaces in prospect and mine workings (Erd *et al.*, 1961, p. 562; McAllister, 1961, p. B300). Boron of the hungchaoite, which was released from weathered priceite and colemanite, apparently migrated much earlier from bedded ulexite in the ore zone.

Hungchaoite on the Meridian claim was collected (specimen JFM58-1-8C) from a small pad of puffed ground that was not in contact with any of the exposed veins of colemanite or priceite. Anhedral and subhedral hungchaoite or exceedingly fine textured ulexite forms commonly 1- to 2-mm clots in a porous, scarcely coherent aggregate of montmorillonite and residual analcime. Gowerite, nobleite, and mcallisterite are very minor constituents. On the South Meridian claim, hungchaoite occurs with more abundant boron minerals (although very minor ulexite), in puffed ground of clay and analcime, down a moderate slope 1.7 m from the nearest exposed colemanite vein. The closely associated minerals in irregular clots or nodules, generally less than 5 mm in diameter, are ginorite, mcallisterite, sborgite, sassolite, nobleite, and ulexite. Other borate minerals thus far identified from the South Meridian locality are gowerite, ward-smithite, and aristarainite. The aristarainite is the second known occurrence (McAllister, 1976) after Salta, Argentina (Hurlbut and Erd, 1974).

Hungchaoite on the Hard Scramble claim, in contrast to the other localities, occurs in a surficial aggregate that contains much gypsum and ulexite, at veins of priceite and colemanite. It is closely associated with kurnakovite, inderite, and mcallisterite, and is within a few meters of an assemblage containing rivadavite, mcallisterite, ulexite, gypsum, and conspicuous quantities of thenardite and mirabilite. Euhedral crystals of hungchaoite (specimen no. JFM69-5-5G7) for this report are from the Hard Scramble locality. Three other specimens from the same grab sample show the following mineral relations. (1) Nodules of hungchaoite coalesce on a gypsum–kurnakovite intergrowth on corroded vein colemanite. The opposite side of the colemanite is encrusted with finer grained inderite and ulexite. (2) An irregular veinlet of hungchaoite penetrates an aggregate of gypsum and weathered basalt on a core of colemanite. Fine-grained inderite was deposited on a somewhat corroded surface of the hungchaoite veinlet and as nodules next to nodules of hungchaoite on gypsum. (3) Ulexite, inderite, and hungchaoite occur separately in nodules or crusts on an aggregate of gypsum and kurnakovite. Clots of very fine grained mcallisterite are in a matrix of weathered basalt attached to the aggregate.

## Crystallography

### Morphology

Hungchaoite occurs as euhedral to anhedral, tabular  $\{100\}$  to equant, untwinned crystals (Fig. 1) up to 0.5 mm in largest dimension. The forms observed are listed in Table 1. A numerical description of the habit development is provided by column D of Table 1, which lists the normal distance of the form from the origin. These data were obtained by Dr. Kenneth L. Keester using a computer program (Keester and Giddings, 1971) which exactly simulates the real crystal (Fig. 1) and thus allows quantitative determination of relative growth velocities. Although D values were not determined for six forms (Table 1), they are all smaller than  $k \{011\}$  and have D values in excess of 1.400. The crystal morphology indicates that hungchaoite is triclinic pinacoidal. Furthermore, both natural etch pits and those produced by attack of cold water show paired faces in accord with centric symmetry.

### X-ray data

Unit-cell dimensions were determined from precession photographs (Mo radiation, Zr filter) of

Table 1. Angle table and morphological data for hungchaoite

Triclinic; pinacoidal $\bar{1}$								
$a:b:c = 0.8278:1:0.7411$ $\alpha = 103^\circ 23'$ , $\beta = 108^\circ 35'$ , $\gamma = 97^\circ 09'$								
$p_o:q_o:r_o = 0.8778:0.7079:1$ $\lambda = 73^\circ 15'$ , $\mu = 68^\circ 54'$ , $\nu = 77^\circ 35'$								
$p_o = 0.9672$ , $q_o = 0.7800$ , $x_o = 0.3362$ , $y_o = 0.3179$								
Form	$\phi^*$	$\rho^*$	A	B	C	D**		
						Tabular	Equant	
$\bar{c}$ 001	46° 36'	24° 50'	68° 54'	73° 14'	---	1.000	0.800	
$\bar{b}$ 010	0° 00'	90° 00'	77° 35'	---	73° 14'	0.800	0.800	
$\bar{a}$ 100	77° 35'	90° 00'	---	77° 35'	68° 54'	0.125	0.125	
$\bar{f}$ 4 $\bar{1}0$	89° 13'	90° 00'	11° 38'	89° 13'	72° 00'	0.765	0.765	
$\bar{n}$ 2 $\bar{1}0$	100° 55'	90° 00'	23° 20'	100° 55'	75° 49'	0.525	0.525	
$\bar{m}$ 1 $\bar{1}0$	121° 12'	90° 00'	43° 36'	121° 12'	83° 36'	0.450	0.450	
$\bar{k}$ 011	17° 02'	48° 57'	68° 15'	43° 52'	29° 22'	1.400	1.400	
$\bar{q}$ 0 $\bar{1}1$	143° 58'	29° 45'	78° 32'	113° 39'	40° 25'	not determined		
$\bar{y}$ 101	67° 41'	54° 10'	37° 00'	72° 04'	31° 54'	not determined		
$\bar{t}$ 1 $\bar{0}1$	-79° 45'	31° 44'	119° 02'	84° 38'	50° 08'	0.975	0.800	
$\bar{r}$ 1 $\bar{1}1$	101° 14'	52° 33''	43° 20''	98° 54'	41° 51'	0.950	0.750	
$\bar{z}$ 4 $\bar{1}4$	-63° 22'	34° 14'	115° 55'	75° 24'	47° 58'	not determined		
$\bar{x}$ 2 $\bar{1}2$	-50° 35'	38° 13'	112° 29'	66° 52'	47° 07'	not determined		
$\bar{u}$ 1 $\bar{1}1$	-34° 21'	47° 09'	105° 54'	52° 45'	48° 16'	1.230	1.050	
$\bar{s}$ 1 $\bar{3}1$	-13° 57'	68° 23'	91° 26'	25° 32'	58° 15'	not determined		
$\bar{p}$ 1 $\bar{1}1$	-137° 46'	42° 09'	123° 11'	119° 47'	66° 55'	0.975	0.975	
$\bar{w}$ 1 $\bar{2}1$	-157° 14'	57° 33'	119° 05'	141° 05'	80° 37'	not determined		

\*Values calculated from unit-cell parameters shown in Table 2.

\*\*Distance from the origin. Determination by K. L. Keester

single crystals from the Hard Scramble claim (specimen no. JFM69-5-5G7). These data were refined by least-squares analysis of the X-ray powder data and are shown in Table 2 compared with those obtained from the synthetic compound,  $MgO \cdot 2B_2O_3 \cdot 9H_2O$ . The crystal structure of hungchaoite has been determined by Wan and Ghose (1977) using our crystals from the Hard Scramble occurrence. They show hungchaoite to be  $Mg[B_4O_5(OH)_4] \cdot 7H_2O$ . Tung (1974) calculated a triclinic unit cell based on the X-ray powder data for the synthetic compound given by Chu *et al.* (1964b). Unfortunately, lines at 8.68 and 7.95Å, indexed by Tung as (100) and (010) respectively, are not due to hungchaoite and have led to an incorrect unit cell. The density calculated from Tung's cell, with  $Z = 1$ , is 1.599 g cm<sup>-3</sup>.

The synthetic compound,  $MgO \cdot 2B_2O_3 \cdot 9H_2O$ , may be dimorphous. According to Abdullaev and Mamedov (1969) the synthetic compound is monoclinic; space group  $P2_1/a$ ;  $a = 11.71$ ,  $b = 13.08$ ,  $c = 6.84$ Å,  $\beta = 105^\circ$ ;  $Z = 4$ . However, the density calculated from

these data is 2.242 g cm<sup>-3</sup>, which is unlikely for a dimorph of hungchaoite of specific gravity 1.703(5) (Table 2). Furthermore, Wan and Ghose (1977, p. 1141) have questioned the validity of the crystal structure proposed for this phase by Abdullaev and Mamedov on the basis of "... a number of impossibly short (<2A) oxygen-oxygen contacts. . ." On the other hand, Eyubova *et al.* (1967) give X-ray powder diffraction data for synthetic  $MgO \cdot 2B_2O_3 \cdot 9H_2O$  that do not agree with ours for the synthetic triclinic compound nor with the  $d(hkl)$  calculated from the monoclinic unit cell of Abdullaev and Mamedov. X-ray powder diffraction data for natural and synthetic hungchaoite are given in Table 3.

#### Physical properties

Hungchaoite is brittle with good to perfect  $\{\bar{1}11\}$ , good  $\{\bar{1}\bar{1}1\}$ , and imperfect  $\{010\}$  cleavages. Specific gravities of 1.706(5) (mineral) and 1.703(5) (synthetic compound) were obtained by suspension in bromo-

Table 2. Crystallographic data for hungchaoite

	Death Valley*	Synthetic**
System	Triclinic	Triclinic
Space Group	$\bar{P}1$	$\bar{P}1$
$a$ (Å)	8.811(1)†	8.800(1)†
$b$	10.644(2)	10.648(2)
$c$	7.888(1)	7.895(2)
$\alpha$	103° 23(1)'	103° 23(1)'
$\beta$	108° 35(1)'	108° 34(1)'
$\gamma$	97° 09(1)'	97° 08(1)'
$V$ (Å <sup>3</sup> )	666.2(1)	666.3(1)
$a:b:c$	0.828:1:0.741	0.826:1:0.742
$Z$	2	2
$G$ (meas)	1.706(5) ††	1.703(5) ††
$\rho$ (calc)	1.703 g cm <sup>-3</sup>	1.703 g cm <sup>-3</sup>

\*Specimen No. JFMS8-1-8C.

\*\*Material synthesized by Dr. W. T. Schaller.

†Data obtained from refinement of X-ray powder data (Table 3) using the least-squares program of Apfleman and Evans (1973). Error in parentheses is one standard deviation.

††Determined in bromoform-acetone mixture checked with a Westphal balance.

form-acetone. The hardness is 2½. The mineral and synthetic compound are colorless, have a vitreous luster, and are nonfluorescent.

#### Optical properties (G.D.E.)

The optical properties of hungchaoite from the Death Valley region are listed in Table 4 and compared with those reported by previous workers. Indices of refraction were determined in sodium light by the immersion method in phase contrast (Zernike) using a spindle stage similar to that described by Wilcox (1959). Refractive indices of the immersion media were checked with an Abbé refractometer using sodium light.

The mean index of refraction of hungchaoite calculated by the Gladstone and Dale law from the ideal composition,  $\text{MgO} \cdot 2\text{B}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ , and calculated density (1.703 g cm<sup>-3</sup>) is 1.468. The measured mean refractive index ( $\bar{R}/\alpha\beta\gamma$ ) is 1.473.

Figure 2 illustrates the relations between principal optical and observed crystallographic elements. Data for the projection were obtained by means of a universal stage equipped with a Waldmann hollow-glass sphere. Single crystals, previously oriented by optical goniometry and X-ray precession procedures, were mounted within the sphere in an immersion liquid of  $N_D(25^\circ\text{C}) = 1.485$ , the  $\beta$  index of the mineral. From the projection it is evident that the  $Z$  vibration direction is almost coincident with  $[0\bar{1}1]$ . Also, fragments lying on the best cleavage,  $\{\bar{1}11\}$ , give an off-centered negative  $Bxa$  interference figure which might be interpreted as uniaxial because of the small  $2V$ . This may

explain the incorrect axiality reported by Nikolaev (1947) for the identical synthetic compound.

The relatively large variation given for the observed  $2V$  (Table 4) is due to the difficulty in judging the exact position of the diffuse melatopes even though both lay close to  $X$  and were easily reachable by means of the universal stage. Nevertheless, the measured  $2V$  is really significantly lower than calculated values for this angle using either our data or those of Chu *et al.* (1964b). The limitations of such calculations have been stressed clearly by Willard (1961).

#### Synthesis and stability of hungchaoite in solution

The compound  $\text{MgO} \cdot 2\text{B}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$  was first synthesized by Nikolaev and Chelishcheva in 1940. Their name for this salt, "magnesium diborate," is followed in the Russian and Chinese nomenclature. Synthetic hungchaoite was subsequently encountered in studies of the  $\text{MgO}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$  system by Kurnakova (1947), Nikolaev (1947), D'Ans and Behrendt (1957), and Rza-Zade *et al.* (1964). Our synthetic material was prepared by the late Dr. Waldemar T. Schaller (oral communication, 1957), but the details of its synthesis are unknown. He may have been the first to recognize the triclinic nature of synthetic hungchaoite, for he reported that the material showed inclined extinction, was biaxial negative, and had a very small  $2V$ . D'Ans and Behrendt's comprehensive study of the solubility isotherms of the  $\text{MgO}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$  system at 25°, 35°, and 83°C showed that hungchaoite is formed only as a metastable phase, in solutions at temperatures less than 35°C. This is confirmed by other studies of the system at temperatures ranging from 45° to 200°C (Rza-Zade *et al.*, 1966, and others). Stable phases found in the system at 25°C are sassolite (orthoboric acid), inderite, kurnakovite, and mcallisterite. Rza-Zade *et al.* (1964) noted that hungchaoite behaves as a metastable phase with respect to inderite and mcallisterite and is eventually converted to one of these phases after prolonged periods at normal temperature (less than 35°C) and pressure conditions. Abdullaev and Mamedov (1966) have offered an explanation of the metastability of  $\text{MgO} \cdot 2\text{B}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$  and its conversion to inderite in terms of the crystal structure model that they proposed for this compound. However, as noted above, this structure is probably in error. Wan and Ghose (1977) have pointed out that while molecular complexes of neutral charge involving a borate polyanion and a hydrated metal cation are relatively rare, they are present in hungchaoite, inderite, and mcallisterite. We did not attempt to determine the time necessary for the

Table 3. X-ray powder diffraction data for hungchaoite

Calculated*			Observed					
hkl	$d_{hkl}$ (Å)	Synthetic**			Death Valley***		China#	
		$d_{hkl}$ (Å)	I	$d_{hkl}$ (Å)	I	$d_{hkl}$ (Å)	I	
010	10.116	10.1	5	10.1	4	---	---	
100	8.147	8.13	16	8.15	8	8.01	10	
$\bar{1}$ 10	7.139	7.13	52	7.14	59	7.18	60	
0 $\bar{1}$ 1	6.853	6.83	10	---	---	---	---	
$\bar{1}$ 01	6.709	6.71	59	6.71	100	6.67	70	
$\bar{1}$ 11	5.847	5.84	36	5.85	58	5.84	60	
$\bar{1}$ 11	5.367	5.36	38	5.36	85	5.34	60	
011	5.186	5.18	2	5.18	6	---	---	
020	5.058	5.06	26	5.05	35	5.05	40	
$\bar{1}$ 20	4.782	4.786	24	4.787	24	4.80	40	
101	4.620	4.620	8	4.619	6	4.47	30	
$\bar{2}$ 01	4.260	4.255	5	---	---	---	---	
$\bar{1}$ 21	4.232	4.235	6	4.233	8	4.25	10	
$\bar{2}$ 10	4.096	4.096	100	4.093	78	---	---	
121	4.074	4.077	95	4.079	64	4.07	100	
$\bar{1}$ 21	3.870	3.865	27	3.867	36	3.86	50	
111	3.785	3.786	8	3.790	8	---	---	
0 $\bar{1}$ 2	3.733	3.732	2	---	---	---	---	
021	3.665	3.666	19	3.666	31	3.66	50	
002	3.583	3.586	3	---	---	---	---	
$\bar{2}$ 20	3.569	3.574	7	3.574	10	---	---	
0 $\bar{3}$ 1	3.459	3.459	8	3.456	18	3.46	10	
$\bar{1}$ 12	3.357	3.354	53	3.356	92	3.34	90	
$\bar{2}$ 02	3.355	---	---	---	---	---	---	
$\bar{2}$ 12	3.277	3.277	13	3.277	20	---	---	
$\bar{2}$ 11	3.231	3.230	3	3.231	4	3.20	10	
$\bar{2}$ 12	3.099	3.098	12	3.100	12	---	---	
201	3.095	---	---	---	---	---	---	
$\bar{2}$ 21	3.061	3.061	5	3.062	5	---	---	
121	2.984	2.986	4	2.982	5	---	---	
$\bar{3}$ 01	2.910	---	---	---	---	2.916	10	
0 $\bar{3}$ 2	2.909	2.911	70	2.912	73	2.902	100	
$\bar{1}$ 31	2.907	---	---	---	---	---	---	
$\bar{3}$ 11	2.885	2.885	10	---	---	---	---	
220	2.884	---	---	---	---	---	---	
$\bar{1}$ 22	2.787	2.782	14	2.783	12	---	---	
$\bar{3}$ 10	2.776	2.775	15	---	---	---	---	
211	2.747	2.747	42	2.748	37	2.734	90	
		2.717	15	2.717	18	---	---	
		2.641	5	2.641	6	---	---	
		2.577	24	2.578	32	2.569	70	
		2.517	16	2.516	36	2.510	70	
		2.497	6	---	---	---	---	
		2.447	3	2.446	5	---	---	
		2.419	6	2.419	5	---	---	
		2.407	6	2.408	6	2.405	20	
		2.399	6	2.400	6	---	---	
		2.333	8	---	---	---	---	
		2.326	8	2.325	11	---	---	
		2.306	10	2.304	14	2.304	50	
		2.289	7	---	---	---	---	
		2.283	9	---	---	---	---	
		2.256	6	2.256	6	---	---	
		2.228	7	2.228	14	2.229	10	

Plus additional lines all with:

I &lt; 23

I &lt; 28

I &lt; 60

\*All lines are indexed to  $d_{hkl} < 2.740\text{Å}$ . Indices from least-squares analysis of X-ray powder data using the digital computer program of Appleman and Evans (1973).

\*\*Material synthesized by Dr. W. T. Schaller. X-ray diffractometer conditions are: Chart No. X3507; Cu/Ni radiation,  $\lambda\text{CuK}\alpha_1 = 1.54051\text{Å}$ ; silicon used as internal standard; scanned at  $\frac{1}{4}^\circ$  per minute from  $8-88^\circ 2\theta$ .

\*\*\*Specimen No. JFM58-1-8C. X-ray diffractometer conditions are: Chart No. X3508; Cu/Ni radiation;  $\lambda\text{CuK}\alpha_1 = 1.54041\text{Å}$ ; silicon used as internal standard; scanned; scanned at  $\frac{1}{4}^\circ$  per minute from  $8-108^\circ 2\theta$ .

#Data of Chu *et al.* (1964b); Zhen Pei-zu, analyst. Intensities have been converted to base 100 for comparison.

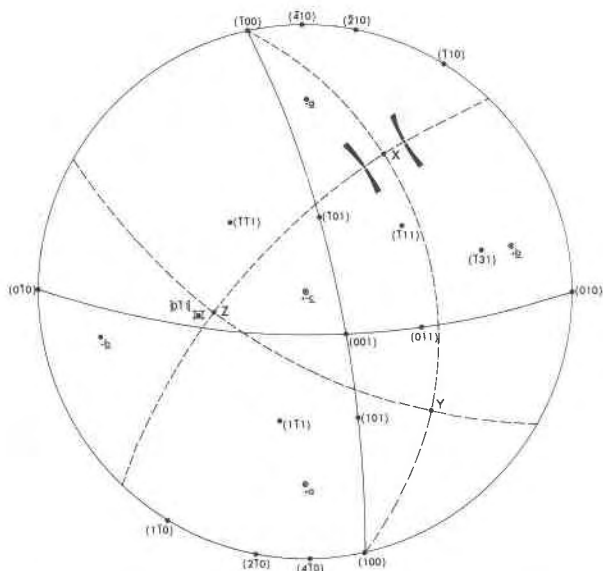


Fig. 2. Stereographic projection showing crystallographic elements and optical orientation of hungchaoite from the Death Valley region, California.

conversion of hungchaoite to the stable phases. However in one experiment, a crystal of hungchaoite suspended over water in a closed vial at 25°C remained unchanged after two months except for the development of etch pits on the crystal faces. The crystal was entirely enclosed by a drop of solution during this time. Hungchaoite is slowly soluble in cold water and easily soluble in cold dilute acids. Quantitative solubility data for the synthetic compound are given by D'Ans and Behrendt (1957).

#### Thermal data and stability of hungchaoite in air

Thermogravimetric and/or differential thermal analytical data for synthetic  $\text{MgO} \cdot 2\text{B}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$  have been given by several authors including Kurnakova (1947), Nikolaev (1947), D'Ans and Behrendt (1957), Eyubova *et al.* (1967), and Chu *et al.* (1964b); the last authors also give corresponding data for natural hungchaoite. The dehydration data are somewhat conflicting. For the following discussion it is convenient to consider the unit-cell content of the synthetic compound as  $2\text{MgO} \cdot 4\text{B}_2\text{O}_3 \cdot 18\text{H}_2\text{O}$ . D'Ans and Behrendt (1957) postulated  $2\text{MgO} \cdot 4\text{B}_2\text{O}_3 \cdot 17\text{H}_2\text{O}$  for the unit-cell content. They found that 12 moles of  $\text{H}_2\text{O}$  are given up on heating to 100°C, forming the compound  $2\text{MgO} \cdot 4\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  (the composition of synthetic halurgite). With further heating the structure collapses; water is driven off gradually; and, above 600°C,  $\text{MgB}_2\text{O}_4$  is formed after a loss of  $\text{B}_2\text{O}_3$ . By

contrast, Chu *et al.* (1964b) show a loss of 20 weight percent (about 8 moles of  $\text{H}_2\text{O}$ ) by 90–100°C and a loss of 40 weight percent (about 15 moles of  $\text{H}_2\text{O}$ ) by 180°C. The data of Eyubova *et al.* (1967) accord with those of Chu *et al.* The dehydration curves shown by D'Ans and Behrendt and by Chu *et al.* are similar in shape but differ in slope, a disparity that may be due to different rates of heating.

We restudied the dehydration of synthetic hungchaoite using 2 g of the material prepared by Dr. Schaller. The material was heated with an infrared lamp to 100°C and kept at this temperature for 24 hours. A loss of 34.00 weight percent (corresponding to 13 moles of  $\text{H}_2\text{O}$ ) occurred by 6 hours, but there was no further weight loss at this temperature. The composition at this point was  $2\text{MgO} \cdot 4\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , in agreement with D'Ans and Behrendt, but the material had become an X-ray amorphous glass with  $n = 1.496(2)$ . The sample was then heated further in an electric furnace to 700°C. There was a gradual loss of water up to 600°C, at which point all of the water had been driven off. The weight loss was 47.50 percent, corresponding to 18 moles of  $\text{H}_2\text{O}$  (47.45 percent for the calculated composition). The material was still amorphous to X-rays at this point. At 630(5)°C it recrystallized to form  $\text{MgB}_4\text{O}_7$ . The X-ray powder data for the  $\text{MgB}_4\text{O}_7$  are in excellent agreement with those of Kuzel (1964), who first synthesized this compound in his study of the  $\text{MgO}-\text{B}_2\text{O}_3$  system. He pointed out that there is no indication for the existence of the compound  $\text{MgB}_2\text{O}_4$  in this system. We found that no further loss in weight occurs up to the melting point (985°C; Kuzel, 1964) of  $\text{MgB}_4\text{O}_7$ .

The DTA curves shown by the various authors are

Table 4. Optical properties of hungchaoite

	Death Valley	China	Synthetic
$\alpha$	1.445(2)*	1.4415**	1.442**
$\beta$	1.485(2)	1.4851	1.485
$\gamma$	1.490(2)	1.4898	1.490
$2V\alpha$	15(2)° (obs)	36° (calc)	36° (calc)
Orientation	X $\Delta$ a = +28° <sup>†</sup> Z $\Delta$ b = +37° Y $\Delta$ c = -66°		
Dispersion	r < v, distinct		

\*Crystals from Hard Scramble claim; specimen no. JFM69-5-5-G7. Determined at 25°C in Na light. Error in parentheses is one standard deviation.

\*\*Data from Chu *et al.* (1964b).

<sup>†</sup>Angle is given as positive if it is measured in the acute angle between the crystallographic axes of reference and negative if it is measured in the obtuse angle.

in fairly good accord and may be explained on the basis of our dehydration study. There is a large endothermic peak at 95–105°C (Chu *et al.*, 1964b, found 170–180°C) corresponding to the loss of 13 moles of H<sub>2</sub>O; a smaller endothermic peak at 944–1040°C corresponds to the melting of MgB<sub>4</sub>O<sub>7</sub>. A medium to large exothermic peak at 630–675°C reflects the recrystallization of the amorphous dehydration product to MgB<sub>4</sub>O<sub>7</sub>. Nikolaev (1947) and Eyubova *et al.* (1967) also show a small endothermic effect at 375–380°C that is not recorded by Chu *et al.* (1964b) and for which we have no explanation.

The alteration of hungchaoite in air proceeds quite differently, however, under natural conditions, as processes other than simple dehydration are operative. The alteration of hungchaoite will be described separately in a forthcoming paper.

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