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REVISION OF THE CRYSTAL STRUCTURE OF MRÁZEKITE, $Bi_2Cu_3(OH)_2O_2(PO_4)_2{\cdot}2H_2O$

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ABSTRACT

Mrázekite, $Bi_2Cu_3(OH)_2O_2(PO_4)_2{\cdot}2H_2O$, is described from its second occurrence in silicified barite veins from Gadernheim and Reichenbach, Odenwald, Hesse, Germany. It forms blue crystals up to 0.5 mm across that are tabular on {101} and elongate parallel to [010]. The most prominent forms are {012}, {101}, and $\{10\bar{3}\}$. Mrázekite is biaxial negative, $2V$ = 66.0(5)°, $r < v$ strong; the mean index of refraction n is 1.86–1.87, $X \wedge c \approx 27°$, $Y \wedge a \approx 15°$, and $Z \parallel b$. Electron-microprobe analyses gave Bi_2O_3 50.1 wt.%, CuO 25.4%, PbO 0.10%, P_2O_5 15.2%, As_2O_5 0.26%, V_2O_5 0.25%, H_2O (calc.) 6.0%, total 97.3%. This yielded the empirical formula $Bi_{2.05}Cu_{2.99}(OH)_{1.98}O_{2.00}[(PO_4)_{1.95}(AsO_4)_{0.02}(VO_4)_{0.02}]_{\Sigma=1.99}{\cdot}1.88\ H_2O$. A reinvestigation of the crystal structure of mrázekite was performed using single-crystal X-ray data. The space group is $P2_1/n$, with a 9.065(1), b 6.340(1), c 21.239(3) Å, β 101.57(1)°, V 1195.8(2) Å^3, Z = 4. The structure refinement converged for 2995 observed unique reflections and 194 free parameters at R = 0.050. The $^{[2+2]}Bi^{3+}O_4$ polyhedra are edge-connected to form Bi_2O_6 dimers, <Bi–O> being 2.12 Å and 2.41 Å for the short and longer bonds. The coordination is completed by four ligands at a distance between 2.71 and 3.09 Å. The Cu atoms have four ligands with <Cu–O> = 1.95 Å; two additional ligands have Cu–O between 2.63 and 2.85 Å. The lengths of the hydrogen bonds in the hydroxyl groups are 2.67 Å; the water molecules have O_w...O contacts greater than or equal to 2.98 Å. Two thirds of the CuO_4 squares are corner-connected to rows in [010]; the PO_4 tetrahedra are linked to these rows to form ribbons that are interconnected by the remaining third part of the Cu atoms. The resulting corrugated sheets parallel to $(10\bar{3})$ are linked by Bi atoms and hydrogen bonds.

Keywords: mrázekite, $Bi_2Cu_3(OH)_2O_2(PO_4)_2{\cdot}2H_2O$, crystal morphology, optical properties, chemical composition, X-ray powder-diffraction pattern, cell parameters, crystal structure.

SOMMAIRE

Nous décrivons le deuxième exemple de la mrázekite, $Bi_2Cu_3(OH)_2O_2(PO_4)_2{\cdot}2H_2O$, découvert dans des veines de baryte silicifiées à Gadernheim et Reichenbach, Odenwald, Hesse, en Allemagne. Elle se présente en cristaux bleus atteignant 0.5 mm, tabulaires sur {101} et allongés parallèles à [010]. Les formes les plus importantes sont {012}, {101}, et $\{10\bar{3}\}$. La mrázekite est biaxe négative, 2V = 66.0(5)°, $r < v$ intense; l'indice de réfraction moyen est entre 1.86 et 1.87, $X \wedge c \approx 27°$, $Y \wedge a \approx 15°$, et $Z \parallel b$. Les analyses à la microsonde électronique ont donné Bi_2O_3 50.1% (poids), CuO 25.4%, PbO 0.10%, P_2O_5 15.2%, As_2O_5 0.26%, V_2O_5 0.25%, H_2O (calculé) 6.0%, total 97.3%. Ces données mènent à la formule empirique $Bi_{2.05}Cu_{2.99}(OH)_{1.98}O_{2.00}[(PO_4)_{1.95}(AsO_4)_{0.02}(VO_4)_{0.02}]_{\Sigma=1.99}{\cdot}1.88H_2O$. Nous avons redéterminé la structure cristalline de la mrázekite sur cristal unique. Le groupe spatial est $P2_1/n$, a 9.065(1), b 6.340(1), c 21.239(3) Å, β 101.57(1)°, V 1195.8(2) Å^3, Z = 4. L'affinement de la structure (194 paramètres libres, 2995 réflexions uniques observées) a atteint un résidu R de 0.050. Les polyèdres $^{[2+2]}Bi^{3+}O_4$ sont articulés par partage d'arêtes avec des dimères Bi_2O_6; <Bi–O> est égal à 2.12 et 2.41 Å pour les distances courtes et plus longues, respectivement. La coordinence est completée par quatre groupes anioniques situés à une distance de 2.71 à 3.09 Å. Les atomes de Cu sont agencés avec quatre ligands, avec <Cu–O> = 1.95 Å; pour deux ligands additionnels, Cu–O est entre 2.63 et 2.85 Å. Les liaisons hydrogène des groupes hydroxyle ont une longueur de 2.67 Å, et les molécules d'eau ont un contact O_w...O supérieur ou égal à 2.98 Å. Deux tiers des groupes planaires CuO_4 partagent leurs coins pour former des rangées le long de [010]. Les tétraèdres PO_4 sont articulés à ces rangées pour former des rubans liés aux autres groupes CuO_4. Les feuillets ondulés qui en résultent, parallèles à $(10\bar{3})$, sont liés par les atomes de Bi et les liaisons hydrogène.

(Traduit par la Rédaction)

Mots-clés: mrázekite, $Bi_2Cu_3(OH)_2O_2(PO_4)_2{\cdot}2H_2O$, morphologie, propriétés optiques, composition chimique, diffraction X, maille élémentaire, structure cristalline.

Introduction

Weathering of small segregations of ore in silicified veins from the Odenwald area, Germany, gave rise to the formation of numerous secondary minerals. In 1989, a blue bismuth–copper phosphate was found by Mr. Klaus Petitjean. X-ray and chemical data pertaining to this material did not match that of any known mineral, and it proved to be a new mineral. During contact with the IMA Commission on New Minerals and Mineral Names, it became evident that this species had been already approved a short time before. The mineral was named mrázekite, and the first description, based on samples from Ľubietová, Slovakia, was then in progress (Řídkošil *et al.* 1992).

We report here on physical, chemical, and structural data for mrázekite from the Odenwald area, Germany. In some respects (optical data, cell parameters, space-group symmetry, and crystal structure), the results differ from those given by Řídkošil *et al.* (1992).

Occurrence and General Appearance

The system of silicified barite veins at Reichenbach, near Bensheim, Odenwald, Hesse, Germany, is the largest among a number of similar silicified veins occurring in the crystalline rocks of the northwestern Odenwald area. The Reichenbach system of veins strikes west–northwest and dips nearly vertically; its length is about 5 km, and locally it reaches a width of more than 10 m. The silicified barite vein near Gadernheim, which can be regarded as the eastern continuation of the Reichenbach system, is much smaller (about 100 m in length and up to 4.5 m in width). A more detailed description of these localities was given by Krause *et al.* (1993). Small isolated grains of ore minerals (galena, chalcopyrite, tetrahedrite, tennantite, emplectite, and wittichenite) occur inside the vein material. Weathering of these primary minerals leads to a great number of secondary minerals, predominantly phosphates, arsenates, and vanadates of copper, lead, and bismuth.

A few milligrams of mrázekite crystals were found at Gadernheim (map coordinates r: 3481300, h: 5508150, topographic map sheet TK 6218) and at Reichenbach (map coordinates r: 3477260, h: 5508500, topographic map sheet TK 6218). Associated minerals at Gadernheim are chalcopyrite, chalcocite, malachite, goethite, pyromorphite, and beudantite, and at Reichenbach, bismutite, preisingerite, mixite, and reichenbachite. Mrázekite forms crusts and spherical aggregates; idiomorphic crystals (<0.5 mm) with well-developed faces are rare. Physical and chemical data of mrázekite from Gadernheim and Reichenbach were found to be identical and in good agreement with the data given by Řídkošil *et al.* (1992), except for part of the optical data.

Morphological and Optical Data

Mrázekite crystals are tabular on {101} and elongate parallel to [010] (Fig. 1). In general, the crystal faces are poorly developed, and measurements with a two-circle optical goniometer revealed values with uncertainties of about 0.5 to 1°. Parallel to [010], four

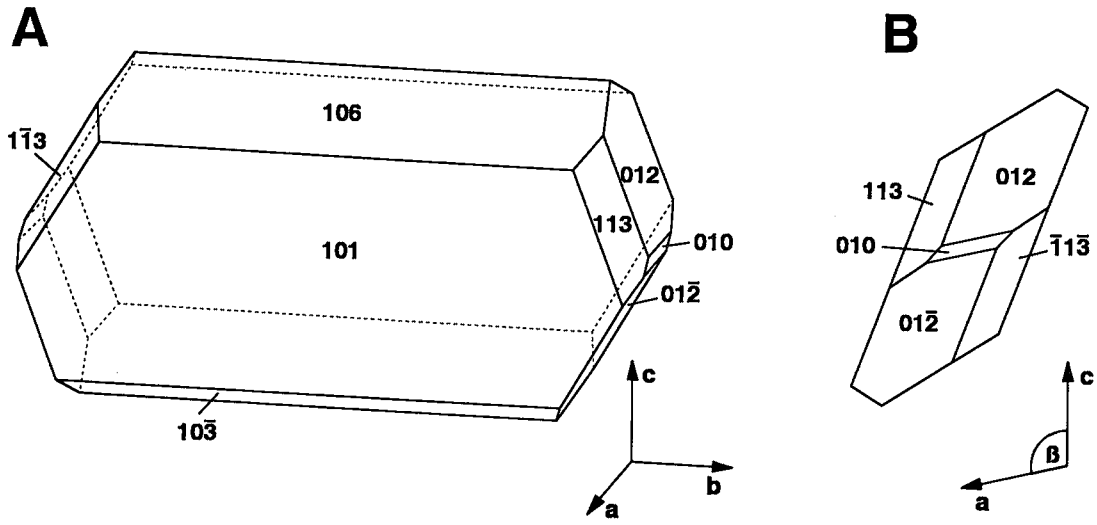

FIG. 1. Morphology of mrázekite: A) perspective view, B) view parallel to [010].

pinacoids {*h*0*l*} were observed: {101} is the dominant form, {10$\bar{3}$} is common and forms small faces, {001} is rare and generally poorly developed. In addition, all crystals investigated show a large pinacoid with a relatively high *l* index. Though it is close to {001}, the deviation with respect to the calculated position of {001} is about 20°, and therefore much greater than the uncertainty of the measurement. Because of its poor development, this form cannot be indexed precisely; the indices may therefore range between {105} and {107}; as an average, {106} is shown. Oblique to [010], the crystals are usually terminated by {012} (dominant), {113} (minor), and {010} (rare).

The optical data could not be determined in detail, because the crystals were rapidly attacked by the immersion liquids, the Cargille oils as well as mixtures of phosphorus and CH_2I_2, with (West solution) and without sulfur. Therefore, only a mean index of refraction, between 1.86 and 1.87, is reported. This is in good agreement with the calculated index of refraction, 1.87, based on the Gladstone–Dale relationship (Mandarino 1981). The optic axis angle 2*V* has been measured by a straightforward method described in detail by Medenbach (1985). Subsequent to the orientation with a spindle stage, the crystal was transferred with its n_y direction parallel to the axis of a second goniometer head. Precise measurements of 2*V* and observations of dispersion effects were then possible in an appropriate immersion liquid with $n = n_y$ of the crystal. Because of the decomposition of mrázekite in higher-index liquids, the determinations have been carried out in methylene iodide and corrected according to Snell's law. Strong dispersion was found, with $r < v$; $2V_x = 63.0(5)°$ (670 nm), 66.0(5)° (589 nm), and 73.5(5)° (435 nm). The orientation is $X \wedge c \approx 27°$, $Y \wedge a \approx 15°$ and $Z \parallel b$, with strong horizontal dispersion. Pleochroism is very faint in ink-blue colors, and absorption is $X < Y < Z$. Note that the orientation of the optical indicatrix differs markedly from that given by Řídkošil *et al.* (1992).

Chemical Composition

An electron microprobe (CAMECA Camebax, 20 kV, 14 nA) was used for chemical analysis. The following standards were used: Bi_2S_3 (Bi), mimetite (Pb, As), $AlPO_4$ (P), vanadium metal (V), and $SrCuSi_4O_{10}$ (Cu). Table 1 gives average results of 14 analyses. No other elements with atomic numbers greater than 8 were detected. H_2O was calculated according to the ideal formula; the infrared spectrum of a single crystal, recorded with a Bruker FTIR spectrometer, clearly indicates the existence of both hydroxyl groups and molecular water. The empirical formula based on 14 oxygen atoms is $Bi_{2.05}Cu_{2.99}(OH)_{1.98}O_{2.00}[(PO_4)_{1.95}(AsO_4)_{0.02}(VO_4)_{0.02}]_{\Sigma=1.99}\cdot 1.88H_2O$ or, ideally, $Bi_2Cu_3(OH)_2O_2(PO_4)_2\cdot 2H_2O$.

TABLE 1. CHEMICAL COMPOSITION (WT.-%) OF MRÁZEKITE FROM REICHENBACH, ODENWALD, GERMANY

constituent	range	1	2
Bi_2O_3	48.87 - 51.76	50.09	51.74
CuO	24.73 - 25.85	25.44	26.50
PbO	0.04 - 0.20	0.10	—
P_2O_5	14.67 - 15.58	15.16	15.76
As_2O_5	0.10 - 0.52	0.26	—
V_2O_5	0.06 - 0.42	0.25	—
H_2O (calc.)		6.00	6.00
total		97.30	100.00

1: mean of 14 analyses
2: calculated for the ideal formula $Bi_2Cu_3(OH)_2O_2(PO_4)_2\cdot 2\ H_2O$

X-Ray Data and Structure Investigation

Řídkošil *et al.* (1992) described mrázekite from Ľubietová as monoclinic, with *a* 12.359(6), *b* 6.331(4), *c* 9.060(4) Å, and β 122.71(4)°. The crystal structure was determined and refined in space group *C*2/*m*. Independently, we investigated crystals of this mineral species from Gadernheim, Odenwald, Germany. Single-crystal Weissenberg film investigations clearly proved Laue symmetry 2/*m*, and from extinction rules the space group $P2_1/n$ was found. The unit-cell parameters were refined from the 2θ values of an X-ray powder-diffraction pattern by least-squares methods (indexed according to the cell parameters ascertained from single-crystal investigations): *a* 9.065(1), *b* 6.340(1), *c* 21.239(3) Å, β 101.57(1)°. The cell volume is doubled compared to that of Řídkošil *et al.* (1992).

The atomic coordinates of the Bi atoms and parts of those of the Cu atoms were derived from a Patterson map. The other atoms (except for the hydrogen atoms) were found from successive Fourier and difference-Fourier maps. A subsequent structural reinvestigation of the type material of mrázekite from Ľubietová verified the results determined on crystals from Gadernheim within limits of error and proved the identity of the two mineral species.

The crystal structure of mrázekite shows a pronounced pseudosymmetry. Řídkošil *et al.* (1992) gave the pseudocell and the *average* structure only. It is noteworthy that the pseudocell found by the previous authors shows a *C*-centering, whereas the *true* cell has a primitive Bravais lattice; consequently, the pseudocell has a quarter of the cell volume of the true cell with respect to translation symmetry. A remark is necessary regarding the pseudocell given by Řídkošil *et al.* (1992): the *C*2/*m* setting implies an unreduced cell; the reduced pseudocell has space group setting *I*2/*m* (the relationships are illustrated in Fig. 2 and Table 2, respectively). The calculated powder-patterns for the average and true structures, respectively, show only very slight differences. Mainly, these are mani-

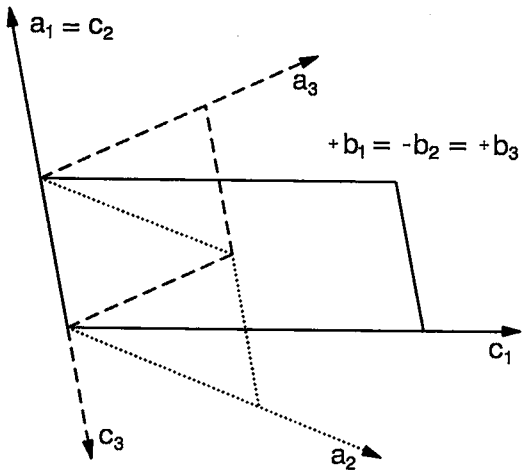

FIG. 2. Relation between the true cell and the pseudocell of mrázekite. a_1, b_1, c_1: true cell, space group $P2_1/n$; a_2, b_2, c_2: pseudocell, space group $C2/m$ (used by Řídkošil *et al.* 1992); a_3, b_3, c_3: reduced pseudocell, space group $I2/m$.

fested in a few additional diffraction lines (Table 3) of minor intensity, as can clearly be seen in a high-resolution powder-diffraction pattern. The pseudo-symmetry of mrázekite is responsible for the large number of unobserved reflections in the single-crystal data set used for structure refinements in space group $P2_1/n$.

Details of the data collection and structure refinements are compiled in Table 4. Final structural parameters and selected interatomic bond-lengths, as well as bond angles, are given in Table 5 and 6, respectively. For convenience throughout this paper, oxygen atoms belonging to the PO_4 tetrahedra, hydroxyl groups, and water molecules are denoted as O_p, O_h, and O_w, respectively, and the oxo-oxygen atoms as O_o; ϕ is an unspecified oxygen ligand. The observed and calculated structure-factors are available from the

TABLE 2. CRYSTALLOGRAPHIC DATA OF MRÁZEKITE *

	true cell	*true* cell	*pseudo*-cell not reduced	*pseudo*-cell reduced
locality	Gadernheim	Ľubietová	Gadernheim	Gadernheim
space group	$P2_1/n$	$P2_1/n$	$C2/m$	$I2/m$
a [Å]	9.065(1)	9.065(1)	12.354(2)	10.678(1)
b [Å]	6.340(1)	6.341(1)	6.340(1)	6.340(1)
c [Å]	21.239(3)	21.238(2)	9.065(1)	9.065(1)
ß [°]	101.57(1)	101.61(1)	122.63(1)	103.00(1)
V [Å³]	1195.8(2)	1195.8(2)	597.9(1)	597.9(1)
Z	4	4	2	2

* Cell parameters refined from powder data; for measuring conditions see Table 3.
transformation matrix $C2/m \rightarrow P2_1/n$: [0 0 1 , 0 1 0 , 2 0 1]
transformation matrix $C2/m \rightarrow I2/m$: [1 0 1 , 0 1 0 , 0 0 $\bar{1}$]

TABLE 3. CALCULATED AND OBSERVED X-RAY POWDER DIFFRACTION PATTERN OF MRÁZEKITE FROM GADERNHEIM, ODENWALD, GERMANY *

h	k	l	I_{calc}	d_{calc}	I_{obs}	d_{obs}
1	0	1	99	7.634	100	7.630
$\bar{1}$	0	3	48	6.091	42	6.089
0	1	2	48	5.414	56	5.407
0	0	4	53	5.202	46	5.198
$\bar{1}$	1	1	43	5.150	49	5.146
$\bar{1}$	1	2	4	# 4.853	5	4.851
0	1	3	3	# 4.679	8	4.671
$\bar{2}$	0	2	30	4.416	29	4.417
2	0	2	22	3.817	21	3.817
2	1	0	32	3.637	35	3.637
$\bar{1}$	1	5	36	3.441	28	3.440
0	2	0	31	3.170	35	3.170
0	2	1	4	# 3.133	6	3.135
$\bar{2}$	0	6	11	3.045	87	3.042
0	1	6	100	3.043		
$\bar{3}$	0	1	70	3.016	77	3.016
$\bar{1}$	0	7	18	3.006		
1	2	0	5	# 2.985	10	2.986
1	2	1	70	2.927	76	2.927
1	2	2	7	# 2.820	11	2.817
2	1	4	20	2.774	19	2.773
$\bar{3}$	0	5	15	2.679	13	2.681
3	1	1	15	2.601	18	2.601
$\bar{2}$	2	2	22	2.575	20	2.574
1	2	4	4	# 2.517	7	2.516
2	0	6	17	2.501	20	2.500
1	1	7	19	2.455	16	2.454
1	2	5	31	2.352	22	2.351
$\bar{2}$	2	5	3	# 2.317	16	2.301
$\bar{2}$	1	8	18	2.302		
4	0	0	11	2.220	12	2.220
$\bar{4}$	0	4	3	2.208	11	2.209
$\bar{1}$	1	9	8	2.208		
$\bar{3}$	1	7	23	2.200	31	2.197
$\bar{2}$	2	6	24	2.196		
$\bar{3}$	2	1	22	2.185	24	2.184
$\bar{1}$	2	7	6	2.181		
$\bar{4}$	1	2	8	2.134	11	2.134
3	1	5	29	2.088	28	2.088
$\bar{1}$	3	1	4	2.055	6	2.056
$\bar{3}$	2	5	3	2.046	5	2.045
$\bar{1}$	3	2	3	# 2.035	5	2.035
0	2	8	12	2.011	7	2.010
2	1	8	3	1.968		
$\bar{4}$	1	6	16	1.966	15	1.965
2	2	6	3	1.963		
$\bar{1}$	3	4	4	# 1.943	4	1.944
$\bar{1}$	0	11	8	1.931	8	1.931
3	0	7	3	1.914	4	1.914
2	3	0	2	1.908	4	1.908
$\bar{4}$	0	8	8	1.886	10	1.885
0	3	5	4	# 1.884		
$\bar{1}$	3	5	9	1.878	9	1.879
4	2	0	22	1.819	17	1.819
0	3	6	14	1.805	14	1.805
2	0	10	8	1.754	8	1.755
2	3	4	3	1.743	8	1.740
5	0	1	8	1.740		
0	0	12	7	1.734	7	1.733
$\bar{5}$	1	1	9	1.732		
0	3	7	3	1.722	5	1.723
1	1	11	4	1.713	4	1.713
$\bar{5}$	1	5	3	1.702	5	1.699
$\bar{3}$	1	11	3	1.698		
$\bar{2}$	1	12	9	1.676	7	1.675
4	1	6	10	1.660	10	1.660
1	3	7	7	1.655		
3	2	7	12	1.639	10	1.639
4	2	4	4	1.635		
$\bar{2}$	3	8	5	1.606	5	1.606
0	4	0	8	1.585	7	1.586
$\bar{1}$	1	13	4	1.582	9	1.580
0	4	1	6	# 1.580		
3	3	4	3	# 1.579		
$\bar{5}$	2	3	7	1.572	9	1.571
$\bar{3}$	3	7	10	1.570		
3	3	5	11	1.528	11	1.527
5	0	5	5	1.527		
1	0	13	10	1.523	19	1.523
$\bar{5}$	1	9	5	1.523		
$\bar{4}$	0	12	8	1.523		
0	2	12	15	1.521		
$\bar{6}$	0	2	7	1.508	6	1.508
$\bar{2}$	0	14	8	1.503	6	1.504
$\bar{5}$	2	7	15	1.485	10	1.485
$\bar{4}$	3	6	5	1.478	7	1.478

* The powder diffraction pattern was calculated with program LAZY PULVERIX (Yvon *et al.* 1977) according to recent structure refinement in space group $P2_1/n$; only intensities with $I_{calc} \geq 3$ were considered. The observed pattern was taken with a STOE powder diffractometer STADI P; $CuK\alpha_1$-radiation; external standard Si; $0° < 2\vartheta < 80°$.
# diffraction lines not possible in the *pseudo*-cell.

TABLE 4. SUMMARY OF CRYSTAL DATA, X-RAY DATA COLLECTION AND STRUCTURE REFINEMENTS OF MRÁZEKITE *

a = 9.065(1) Å	specimen from Gadernheim, Odenwald, Germany
b = 6.340(1) Å	Z = 4 $\{Bi_2Cu_3(OH)_2O_2(PO_4)_2 \cdot 2\,H_2O\}$
c = 21.239(3) Å	crystal dimensions: 0.11 x 0.22 x 0.28 mm³
ß = 101.57(1)°	$2\vartheta/\omega$ scan mode, scan time 0.90 to 3.60°/min
V = 1195.8(2) Å³	scan width: 0.84° (increased for α_1-α_2 dispersion)
space group $P2_1/n$	3 standard reflections measured each 120 min
X-ray density 5.00 gcm⁻³	maximal variation of intensity ±2.3%
$\mu(MoK\alpha)$ = 346 cm⁻¹	range of data collection: $5° < 2\vartheta < 70°$
R_{int} = 0.083	13318 total measured reflections
R = 0.050	5066 unique reflections
R_w = 0.044	2995 reflections for refinements: $F_o > 3\sigma(F_o)$
$w = 2.25/[\sigma(F_o)]^2$	absorption correction according to crystal shape
194 variable parameters	transmission factors from 0.026 to 0.146
max Δ/σ < 0.001	program SHELX-76 (Sheldrick 1976)

* STOE four circle diffractometer AED2, Mo tube, graphite monochromator. Corrections for Lorentz and polarization effects. Complex neutral atomic scattering functions (International Tables for X-ray Crystallography 1974).

TABLE 5. STRUCTURAL PARAMETERS (E.S.D.'S IN PARENTHESES) FOR MRÁZEKITE *

atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B_{eq}
Bi(1)	0.36464(9)	0.25135(8)	0.04570(3)	0.0185(3)	0.0160(2)	0.0155(2)	0.0003(1)	0.0034(1)	0.0002(1)	1.31
Bi(2)	0.38662(8)	0.19971(7)	0.20523(3)	0.0173(3)	0.0161(2)	0.0147(2)	0.0000(1)	0.0031(1)	0.0000(1)	1.27
Cu(1)	0.0	0.0	0.0	0.0171(14)	0.0173(11)	0.0248(14)	-0.0016(6)	0.0037(6)	-0.0001(4)	1.56
Cu(2)	0.0	0.5	0.0	0.0174(14)	0.0167(11)	0.0248(14)	0.0023(6)	0.0039(6)	0.0007(4)	1.55
Cu(3)	0.3719(3)	0.7251(3)	0.1251(1)	0.0276(9)	0.0134(7)	0.0151(7)	0.0000(3)	0.0035(3)	0.0002(3)	1.49
Cu(4)	0.7461(2)	0.4532(3)	0.2469(1)	0.0171(10)	0.0188(8)	0.0247(11)	-0.0024(4)	0.0041(4)	0.0001(3)	1.60
P(1)	0.7237(5)	0.2688(5)	0.0281(2)	0.0178(21)	0.0164(16)	0.0166(19)	0.0007(7)	0.0042(8)	0.0004(6)	1.32
P(2)	0.0284(5)	0.2192(5)	0.2226(2)	0.0181(21)	0.0160(15)	0.0147(18)	-0.0001(7)	0.0042(8)	0.0001(6)	1.27
$O_p(11)$	0.631(2)	0.247(2)	0.0803(6)	0.020(7)	0.036(6)	0.028(7)	0.002(3)	0.007(3)	0.000(2)	2.17
$O_p(12)$	0.809(1)	0.064(2)	0.0224(6)	0.026(7)	0.015(5)	0.037(7)	-0.002(3)	0.006(3)	0.000(2)	2.08
$O_p(13)$	0.610(2)	0.315(2)	-0.0345(5)	0.030(8)	0.033(6)	0.014(6)	-0.006(3)	0.004(3)	-0.003(2)	2.03
$O_p(14)$	0.832(1)	0.460(2)	0.0417(5)	0.022(6)	0.022(5)	0.031(6)	0.000(3)	0.005(3)	0.000(2)	1.97
$O_p(21)$	0.115(1)	0.189(2)	0.1690(5)	0.012(6)	0.027(5)	0.017(5)	-0.002(2)	0.001(2)	0.000(2)	1.51
$O_p(22)$	-0.056(1)	0.013(1)	0.2299(6)	0.020(6)	0.020(5)	0.033(6)	0.000(3)	0.006(3)	-0.002(2)	1.95
$O_p(23)$	-0.081(1)	0.407(2)	0.2086(6)	0.022(7)	0.022(5)	0.039(7)	0.000(3)	0.009(3)	0.002(2)	2.15
$O_p(24)$	0.147(2)	0.267(2)	0.2847(6)	0.023(7)	0.032(6)	0.019(7)	0.001(2)	0.005(3)	-0.001(2)	1.92
$O_o(1)$	0.378(1)	0.025(1)	0.1200(5)	0.023(5)	0.018(5)	0.019(5)	0.004(2)	0.004(2)	0.003(2)	1.59
$O_o(2)$	0.372(1)	0.425(1)	0.1307(5)	0.022(5)	0.014(4)	0.020(5)	0.002(2)	0.005(2)	0.000(2)	1.45
$O_h(1)$	0.652(1)	0.195(1)	0.2068(5)	0.024(6)	0.020(5)	0.019(5)	-0.001(2)	0.005(2)	0.000(2)	1.63
$O_h(2)$	0.099(1)	0.254(1)	0.0436(6)	0.018(6)	0.018(5)	0.026(6)	0.002(2)	0.003(2)	0.002(2)	1.63
$O_w(1)$	0.065(2)	0.769(2)	0.1050(8)	0.034(10)	0.052(8)	0.026(8)	-0.008(3)	0.004(4)	-0.001(3)	2.97
$O_w(2)$	0.685(3)	0.735(2)	0.1403(8)	0.064(15)	0.065(9)	0.021(8)	-0.012(4)	-0.002(4)	0.000(4)	4.05

* Anisotropic displacement parameters: $\exp [-2 \pi^2 \Sigma_{i=1}^{3} \Sigma_{j=1}^{3} U_{ij} a_i^* a_j^* h_i h_j]$, B_{eq} after Fischer & Tillmanns (1988)

TABLE 6. INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) *

Bi(1)	$O_o(2)$	$O_o(1)$	$O_p(11)$	$O_h(2)$	**Bi(2)**	$O_o(1)$	$O_o(2)$	$O_h(1)$	$O_p(21)$
$O_o(2)$	**2.10**	2.54	2.99	2.98	$O_o(1)$	**2.11**	2.54	2.98	2.97
$O_o(1)$	74.1	**2.12**	2.96	3.08	$O_o(2)$	74.1	**2.11**	3.09	3.01
$O_p(11)$	83.5	82.0	**2.38**	4.73	$O_h(1)$	82.6	86.1	**2.40**	4.77
$O_h(2)$	82.6	85.8	163.5	**2.40**	$O_p(21)$	81.5	82.8	162.5	**2.43**

Cu(1)	$O_p(12)$	$O_p(12)$	$O_h(2)$	$O_h(2)$	**Cu(2)**	$O_p(14)$	$O_p(14)$	$O_h(2)$	$O_h(2)$
$O_p(12)$	**1.93**	3.86	2.69	2.84	$O_p(14)$	**1.93**	3.86	2.74	2.73
$O_p(12)$	180	**1.93**	2.84	2.69	$O_p(14)$	180	**1.93**	2.73	2.74
$O_h(2)$	86.8	93.2	**1.98**	3.96	$O_h(2)$	90.4	89.7	**1.94**	3.87
$O_h(2)$	93.2	86.8	180	**1.98**	$O_h(2)$	89.7	90.4	180	**1.94**

Cu(3)	$O_o(1)$	$O_o(2)$	$O_p(24)$	$O_p(13)$	**Cu(4)**	$O_p(22)$	$O_p(23)$	$O_h(1)$	$O_h(1)$
$O_o(1)$	**1.91**	3.82	2.65	2.84	$O_p(22)$	**1.93**	3.84	2.84	2.66
$O_o(2)$	178.4	**1.91**	2.85	2.66	$O_p(23)$	169.9	**1.93**	2.73	2.77
$O_p(24)$	86.0	94.2	**1.98**	3.96	$O_h(1)$	94.3	89.4	**1.95**	3.91
$O_p(13)$	93.7	86.2	180.0	**1.98**	$O_h(1)$	86.6	90.6	174.9	**1.96**

P(1)	$O_p(11)$	$O_p(12)$	$O_p(13)$	$O_p(14)$	**P(2)**	$O_p(21)$	$O_p(22)$	$O_p(23)$	$O_p(24)$
$O_p(11)$	**1.53**	2.50	2.44	2.53	$O_p(21)$	**1.52**	2.47	2.52	2.47
$O_p(12)$	110.0	**1.53**	2.52	2.54	$O_p(21)$	108.0	**1.54**	2.54	2.54
$O_p(13)$	105.9	110.8	**1.54**	2.49	$O_p(23)$	111.2	111.4	**1.54**	2.51
$O_p(14)$	110.7	111.6	107.6	**1.55**	$O_p(24)$	106.7	110.7	108.8	**1.56**

additional Bi—Ø bonds		additional Cu—Ø bonds		hydrogen bonds	
Bi(1)-O_p(12)	2.77	Cu(1)-O_w(1)	2.63	O_h(1)···O_p(11)	2.68
Bi(1)-O_p(13)	2.77	Cu(1)-O_w(1)	2.63	O_h(2)···O_p(21)	2.67
Bi(1)-O_p(14)	2.94	Cu(2)-O_w(1)	2.77	O_w(1)···Ø ≥	2.98
Bi(1)-O_p(13)	3.09	Cu(2)-O_w(1)	2.77	O_w(2)···Ø ≥	3.21
Bi(2)-O_p(22)	2.71	Cu(3)-O_w(1)	2.74		
Bi(2)-O_p(24)	2.77	Cu(3)-O_w(2)	2.79		
Bi(2)-O_p(23)	2.93	Cu(4)-O_w(2)	2.73		
Bi(2)-O_p(24)	3.04	Cu(4)-O_w(2)	2.85		

* E.s.d.'s for bonds and angles are 0.01 Å for Bi—Ø, Cu—Ø, and P—Ø, 0.02 Å for Ø—Ø, 0.4° for Ø—Bi—Ø and Ø—Cu—Ø, and 0.6° for O_p—P—O_p.

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Crystal Structure

The two Bi^{3+} atoms show a [2+2]-coordination; the ligands are one-sided, arranged as is characteristic for elements with lone-pair electrons. The coordination polyhedra could be described as trigonal bipyramids: two O_o atoms and the lone-pair electrons are in the equatorial plane, and O_h and O_p atoms are at the apices; the average bond-length <Bi–O_o>, 2.12 Å, is definitely shorter than <Bi–O_h/O_p>, 2.40 Å. Owing to the larger space-requirement of the lone-pair electrons, as compared to the oxygen atoms, the <O_o–Bi–O_o> angles are reduced to 74°, whereas <O_o–Bi–O_h/O_p> is 83°. The sums of bond valences for these four nearest neighbors are 2.79 and 2.72 v.u. (valence units), respectively [all bond-valence calculations were made according to Brese & O'Keeffe (1991)]. Four additional ϕ ligands are on the side of the lone-pair electron region, and the corresponding bond-valences are smaller than 0.16 v.u. In the synthetic compound Bi_2CuO_4, the Bi^{3+} atom has a [2+2] coordination most similar to that in mrázekite [Effenberger (1993); for a previous investigation of the structure, see Boivin *et al.* (1976); the structure model given by Arpe & Müller-Buschbaum (1976) is incorrect].

Two of the four crystallographically different copper atoms have site symmetry $\bar{1}$, and that of the others is 1. Considering the nearest-neighbor environment, all Cu atoms show the common square coordination; the ligands are two hydroxyl groups and two oxo-oxygen atoms. The ϕ–Cu–ϕ bond angles deviate less than 5° from rectangularity. The coordination figure of each of the four Cu atoms is completed by two additional O_w ligands to a tetragonal dipyramid; because the Cu–O_w distances are larger than 2.64 Å, only weak chemical interactions are assumed (bond valences 0.08 to 0.04 v.u.).

The PO_4 groups have the usual dimensions. The O_p atoms are [2]-coordinated to P and Bi or P and Cu (short Bi–ϕ and short Cu–ϕ bonds). The angles P–O_p–Bi (113.7° and 116.6°) are smaller than P–O_p–Cu (123.2° to 133.9°); the former act as the acceptor atoms of the hydrogen bonds from the hydroxyl groups O_h...O_p, and the latter are the additional ligands at the Bi atoms. The O_o atoms are approximately planar coordinated by two Bi atoms and by one Cu atom. The O_h atoms are in a trigonal pyramidal arrangement, attached to two Cu and one Bi atom; the mean angles at the O_h atoms are 115°. Atoms that most probably act as the acceptor atoms of the hydrogen bonds complete the coordination around the O_h atoms to an approximate tetrahedron. The hydrogen-bond lengths $O_h(1)$...O(11) and $O_h(2)$... O(21) are 2.68(2) Å and 2.67(2) Å, respectively (other O_h–ϕ distances less than 3.2 Å are edges in either a $^{[2+2]}Bi\phi_4$ or a $^{[4]}Cu\phi_4$ polyhedron). The O_w atoms are the distant ligands in three $^{[4+2]}Cu\phi_6$ polyhedra, average <Cu–O_w–Cu> angles are 89°; owing to their low bonding interaction to these cations, they have to be

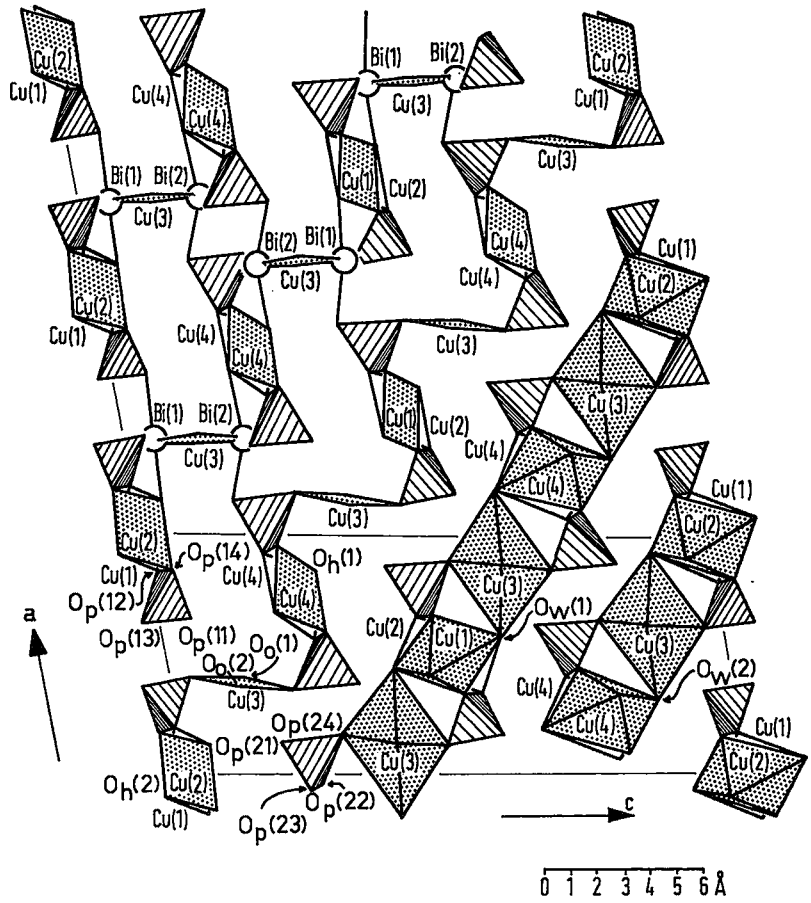

FIG. 3. Projection of the crystal structure of mrázekite on (010). The connection of the coordination polyhedra around the Cu atoms (dotted) and of the PO_4 tetrahedra (hatched) to sheets parallel ($10\bar{3}$) is shown. In the lower right-hand corner, the additional Cu–O_w bonds are considered to form tetragonal dipyramids $^{[4+2]}Cu\phi_6$. The Bi atoms are given only in the upper left-hand corner.

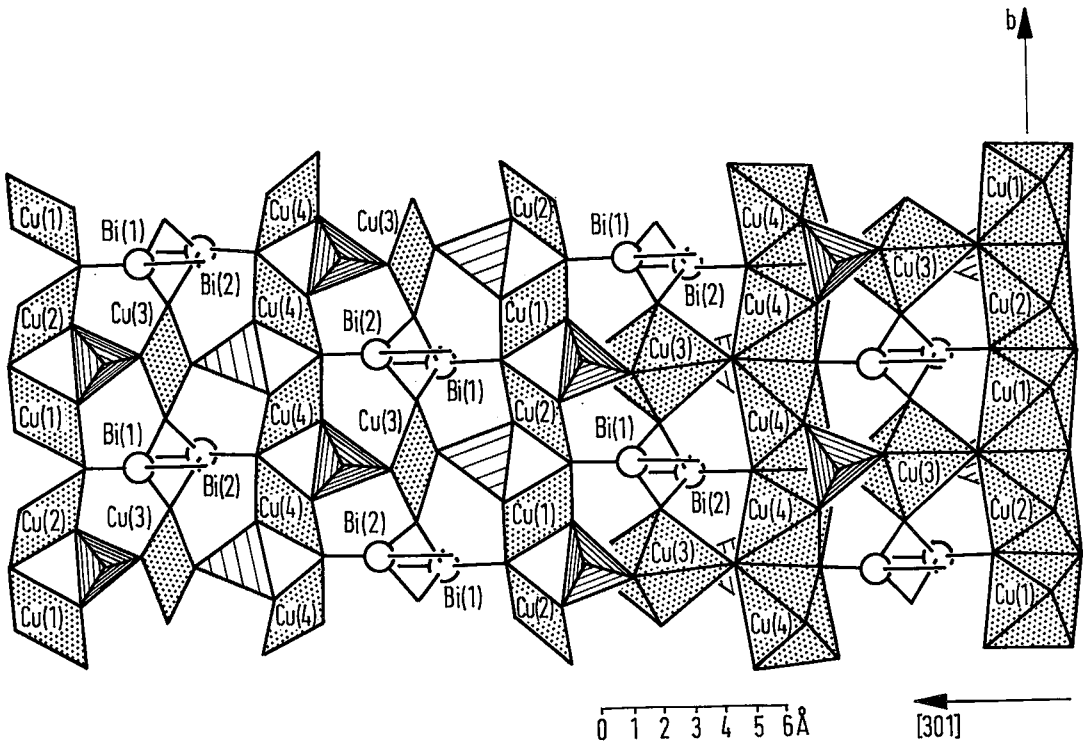

FIG. 4. Projection of one of the sheets of mrázekite on (10$\bar{3}$). The connection of the coordination polyhedra around Cu atoms (dotted) and PO_4 tetrahedra (hatched) to a two-dimensional net is shown. To the right, the additional Cu–O_w bonds are considered to form tetragonal dipyramids ($^{[4+2]}Cu\phi_6$).

assumed to belong to the water molecules. The scheme of hydrogen bonding of the O_w atoms is not clear: the shortest contacts (no O_w–ϕ edges in the $^{[4+2]}Cu\phi_6$ polyhedron) to any ϕ atoms are greater or equal to 2.98(2) Å, as is characteristic for "free" O_w...ϕ dipoles. As expected for such a water molecule, its displacement parameters are large.

The atomic arrangement of mrázekite (Fig. 3) is characterized by edge connection of $Bi\phi_4$ polyhedra to form $Bi_2\phi_6$ dimers and by two crystallographically different $Cu_2(O_p)_4(O_h)_2$ rows parallel [010], formed by corner connection of $Cu(1)\phi_4$ and $Cu(2)\phi_4$ squares on the one hand, and of $Cu(4)\phi_4$ squares on the other. The PO_4 tetrahedra are linked *via* corners to these rows forming $Cu_2(O_h)_2(PO_4)_2$ ribbons. $Cu(3)\phi_4$ squares have two different corners in common with PO_4 tetrahedra of neighboring rows (Fig. 4), resulting in layers parallel (10$\bar{3}$) that are responsible for the good cleavage of mrázekite. Consideration of the additional Cu–O_w bonds leads to a two-dimensional net formed solely by connecting the $^{[4+2]}Cu\phi_6$ polyhedra. Hydrogen bonds and Bi atoms link the copper–phosphate sheets to a three-dimensional framework.

The coordination figures around atoms related by pseudosymmetry are similar to each other. Figures 3 and 4 illustrate the error if only the pseudocell instead of the true $P2_1/n$ cell is chosen for description of the atomic arrangement of mrázekite: the rows $Cu(1)Cu(2)O_2(PO_4)_2$ and $Cu(4)_2O_2(PO_4)_2$ of $P2_1/n$ are identical by translation symmetry in the pseudocell. The refinement in the pseudocell caused the large residual electron-density (from –7.82 to +5.95 eÅ^{-3}) and the large displacement parameters observed by Řídkošil *et al.* (1992). Obviously, crystal-chemical reasons cause the larger cell: in the *average* structure, one of the Cu–O_o bond lengths is 1.85(2) Å, which seems to be one of the reasons necessitating violation of the small cell.

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References

ARPE, R. & MÜLLER-BUSCHBAUM, H. (1976): Isolierte quadratisch planare CuO^{6-}_4-Polyeder in $CuBi_2O_4$, ein neuer Bautyp zur Formel $M^{3+}_2M^{2+}O_4$. *Z. anorg. allgem. Chem.* **426**, 1-6.

BOIVIN, J.-C., TRÉHOUX, J. & THOMAS, D. (1976): Étude structurale de $CuBi_2O_4$. *Bull. Soc. fr. Minéral. Cristallogr.* **99**, 193-196.

BRESE, N.E. & O'KEEFFE, M. (1991): Bond valence parameters in solids. *Acta Crystallogr.* **B47**, 192-197.

EFFENBERGER, H. (1993): Symmetrie und Kristallstruktur von Bi_2CuO_4. *Z. Kristallogr., suppl. issue* **7**, 39 (abstr.).

FISCHER, R.X. & TILLMANNS, E. (1988): The equivalent isotropic displacement factor. *Acta Crystallogr.* **C44**, 775-776.

INTERNATIONAL TABLES FOR X-RAY CRYSTALLOGRAPHY, VOL. IV (1974): Revised and supplementary tables (J.A. Ibers & W.C. Hamilton, eds.). The Kynoch Press, Birmingham, England.

KRAUSE, W., BELENDORFF, K. & BERNHARDT, H.-J. (1993): Petitjeanite, $Bi_3O(OH)(PO_4)_2$, a new mineral, and additional data for the corresponding arsenate and vanadate, preisingerite and schumacherite. *Neues Jahrb. Mineral. Monatsh.*, 487-503.

MANDARINO, J.A. (1981): The Gladstone–Dale relationship. IV. The compatibility concept and its application. *Can. Mineral.* **19**, 441-450.

MEDENBACH, O. (1985): A new microrefractometer spindle-stage and its application. *Fortschr. Mineral.* **63**, 111-133.

ŘÍDKOŠIL, T., ŠREIN, V., FÁBRY, J., HYBLER, J. & MAXIMOV, B.A. (1992): Mrázekite, $Bi_2Cu_3(OH)_2O_2(PO_4)_2{\cdot}2H_2O$, a new mineral species and its crystal structure. *Can. Mineral.* **30**, 215-224.

SHELDRICK, G.M. (1976): *SHELX-76. Programs for Crystal Structure Determination*. University of Cambridge, Cambridge, England.

YVON, K., JEITSCHKO, W. & PARTHÉ, E. (1977): LAZY PULVERIX, a computer program for calculating X-ray and neutron diffraction powder patterns. *J. Appl. Crystallogr.* **10**, 73-74.

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