

THE CRYSTAL STRUCTURE OF KUDRIAVITE, (Cd,Pb)Bi₂S₄

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ABSTRACT

The crystal structure of kudriavite, (Cd,Pb)Bi₂S₄, a new mineral species, was solved from single-crystal X-ray-diffraction data and refined to R = 4.9% (4.3% for a model with split mixed-cation sites). Lattice parameters are *a* 13.095(1), *b* 4.0032(3), *c* 14.711(1) Å, β 115.59(1)°, *V* 695.6(1) Å³. The structure is equivalent to that of synthetic CdBi₂S₄, space group *C2/m*, *Z* = 4, and represents a pavonite homologue, *N* = 3. It is built of three-octahedron-thick columns of (311)PbS-like slabs combined by “unit-cell twinning” in a quasi-mirror-glide succession. The slabs, which are intrinsically of the same topology, differ in the coordination state of bordering cations because of the relative positions of the adjacent layers. In the slabs of type I (the “non-accreting” slab common to all pavonite homologues), the central columns of octahedra are flanked by half-octahedral (square-pyramidal) coordinations completed to split-octahedra by the addition of two S atoms from the adjacent slab. The central columns of octahedra in the slabs of type II (of varying thickness, *i.e.*, “accreting” in pavonite homologues) are flanked by octahedral coordinations involving a S atom from the adjacent slab. The observed chemical Cd ↔ Pb and Bi ↔ In substitutions are, according to the crystal-chemical analysis, structurally limited to Bi-containing sites. They are distributed predominantly in the boundary coordinations of the type-I slabs, and the central octahedra of the type-II slabs, with Pb preferentially entering the former, and In the latter. The marginal octahedral sites of the type-II slabs, and the central octahedral sites of the type-I slabs, have been refined as pure Bi and Cd sites, respectively. The crystal-chemical analysis suggests that the observed 1:1 Pb:Cd ratio in natural kudriavite represents the upper limit for the substitution of Pb in the structure. A limit of the In substitution is not possible to determine from the present data, but it most probably is less than In:Bi = 1:3. The ratio observed in type kudriavite is less than 1:10.

Keywords: kudriavite, crystal structure, Cd–Bi sulfosalt.

SOMMAIRE

Nous avons résolu la structure cristalline de la kudriavite, (Cd,Pb)Bi₂S₄, nouvelle espèce minérale, à partir de données prélevées sur monocristal, et nous l'avons affiné jusqu'à un résidu R de 4,9% (4,3% pour un modèle ayant des sites subdivisés des cations). Les paramètres réticulaires sont *a* 13,095(1), *b* 4,0032(3), *c* 14,711(1) Å, β 115,59(1)°, *V* 695,6(1) Å³. La structure est équivalente à celle du composé synthétique CdBi₂S₄, groupe spatial *C2/m*, *Z* = 4, et représenterait un homologue de la pavonite, *N* = 3. Elle est faite de colonnes trois octaèdres de large d'un module ressemblant une tranche (311) de PbS, agencées par maclé à l'échelle de la maille dans une séquence simulant un plan de glissement avec miroir. Ces modules, qui possèdent intrinsèquement la même topologie, diffèrent dans la coordinence des cations en bordure à cause des positions relatives des couches adjacentes. Dans les modules de type I (le module “non-accrétionnel” présent dans tout homologue de la pavonite), les colonnes centrales d'octaèdres ont, en bordure, des coordinences de demi-octaèdres (pyramide carrée) avec complément d'un octaèdre divisé, résultat de l'addition de deux atomes de S provenant d'un module voisin. Les colonnes centrales d'octaèdres des modules de type II (d'épaisseur variable, c'est-à-dire, module dit “d'accrétion” dans les homologues de la pavonite) ont, sur leurs flancs, une coordinence octaédrique impliquant un atome S provenant d'un module adjacent. Les substitutions observées, Cd ↔ Pb et Bi ↔ In, n'impliqueraient, selon notre analyse cristalochimique, que les sites contenant le Bi. Elles affectent surtout les coordinences limitrophes des modules de type I, et les octaèdres centraux des modules de type II, le Pb entrant de préférence dans le premier, et l'In, dans le second. Nous avons affiné les sites octaédriques limitrophes des modules de type II, et ceux des sites octaédriques centraux des modules de type I, comme sites Bi et Cd, respectivement. D'après notre analyse cristalochimique, le rapport Pb:Cd égal à 1:1 observé dans la kudriavite représenterait la limite maximale de l'incorporation du Pb dans la structure. Il nous est impossible de fixer une limite sur l'incorporation de l'In à partir des données disponibles, mais il est probable que le rapport In:Bi est inférieur à 1:3. Le rapport dans la kudriavite-type est inférieur à 1:10.

(Traduit par la Rédaction)

Most-clés: kudriavite, structure cristalline, sulfosel de Cd–Bi.

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INTRODUCTION

Kudriavite, (Cd,Pb)Bi₂S₄, is the first known natural Cd–Pb–Bi sulfosalt, found recently in fumaroles of the Kudriav volcano on Iturup Island in the Kurili Archipelago, Russia. The mineral description was published by Chaplygin *et al.* (2005). Here, we publish full data about the crystal structure of this mineral, which is based on the same model as the crystal structures of synthetic CdBi₂S₄ (Choe *et al.* 1997) and the isostructural HgBi₂S₄ (Mumme & Watts 1980). The main focus of the present structure-analysis is the influence of extensive atomic substitutions observed in the mineral, which largely departs from the ideal stoichiometry of the synthetic analogue. A chemical analysis of the type kudriavite gave the composition (Cd_{0.51}Pb_{0.44}Fe_{0.02}Mn_{0.03}Σ_{1.00}(Bi_{1.83}In_{0.17})Σ_{2.00}(S_{3.81}Se_{0.19})Σ_{4.00} (Chaplygin *et al.* 2005).

EXPERIMENTAL

A crystal of a tabular form {001} bounded by faces of the forms {201} and {211}, with (613) as an additional face, giving it an elongate arrow-like habit along [010], was used for the crystal-structure analysis. It was analyzed with a Bruker–AXS four-circle diffractometer equipped with a 1000K area detector (6.25 × 6.25 cm active area, 512 × 512 effective pixels) and a flat graphite monochromator, using MoK α radiation from a fine-focus sealed X-ray tube. The sample-to-detector distance was 4 cm. A total of 2880 exposures (step = 0.25°, time/step = 60 s) covering a full reciprocal sphere were collected.

TABLE 1. CRYSTAL DATA AND PARAMETERS DESCRIBING THE MEASUREMENT AND CRYSTAL-STRUCTURE REFINEMENT OF KUDRIAVITE

Empirical formula (EMP)	Pb _{0.44} Cd _{0.51} Fe _{0.02} Mn _{0.03} Bi _{1.83} In _{0.17} Se _{0.19} S _{3.81}
Empirical formula (XRD)	Pb _{0.53} Cd _{0.50} Bi _{1.78} In _{0.19} Se _{0.20} S _{3.80}
Formula weight (EMP, XRD)	1376.49, 1414.14
Crystal dimensions	0.01 × 0.09 × 0.24 mm
Crystal system, space group (No.)	Monoclinic, C2/m (12)
<i>a</i> (Å)	13.095(1)
<i>b</i> (Å)	4.0032(3)
<i>c</i> (Å)	14.711(1)
β (°)	115.59(1)
<i>V</i> (Å ³)	695.6(1)
<i>Z</i>	4
Temperature (K)	296
<i>D_x</i> (Mg m ⁻³) (EMP, XRD)	6.571, 6.750
μ (mm ⁻¹)	61.71
<i>F</i> (000)	1182
Range for data collection, θ (°)	4.34–33.11
Limiting indices	–20 ≤ <i>h</i> ≤ 17, –5 ≤ <i>k</i> ≤ 6, –21 ≤ <i>l</i> ≤ 22
Completeness / average redundancy	98.6 % / 3.9
Reflections collected / unique	5797 / 1473 (<i>R_m</i> = 0.0356)
Reflections unique observed [<i>I</i> > 2 σ (<i>I</i>)]	1339
Data / restraints / parameters	1473 / 0 / 57
Goodness-of-fit, <i>S</i>	1.137
<i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 4.87(4.50)%*, <i>wR</i> ₂ = 11.43(10.70)% [‡]
<i>R</i> indices (all data)	<i>R</i> ₁ = 5.36(4.99)%*, <i>wR</i> ₂ = 11.65(10.92)%

* The values in parentheses are for the unconstrained refinement of cation sites 2 and 3. [‡] $w = 1/[\sigma^2(F_o^2) + (0.0207P)^2 + 80.5857P]$, where $P = (F_o^2 + 2F_c^2)/3$.

The SMART software was used for data collection. The orientation of the crystal lattice was determined from 800 strong reflections evenly distributed in reciprocal space and used for a subsequent integration of all collected intensities. The latter was accomplished by the program SAINT, with which we also performed *Lp* corrections and calculation of the final unit-cell parameters. These were determined from 802 reflections with *I* > 10 σ (*I*) in the range 10° < 2 θ < 78°. A determination of the space group and a gaussian face-indexed absorption correction (which decreased *R*_{INT} from initial 0.143 to 0.0719) were done using the program XPREP. The only observed extinctions were those of a C-centered lattice, suggesting the space groups C2/m, C2, or Cm. The centrosymmetric C2/m was chosen in accordance with the statistical test on centricity (*E*² – 1 = 0.908). It was further confirmed by a satisfactory solution of the structure. Observed irregularities in crystal shape, as well as shading by the glass stick on which the crystal was mounted, supposedly caused some systematic errors in intensities. Therefore, a subsequent data-correction was applied using the program SADABS. This further decreased the *R*_{INT} to 0.0356. The data were truncated to 0.65 Å resolution, as suggested by the statistics. All programs used are Bruker–AXS products. The crystal data, as well as details of data collection and refinement are given in Table 1.

SOLUTION AND REFINEMENT OF THE STRUCTURE

The structure was solved by direct methods (SHELXS97, Sheldrick 1997a), which revealed the positions of all the atoms, together with some spurious maxima in the E-Fourier map. The assignment of atoms was made on the basis of interatomic distances and heights of maxima (Table 2). Inspection of the difference-Fourier results during the subsequent stages of refinement by full-matrix least-squares on *F*² (SHELXL97, Sheldrick 1997b) showed a minimum in the cation site 2 flanked by two close maxima, whereas there were additional low maxima around the central maximum at cation site 3. As both sites turned out to have mixed cation-occupancies, a refinement with unconstrained coordinates for various atomic species was attempted at the last stage. Refinements with free occupancy-factors for cations suggested that sites 1 and 2 are completely occupied by heavy cations (Bi and Pb). Site 3 showed electron density intermediate between those of Bi (Pb) and Cd (In). Site 4 appeared to be occupied by the light cations alone (Cd or In). According to the results of chemical analysis, site 1 was defined as a Bi site, site 2 as a mixed Pb,Bi site, site 3 as a mixed Bi,In site, and site 4 as a pure Cd site. The final refinements were made with these attributions and by constraining the sums of occupancies to full sites. Owing to very small differences in the atomic numbers of Bi and Pb, and In and Cd, respectively, the attributions should be considered only tentative and subject

to crystal-chemical considerations (see Description of the Crystal Structure and Crystal-Chemical Analysis). In the final refinement with the constrained coordinations and displacement factors of atoms occupying the same structural site, the anisotropic displacement-factors were used for all the atoms. In the final unconstrained refinement, In was apportioned in site 3 to two symmetrical positions around the central Bi position and refined with an isotropic displacement-factor. In site 2, the unconstrained refinement gave large correlations between the positions of Bi and Pb and their occupancies. The constrained refinement, on the contrary, produced no correlations larger than 0.6. In accordance with the chemical composition (Chaplygin *et al.* 2005) and a refinement with free occupancy-parameters for anions, all anion positions were defined as 95% S and 5% Se. The atomic parameters are given in Tables 2 and 3. In Table 4, the interatomic distances and angles are represented. A table of observed and calculated structure-factors is available from the Depository of Unpublished Data on the MAC web site [document Kudriavite CM45_437].

DESCRIPTION OF THE CRYSTAL STRUCTURE AND CRYSTAL-CHEMICAL ANALYSIS

The crystal structure of kudriavite (Fig. 1) reveals that this mineral is a pavonite homologue, $N = 3$. It follows closely the structural principles of the pavonite series. It is built of three-octahedron-wide columns of (311)PbS-like slabs combined by "unit-cell twinning" in a quasi mirror-glide succession, parallel to (001) of kudriavite. The slabs, which are intrinsically of the same topology, differ in the coordinations of marginal

cations resulting from the relative positions of the adjacent layers. In the slabs of type I (the "non-accreting" slab common to all pavonite homologues), the central columns of octahedra are flanked by half-octahedron (square-pyramidal) coordinations completed to split-octahedra by two additional S atoms from the adjacent slab. The central columns of octahedra in the slabs of type II (which in other pavonite homologues are of varying thickness, *i.e.*, "accreting") are flanked by octahedral coordinations completed by one S atom from the adjacent slab of type I. The cation sites described in the following are as follows: site 1 is the marginal octahedral site in the type-II slabs, site 2 is the marginal square-pyramidal (split-octahedron) site in the type-I slab, site 3 is the central octahedral site of the type-II slab, site 4 is the central octahedral site of the type-I slab. The sulfur atoms (with 5% substitution by Se) occupy four distinct sites with one tetrahedral (S3), and three square-pyramidal (S1, S2, S4) coordinations.

An analysis of atom coordinations was done by calculations of centroid parameters and atomic volumes (Balić-Žunić & Makovicky 1996, Makovicky & Balić-Žunić 1998) and bond-valence calculations (Brown & Altermatt 1985). All calculations were done by the program IVTON (Balić-Žunić & Vicković 1996). The values are represented in Table 5.

The pure Cd-Bi phase (Choe *et al.* 1997) exhibits mixed cation sites, which shows that some of them can host both divalent and trivalent elements and atoms of significantly different sizes as well. The situation in synthetic CdBi_2S_4 in terms of the present labeling of sites is: Site 1: 82% Bi, 18% Cd, Site 2: 100% Bi, Site 3: 60% Cd, 40% Bi, Site 4: 100% Cd.

Cation site 1 shows characteristics of a pure Bi coordination-polyhedron. The size of this octahedron corresponds to that found for a pure or almost pure Bi

TABLE 2. FRACTIONAL COORDINATES, EQUIVALENT DISPLACEMENT AND OCCUPANCY FACTORS OF THE ATOMS IN THE STRUCTURE OF KUDRIAVITE

atom	x	y	z	U_{eq} (Å ²) ^a	occupancy
Bi1	0.34837(5)	½	0.13540(5)	0.0205(2)	1
Pb2	0.21088(6)	0	0.35684(6)	0.0269(2)	1
Bi2*	0.219(1)	0	0.366(1)	0.0183(9)	0.47(8)
Pb2*	0.203(2)	0	0.348(2)	0.023(1)	0.53(8)
Bi3	½	0	0	0.0205(4)	0.603(6)
In3	½	0	0	0.0205(4)	0.397(6)
Bi3*	½	0	0	0.0178(9)	0.63(2)
In3*	0.519(2)	0	0.008(2)	0.017(4)	0.187(8)
Cd4	½	½	½	0.0183(3)	1
S1	0.5036(3)	0	0.1882(3)	0.0191(7)	0.95
Se1	0.5036(3)	0	0.1882(3)	0.0191(7)	0.05
S2	0.1633(3)	0	0.0603(3)	0.0212(7)	0.95
Se2	0.1632(3)	0	0.0603(3)	0.0212(7)	0.05
S3	0.3337(4)	½	0.3213(3)	0.0216(7)	0.95
Se3	0.3337(4)	½	0.3213(3)	0.0216(7)	0.05
S4	0.1215(3)	½	0.4590(3)	0.0174(6)	0.95
Se4	0.1215(3)	½	0.4590(3)	0.0174(6)	0.05

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. Inserted atoms marked with * are from the unconstrained refinement. Parameters of the other atoms show only negligible differences in the two refinements.

TABLE 3. ANISOTROPIC DISPLACEMENT PARAMETERS, U_{ij} (Å²), FOR KUDRIAVITE

atom	U_{11}	U_{22}	U_{33}	U_{13}
Bi1	0.0206(3)	0.0170(3)	0.0223(3)	0.0076(2)
Pb2	0.0265(3)	0.0189(3)	0.0351(4)	0.0131(3)
Bi2*	0.013(2)	0.0194(9)	0.014(2)	-0.003(1)
Pb2*	0.020(3)	0.0186(8)	0.024(3)	0.003(3)
Bi3, In3	0.0183(5)	0.0150(5)	0.0281(6)	0.0100(4)
Bi3*	0.007(2)	0.015(1)	0.028(2)	0.005(1)
Cd4	0.0151(6)	0.0163(7)	0.0206(7)	0.0050(5)
S1	0.015(1)	0.015(2)	0.022(2)	0.003(1)
Se1	0.015(1)	0.015(2)	0.022(2)	0.003(1)
S2	0.018(1)	0.018(2)	0.026(2)	0.007(1)
Se2	0.018(1)	0.018(2)	0.026(2)	0.007(1)
S3	0.026(2)	0.019(2)	0.022(2)	0.012(1)
Se3	0.026(2)	0.019(2)	0.022(2)	0.012(1)
S4	0.019(1)	0.016(2)	0.018(1)	0.008(1)
Se4	0.019(1)	0.016(2)	0.018(1)	0.008(1)

Note: U_{23} and U_{12} are 0 because of symmetry. Inserted atoms marked with * are from the unconstrained refinement. Displacement parameters of the other atoms show only negligible differences in the two refinements.

TABLE 4. THE COORDINATION OF CATIONS IN KUDRIAVITE

Atom Bi1, CN: 6, bonded to:						
S1	S1	S2	S3	S2	S2	
S1	2.716(3)	94.9(1)	89.8(1)	94.5(1)	174.0(1)	90.0(1)
S1	4.003(0)	2.716(3)	89.8(1)	94.5(1)	90.0(1)	174.0(1)
S2	3.905(4)	3.905(4)	2.816(5)	173.7(1)	86.8(1)	86.8(1)
S3	4.069(6)	4.069(6)	5.631(7)	2.823(5)	88.5(1)	88.5(1)
S2	5.673(4)	4.019(5)	3.974(6)	4.041(5)	2.964(3)	84.9(1)
S2	4.019(5)	5.673(4)	3.974(6)	4.041(5)	4.003(0)	2.964(3)
Atom Pb2, CN: 7 bonded to:						
S4	S3	S3	S4	S4	S1	S1
S4	2.650(3)	84.3(1)	84.3(1)	79.6(1)	79.6(1)	142.1(1)
S3	3.628(5)	2.756(4)	93.2(2)	89.8(1)	163.2(1)	77.5(1)
S3	3.628(5)	4.003(0)	2.756(4)	163.2(1)	89.8(1)	129.2(1)
S4	3.644(4)	4.085(8)	5.720(5)	3.026(4)	82.8(1)	67.5(1)
S4	3.644(4)	5.720(5)	4.085(8)	4.003(0)	3.026(4)	113.0(1)
S1	5.748(4)	3.900(6)	5.589(4)	3.597(6)	5.382(4)	3.422(3)
S1	5.748(4)	5.589(4)	3.900(6)	5.382(4)	3.597(6)	4.003(0)
						3.422(3)
Atom Bi2*, CN: 7, bonded to:						
S4	S3	S3	S4	S4	S1	S1
S4	2.527(13)	86.8(4)	86.8(4)	82.0(4)	82.0(4)	143.3(5)
S3	3.628(5)	2.746(13)	93.6(4)	90.4(4)	167.9(5)	125.7(4)
S3	3.628(5)	4.003(0)	2.746(13)	167.9(5)	90.4(4)	75.8(3)
S4	3.646(4)	4.084(7)	5.719(5)	3.004(14)	83.6(3)	110.9(4)
S4	3.646(4)	5.719(5)	4.084(7)	4.003(0)	3.004(14)	66.4(2)
S1	5.748(4)	5.587(3)	3.897(5)	5.381(4)	3.596(6)	3.520(9)
S1	5.748(4)	3.897(5)	5.587(3)	3.596(6)	5.381(4)	4.003(0)
						3.520(9)
Atom Pb2*, CN: 7, bonded to:						
S3	S3	S4	S4	S1	S1	
S3	2.769(17)	92.6(6)	81.6(5)	88.9(5)	158.3(7)	133.0(6)
S3	4.003(0)	2.769(17)	81.6(5)	158.3(7)	88.9(5)	79.0(5)
S4	3.628(5)	3.628(5)	2.783(19)	77.2(5)	77.2(5)	140.6(7)
S4	4.084(7)	5.719(5)	3.646(4)	3.054(21)	81.9(5)	115.2(6)
S4	5.719(5)	4.084(7)	3.646(4)	4.003(0)	3.054(21)	68.6(4)
S1	5.587(3)	3.897(5)	5.748(4)	5.381(4)	3.596(6)	3.319(13)
S1	3.897(5)	5.587(3)	5.748(4)	3.596(6)	5.381(4)	4.003(0)
						3.319(13)
Atom Bi3, CN: 6, bonded to:						
S1	S1	S2	S2	S2	S2	
S1	2.749(5)	180.0(1)	90.1(1)	89.9(1)	89.9(1)	90.1(1)
S1	5.497(7)	2.749(5)	89.9(1)	90.1(1)	90.1(1)	89.9(1)
S2	3.914(6)	3.905(4)	2.780(2)	180.0(1)	87.9(1)	92.2(1)
S2	3.905(4)	3.914(6)	5.560(4)	2.780(2)	92.2(1)	87.9(1)
S2	3.905(4)	3.914(6)	3.858(5)	4.003(0)	2.780(2)	180.0(1)
S2	3.914(6)	3.905(4)	4.003(0)	3.858(5)	5.560(4)	2.780(2)
Atom In3*, CN: 6, bonded to:						
S2	S2	S1	S1	S2	S2	
S2	2.632(13)	99.0(7)	93.6(6)	92.4(6)	173.4(8)	87.5(6)
S2	4.003(0)	2.632(13)	93.6(6)	92.4(6)	87.5(6)	173.4(8)
S1	3.914(6)	3.914(6)	2.737(28)	170.8(8)	86.9(5)	86.9(5)
S1	3.904(4)	3.904(4)	5.496(7)	2.777(26)	86.4(5)	86.4(5)
S2	5.560(4)	3.858(5)	3.904(4)	3.914(6)	2.937(15)	85.9(5)
S2	3.858(5)	5.560(4)	3.904(4)	3.914(6)	4.003(0)	2.937(15)
Atom Cd4, CN: 6, bonded to:						
S3	S3	S4	S4	S4	S4	
S3	2.590(3)	180.0(2)	95.1(1)	84.9(1)	84.9(1)	95.1(1)
S3	5.180(5)	2.590(3)	84.9(1)	95.1(1)	95.1(1)	84.9(1)
S4	3.965(4)	3.628(5)	2.780(3)	180.0(1)	87.9(1)	92.1(1)
S4	3.628(5)	3.965(4)	5.561(5)	2.780(3)	92.1(1)	87.9(1)
S4	3.628(5)	3.965(4)	3.860(7)	4.003(0)	2.781(3)	180.0(1)
S4	3.965(4)	3.628(5)	4.003(0)	3.860(7)	5.561(5)	2.781(3)

The numbers shown in bold in the diagonals are the bond distances (Å), the numbers above the diagonal are the bond angles (°), and the numbers below the diagonal are the ligand-ligand distances (Å). As in previous tables, the atoms marked with * are from the unconstrained refinement.

polyhedron in the structure of neyite (Makovicky *et al.* 2001), and the calculated valence is 2.98 valence units (*vu*) in accordance with this. In the synthetic CdBi₂S₄ (Choe *et al.* 1997), this site was refined with a small extent of Cd substitution (see above). The results of the present refinement suggest that no elements lighter than Bi or Pb are present at this site. The size of the coordination polyhedron is only slightly larger in kudriavite than in the synthetic analogue. If the volume of the pure Cd in octahedral coordination from site 4 of the synthetic CdBi₂S₄ (26.31 Å³) is taken as representative, and the volume of the present site 1 is taken as a representative of the pure Bi octahedron, the linear interpolation for the volume differences between kudriavite and the synthetic analogue gives 16% of Cd substitution in site 1 in the latter, in good accordance with the results of the refinement. The anions that surround this site form a very regular octahedron (Table 5).

Results of the difference-Fourier synthesis suggest that site 2 is a split one; the two positions were attributed in the unconstrained refinement to Pb and Bi, respectively, on the basis of their eccentricity parameters (a larger eccentricity is expected for Bi). The volume of the polyhedron (37.87 Å³) has a size characteristic of Bi coordination with coordination number (CN) 7 (typically between 36 and 39 Å³ in Bi sulfosalts), but also close to those characteristic for Pb with the same CN (38 to 42 Å³; Makovicky *et al.* 2001). The valence sum obtained from the result of the constrained refinement is 2.70 *vu*, suggesting a mixed Bi₃Pb site (the bond-valence parameters for Bi³⁺ and Pb²⁺ are equal, and this gives a possibility for a direct calculation). A weighted valence for this position obtained from the unconstrained refinement with different positions

TABLE 5. COORDINATION NUMBERS AND SELECTED POLYHEDRON-DISTORTION PARAMETERS IN KUDRIAVITE

Site	CN	Ave. bond-distance (Å)	Radius, circumscribed sphere (Å)	Sphere volume V _s (Å ³)	Eccentricity Δ	Volume distortion v	Polyhedron volume V _p (Å ³)
Bi1	6	2.83	2.830	94.96	0.062	0.001	30.20(7)
		2.82	2.814	93.29	0.068	0.003	29.60
Pb2	7	3.01	3.019	115.22	0.164	0.131	37.87(9)
		2.97	2.982	111.11	0.171	0.133	36.36
Bi2*	7	3.01	"	"	0.201	"	"
Pb2*	7	3.01	"	"	0.127	"	"
Bi3	6	2.77	2.769	88.97	0.000	0.0007	28.30(6)
		2.76	2.755	87.61	0.000	0.001	27.86
In3*	6	2.77	"	"	0.080	"	"
Cd4	6	2.72	2.717	84.01	0.000	0.011	26.46(7)
		2.72	2.715	83.80	0.000	0.013	26.31

Atoms marked with * are from the unconstrained refinement. Values in the second row of each coordination polyhedron pertain to synthetic CdBi₂S₄ and are shown for comparison. CN: coordination number. The parameters of atomic coordinations are defined in Balić-Žunić & Makovicky (1996) and Makovicky & Balić-Žunić (1998). All calculations were done with IVTON (Balić-Žunić & Vicković 1996).

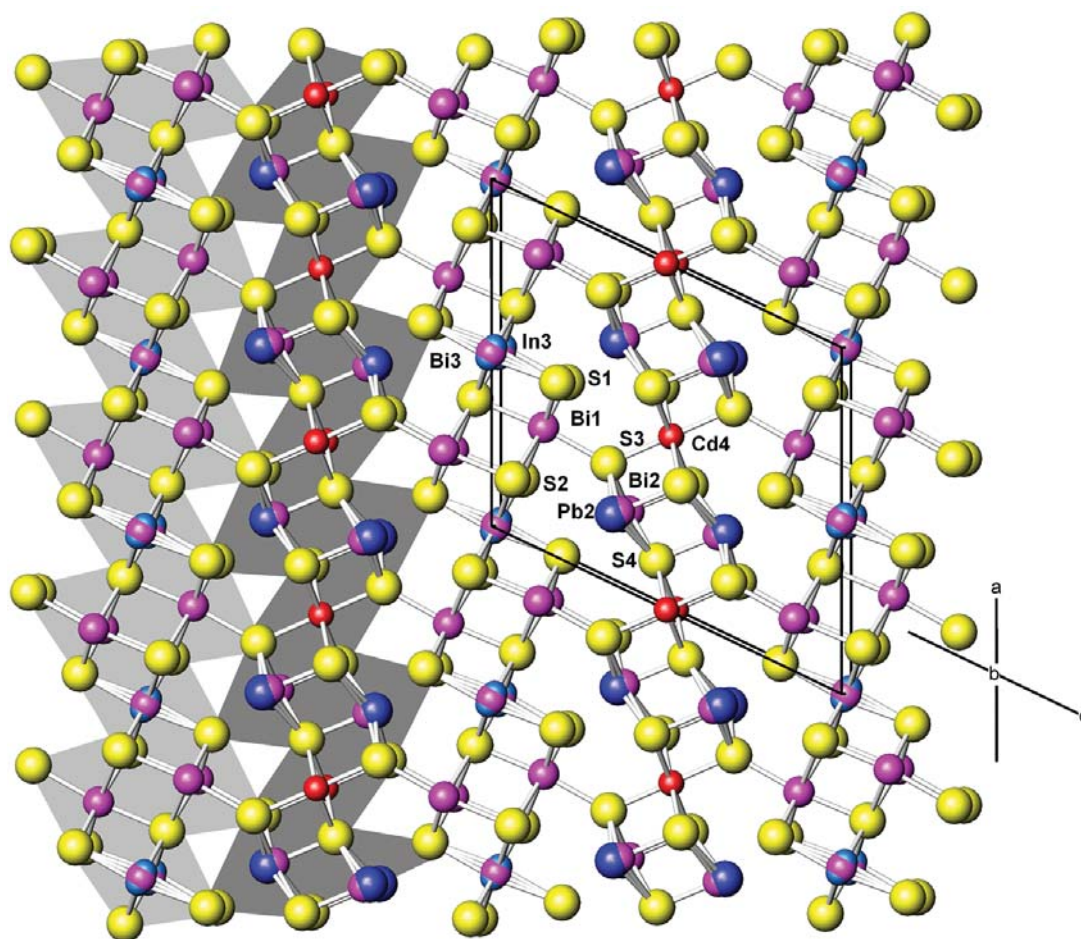


FIG. 1. Projection of the crystal structure of kudriavite. The characteristic structural slabs are marked by different background-shading on the left of the figure. Type-I slab has a darker background, and type-II slab has a lighter background. A trace of the unit cell and the labels of atoms in one asymmetric unit are also indicated.

of Bi2 and Pb2 is 2.74 *vu* (the Bi and Pb positions gave 3.06 and 2.45 *vu*, respectively). Considering that the bond-valence parameters for Bi and Pb are equal, we can expect that a pure Bi site would give a value close to 3, regardless if it is split or not. A very limited accuracy of the bond-valence calculations, based on parameters that represent averages for very different structures and bonding conditions, does not allow us to derive quantitative conclusions, but the results clearly suggest that this site is a mixed Pb,Bi one. In the synthetic CdBi_2S_4 , this site was refined as a pure Bi site, and the sum of valences for it gives 2.97 *vu*. The volume of the coordination polyhedron in the synthetic phase (36.46 \AA^3) is smaller than in kudriavite, which also suggests that Bi is replaced by a larger cation in

the mineral. The value of the ratio of the circumscribed sphere and the volume of the polyhedron (V_s/V_p) for the coordination polyhedron around site 2 (3.042) is the one characteristic of the coordination described as a split octahedron (Makovicky & Balić-Žunić 1998). The unconstrained refinement gave positions of Bi and Pb that correspond relatively well with their expected crystal-chemical characteristics, if the more eccentric position is ascribed to Bi (Table 5). However, many of the correlations between their occupancies, positional and displacement parameters were found to be over 0.8 and even 0.9 (absolute value), so that the unconstrained refinement cannot be regarded as completely satisfactory, and the detailed data on coordination must not be taken as problem-free.

The sizes of coordination polyhedra (both octahedra) for sites 3 and 4 are significantly smaller than the characteristic size of about 30 \AA^3 for a $[\text{BiS}_6]$ octahedron. This corresponds well to the occupancies obtained from the refinement, which suggest for site 4 a very low content of Bi (or Pb), or none at all, and for site 3, a significant amount of an element lighter than Bi. The volume of the coordination octahedron for site 4 is the smallest in the structure, in accordance with the smallest amount of Bi at this position (if any). It is also practically identical (0.6% difference) to the volume of the same site in the synthetic analogue. The bond-valence calculations also give a satisfactory result if a pure Cd position is assumed (1.99 *vu*). The conclusion is further supported by the Cd1 site in the structure of $\text{Cd}_3\text{Bi}_8\text{S}_{15}$ (Choe *et al.* 1997), which was refined as a pure Cd site and has an almost identical volume of the octahedron (26.48 \AA^3). If In were substituting in substantial amounts at this site, a smaller size for the coordination polyhedron would be expected (see below). The distribution of anions around site 4 corresponds to an almost regular octahedron with a very small volume-distortion. The distortion is in a form of a shortened octahedron, with one of the axes being 6% shortened in comparison to the other two.

Site 3 in the synthetic analogue was found to be a mixed site with 60% Cd and 40% Bi. This site presents the most complicated problem in the present analysis, and the attribution of elements to it can only be verified taking into account the results of the chemical analysis, and the situation at other sites. The refinement suggests dominance (60%) of a heavier cation (Bi or Pb) at this site, contrary to the synthetic analogue. The volume of the polyhedron for this site is larger than a corresponding one in the synthetic analogue, but not as much as expected if the site is occupied by Bi and Cd alone. If a calculation is made similar to the one made for site 1 in the synthetic CdBi_2S_4 (assuming the volumes for the pure Bi and Cd octahedra), a satisfactory result with 60% Cd is obtained for the synthetic phase, whereas for kudriavite, the calculation suggests 50% of each element. However, Cd is not the only lighter cation present in significant amounts. The chemical analysis shows a relatively large amount of In in the structure of the mineral. The amount corresponds approximately to the amount of the lighter cation (Cd or In) found at site 3. If we assume that the lighter cation is In, the volume of the polyhedron should be related to the characteristic one for this element. An inspection of the crystal structures of $\text{Bi}_2\text{In}_4\text{S}_9$ (Chapuis *et al.* 1972) and $\text{Bi}_3\text{In}_5\text{S}_{12}$ (Kraemer 1980) reveals that the volumes of the octahedra enclosing In vary between 23.2 and 25.3 \AA^3 . Taking 24.3 \AA^3 as the characteristic value, and making a linear interpolation to the volume of site 1 (considering this to be the pure Bi site), one obtains from the volume of site 3 in kudriavite 33% In, in a good accordance with the refinement of occupancies and results of the chemical analysis. The anions

that surround this site form a very regular octahedron. There remains the question of the incorporation of In in this rather large coordination for this element. In the unconstrained refinement, In moved off the two-fold axis, and distributed symmetrically around the central position in two sites with a 4 + 2 coordination intermediate between the octahedral and tetrahedral cases. However, as the content of In at site 3 of kudriavite is not very high and as the unconstrained refinement gave relatively large correlations between the parameters of the split sites (for In the correlation between the z coordinate and the U_{13} of Bi3 was -0.877), these results should be accepted with caution.

CONCLUSIONS

1. Cadmium is assumed to be concentrated practically exclusively at site 4, which resulted in refinement as a pure light cation (Cd or In) site. In synthetic CdBi_2S_4 , it was also found substituting in lesser and larger amounts, respectively, at sites 1 and 3. However, the amount of Cd found by chemical analysis in the type kudriavite suffices only to fill up site 4. In the mineral, the only site other than 4 that was found to host a cation lighter than Bi or Pb is site 3. The heavier element at this site is assumed to be Bi, and the lighter element, In, on the basis of the volume of the coordination polyhedron, which also gives the expected content of In from the chemical analysis. We cannot exclude the possibility that Cd and In mix on the two sites, but the presented evidence strongly suggests their ordered distribution at sites 4 and 3, respectively.

2. Lead is considered to substitute partially for Bi at site 2. This is supported both by the results of the refinement and the Fourier syntheses, which suggest a splitting of this site into two positions differing in eccentricity (and consequently in the steric activity of the lone electron pair) and by the bond-valence calculations, which suggest a mixture of a divalent and a trivalent element at this site. The amount of Pb calculated for site 2 corresponds well to the total amount established from the chemical analysis. We do not assume that Pb substitutes at other Bi sites in the structure, at least not in a substantial amount. The crystal-chemical data support this conclusion, because site 1 does not show any important increase in the volume of the coordination polyhedron over the value expected for a pure Bi site, and the only other site that contains a heavy cation, site 3, shows even a smaller volume of polyhedron, which corresponds well to a mixed Bi,In site.

3. The main differences in the distribution of Bi between kudriavite and the synthetic CdBi_2S_4 lie in the occupancies of sites 2 and 3. The increased occupancy of site 3 by Bi is evidently a consequence of the presence of Pb, which shows a preference for site 2, and in this way redistributes Bi over these two sites in comparison with the synthetic Pb-free analogue.

4. Assuming that no incorporation of Pb (or In) is possible at site 4, the maximum expected amount of Pb in the structure of kudriavite would be one-half of the sum of the divalent cations; the type sample almost achieves that level. On the other hand, we can assume that larger amounts of In than those present in the type material can enter the structure, substituting at site 3. A full occupancy of In at site 3 would give a 1:3 relation between the atomic proportions of In and Bi. We contend that this value also determines the maximum possible substitution of Bi by In in kudriavite. The relation inferred from the chemical composition observed is well below this value (lower than 1:10).

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REFERENCES

- BALIĆ-ŽUNIĆ, T. & MAKOVICKY, E. (1996): Determination of the centroid or "the best centre" of a coordination polyhedron. *Acta Crystallogr.* **B52**, 78-81.
- BALIĆ-ŽUNIĆ, T. & VICKOVIĆ, I. (1996): IVTON – a program for the calculation of geometrical aspects of crystal structures and some crystal chemical applications. *J. Appl. Crystallogr.* **29**, 305-306.
- BROWN, I.D. & ALTERMATT, D. (1985): Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. *Acta Crystallogr.* **B41**, 244-247.
- CHAPLYGIN, I.V., MOZGOVA, N.M., MAGAZINA, L.O., KUZNETSOVA, O.YU., SAFONOV, Y.G., BRYZGALOV, I.A., MAKOVICKY, E. & BALIĆ-ŽUNIĆ, T. (2005): Kudriavite, (Cd,Pb)Bi₂S₄, a new mineral species from Kudriavyy volcano, Iturup island, Kurile Arc, Russia. *Can. Mineral.* **43**, 695-701.
- CHAPUIS, G., GNEHM, C. & KRAEMER, V. (1972): Crystal structure and crystal chemistry of bismuth indium sulphide, Bi₂In₄S₉. *Acta Crystallogr.* **B28**, 3128-3130.
- CHOE, W., LEE, S., O'CONNEL, P. & COVEY, A. (1997): Synthesis and structure of new Cd–Bi–S homologous series: a study in intergrowth and the control of twinning patterns. *Chem. Mater.* **9**, 2025-2030.
- KRAEMER, V. (1980): Structure of bismuth indium sulphide Bi₃In₅S₁₂. *Acta Crystallogr.* **B36**, 1922-1923.
- MAKOVICKY, E. & BALIĆ-ŽUNIĆ, T. (1998): New measure of distortion for coordination polyhedra. *Acta Crystallogr.* **B54**, 766-773.
- MAKOVICKY, E., BALIĆ-ŽUNIĆ, T. & TOPA, D. (2001): The crystal structure of neyite, Ag₂Cu₆Pb₂₅Bi₁₂₆S₆₈. *Can. Mineral.* **39**, 1365-1376.
- MUMME, W.G. & WATTS, J.A. (1980): HgBi₂S₄: crystal structure and relationship with the pavonite homologous series. *Acta Crystallogr.* **B36**, 1300-1304.
- SHELDRICK, G.M. (1997a): *SHELXS97. Program for the Solution of Crystal Structures*. University of Göttingen, Göttingen, Germany.
- SHELDRICK, G.M. (1997b): *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Göttingen, Germany.

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