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WHAT IS THE REASON FOR THE DOUBLED UNIT-CELL VOLUMES OF COPPER–LEAD-RICH PAVONITE HOMOLOGUES? THE CRYSTAL STRUCTURES OF CUPROMAKOVICKYITE AND MAKOVICKYITE

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Abstract

The crystal structure of cupromakovickyite, ideally $Cu_8Pb_4Ag_2Bi_{18}S_{36}$, from the skarn deposit at Băiţa Bihor, in Romania, has been solved by direct methods and refined to an R_1 index of 5.36% for 2680 unique reflections measured with Mo$K\alpha$ radiation on a four-circle diffractometer equipped with a CCD detector. Cupromakovickyite has a monoclinic cell with a 13.405(8), b 4.016(3), c 29.949(19) Å, β 99.989(16), V 1587.8(17) Å^3, space group $C2/m$ and Z = 1. There are eight metal sites and twelve sulfur sites in each of the four asymmetric units. The thicker, galena-like layers are composed of parallel chains Bi4–Bi1–Bi1–Bi4 four octahedra long. In the thinner layers, the octahedra of Ag are replaced by two tetrahedrally coordinated Cu sites, whereas one of the paired square pyramids of Bi is replaced by Pb. The asymmetry of the thin layer is responsible for the doubling of the c parameter for cupromakovickyite with respect to makovickyite. To be able to compare them, the crystal structure of Cu-bearing makovickyite, $Cu_{2.25}Ag_{1.56}$ $(Pb_{0.27}Cd_{0.13})_{\Sigma 0.4}Bi_{10.46}S_{18}$, from a scheelite deposit at Felbertal, in Austria, has been refined to an R_1 index of 4.36% for 1320 unique reflections measured with the same equipment. Makovickyite has a monoclinic cell with a 13.239(3), b 4.0547(7), c 14.667(3) Å, β 99.397(4), V 776.7(3) Å^3, space group $C2/m$ and Z = 1. There are four metal sites and six sulfur sites in each of the four asymmetric units. The thicker, galena-like layers are composed of parallel chains Bi2–Bi1–Bi1–Bi2 four octahedra long. In the thinner layers, the octahedra of Ag are partially replaced by two tetrahedrally coordinated Cu sites.

Keywords: cupromakovickyite, makovickyite, cupropavonite, sulfosalt, crystal structure, single-crystal X-ray diffraction, pavonite homologous series, Băiţa Bihor, Romania, Felbertal, Austria.

Sommaire

Nous avons résolu la structure cristalline de la cupromakovickyite, de formule idéale $Cu_8Pb_4Ag_2Bi_{18}S_{36}$, provenant d'un gisement de type skarn à Băiţa Bihor, en Roumanie, par méthodes directes, et nous l'avons affiné jusqu'à un résidu R_1 de 5.36% en utilisant 2680 réflexions uniques mesurées avec rayonnement Mo$K\alpha$ et un diffractomètre à quatre cercles muni d'un détecteur CCD. La cupromakovickyite possède une maille monoclinique ayant a 13.405(8), b 4.016(3), c 29.949(19) Å, β 99.989(16), V 1587.8(17) Å^3, groupe spatial $C2/m$ et Z = 1. Il y a huit sites pour métaux et douze sites de soufre dans chacun des quatre unités assymétriques. Les couches plus épaisses, semblables à la galène, sont faites de chaînes parallèles d'octaèdres Bi4–Bi1–Bi1–Bi4 d'une longueur de quatre octaèdres. Dans les couches plus minces, les octaèdres contenant Ag sont remplacés par deux sites Cu à coordinence tétraédrique, tandis que dans une des paires de pyramides carrées, le Bi est remplacé par Pb. L'assymétrie de la couche mince cause un dédoublement du paramètre c de la cupromakovickyite par rapport à la makovickyite. Afin de mieux comparer ces deux structures, nous avons établi la structure cristalline de la makovickyite cuprifère, $Cu_{2.25}Ag_{1.56}$ $(Pb_{0.27}Cd_{0.13})_{\Sigma 0.4}$ $Bi_{10.46}S_{18}$, provenant d'un gisement de scheelite à Felbertal, en Autriche, jusqu'à un résidu R_1 de 4.36% en nous servant de 1320 réflexions uniques mesurées avec le même équipement. La makovickyite possède une maille monoclinique avec a 13.239(3), b 4.0547(7), c 14.667(3) Å, β 99.397(4), V 776.7(3) Å^3, groupe spatial $C2/m$ et Z = 1. Il y a quatre sites pour métaux et six sites de soufre dans chacune des quatre unités assymétriques. Les couches plus épaisses, semblables à la galène, sont faites de chaînes parallèles d'octaèdres Bi2–Bi1–Bi1–Bi2 d'une longueur de quatre octaèdres. Dans les couches plus minces, les octaèdres contenant Ag sont partiellement remplacées par deux sites Cu à coordinence tétraédrique.

(Traduit par la Rédaction)

Mots-clés: cupromakovickyite, makovickyite, cupropavonite, sulfosel, structure cristalline, diffraction X sur monocristal, série d'homologues de la pavonite, Băiţa Bihor, Roumanie, Felbertal, Autriche.

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INTRODUCTION

In 1979, Karup-Møller and Makovicky resolved, by means of single-crystal X-ray diffraction, the problem of intimate lamellar exsolution-induced intergrowths observed in pavonite specimens from the Alaska mine, Colorado. They discovered that the Cu(and Pb)-rich lamellae represent a new mineral species with a *c* parameter doubled in respect to those of pavonite, which in turn formed the lamellae poorer in copper and lead. The new species, with excess of copper and lead reported, received the name *cupropavonite*; it is a modified N = 5 member of the series. It has a monoclinic unit-cell with *a* 13.45, *b* 4.02, *c* 33.06 Å, β 93.50°, space group *C*2/*m* or *Cm*, and is ideally $Cu_{7.2}Ag_4Pb_{4.8}Bi_{20}S_{40}$, Z = 1. The doubling of the *c* axis and intensity differences between the corresponding X-ray reflections of pavonite and cupropavonite showed that some structural positions in the two structures must differ substantially.

Similar exsolution-induced aggregates of makovickyite, the N = 4 homologue of the series, were structurally analyzed by Mumme (1990), whereas those of mummeite, the N = 8 homologue, were studied by X-ray diffraction by Karup-Møller & Makovicky (1992) and structurally by Mumme (1990). In both studies, the investigators detected two distinct chemical compositions and cells, but failed to recognize a doubled *c* parameter. Weak streaking parallel to *c** has since been detected in the N = 8 case. The Cu–Pb-rich phases received the provisional adjective modifier "cuproplumbian" in these publications.

The structure analysis by Mumme (1990) was performed on lamellar intergrowths of the Cu-bearing homologue N = 4 using a Weissenberg film camera for X-ray intensity collection; therefore the diffraction data were limited to the higher angles. The argentian (Cu-free material from Felbertal) N = 4 homologue was refined from a full dataset recorded on film (Mumme 1990).

In the new material from Felbertal, Austria, and Băiţa Bihor, Romania, the electron-microprobe data indicated two homogeneous, almost end-members, N = 4, respectively (Cu, Pb)-poor and (Cu, Pb)-rich, in crystals of a quality sufficient for structure determination. The present material allowed us to recognize a doubled *c* parameter of the (Cu, Pb)-rich variety. In analogy with the pair pavonite–cupropavonite (both with N = 5), the name of the (Cu, Pb)-poorer phase, makovickyite (Žák *et al.* 1994), was used to give the name *cupromakovickyite* to the new, (Cu, Pb)-rich phase with a doubled *c* parameter. A mineralogical description of *cupromakovickyite* has been published in a companion paper (Topa & Paar 2008); in this contribution, we examine analogies and differences between the two N = 4 structures.

EXPERIMENTAL

Chemical analysis

Quantitative chemical data for makovickyite and cupromakovickyite were obtained with an electron microprobe (JEOL Superprobe JXA–8600, controlled by LINK–*eXL* system, operated at 25 kV and 35 nA, beam diameter 5 μm), installed at the Department of Geography and Geology, University of Salzburg. The following standards (all synthetic except galena) and emission lines were selected: Bi_2S_3 (Bi*L*α, S*K*α), galena (Pb*L*α), chalcopyrite (Cu*K*α, Fe*K*α), Ag metal (Ag*L*α), CdTe (Cd*L*β, Te*L*α), and Bi_2Se_3 (Se*L*α). The raw data were corrected with the on-line ZAF–4 procedure. Five to nine point-analyses were made on a homogeneous grain of an individual phase, and results were averaged. Chemical data for the material structurally investigated are compiled in Table 1.

TABLE 1. CHEMICAL DATA FOR THE INVESTIGATED CRYSTALS: 1) MAKOVICKYITE FROM FELBERTAL (FE) AND 2) CUPROMAKOVICKYITE FROM BĂIŢA BIHOR (BB)

No.	sample	NA	Cu	Ag	Pb	Cd	Bi	Sb	Te	Se	S	Total
1	FE-89/9-sm5-gr1m	9	4.55(3)	5.37(9)	1.79(10)	0.45(7)	69.41(10)	0.11(2)	0.20(3)	0.00	18.29(3)	100.16(26)
2	BB-zon.3	5	7.66(1)	4.01(3)	9.45(3)	-	60.02(9)	-	0.76(2)	0.30(1)	17.55(2)	99.75(7)

No.	sample	N_{p2}	N_{p3}	Σmet	*ch*	*ev*	structural formula
1	FE-89/9-sm5-gr1m	3.59	3.09	14.69	0.13	0.12	$Cu_{2.25}Ag_{1.56}(Pb_{0.27}Cd_{0.13})_{\Sigma 0.40}Bi_{10.48}(S_{17.95}Te_{0.05})_{\Sigma 18}$ $^{i}Cu_{0.69}(^{s}Cu_{1.56}Ag_{1.56})_{\Sigma 3.12}\text{“Pb”}_{0.40}\text{“Bi”}_{10.48}S_{18}$
2	BB-zon.3	4.85	3.88	31.69	-0.37	-0.35	$Cu_{7.79}Ag_{2.40}Pb_{2.95}Bi_{18.55}(S_{35.37}Se_{0.25}Te_{0.39})_{\Sigma 36}$

The compositions are expressed in wt.%. NA: number of analyses. Standard deviation for the last digit is shown in parentheses. N_{p2} and N_{p3} represent chemical calculated pavonite homologue number as defined by Karup-Møller & Makovicky (1979). *ch* and *ev* express the absolute and relative error in the charge balance based on the sum of cation and anion charges.

Single-crystal X-ray diffraction

Fragments of cupromakovickyite with an irregular shape and a diameter of 0.03–0.07 mm from Băiţa Bihor and similar fragments of makovickyite from Felbertal, extracted from the grains presented in Topa & Paar (2008, Figs. 1a, f), were measured on a Bruker AXS four-circle diffractometer equipped with a CCD area detector using graphite-monochromated Mo*K*α radiation. Crystal data for the minerals studied are listed in Table 2. The SMART (Bruker AXS, 1998) system of programs was used for unit-cell determination and data collection, SAINT+ (Bruker AXS, 1998) for the calculation of integrated intensities, and XPREP (Bruker AXS, 1998) for an empirical absorption-correction based on pseudo ϕ-scans. The centrosymmetric space-group *C*2/*m*, proposed by the XPREP program, was chosen for both phases. It is consistent with the monoclinic symmetry of the lattices and intensity statistics (mean $|E^*E-1| = 0.994$ [expected values: 0.968 for the centrosymmetric case and 0.736 for the non-centrosymmetric case]). The structure of cupromakovickyite was solved by direct methods (program SHELXS, Sheldrick 1997a) which revealed most of the atom-positions. In subsequent cycles of the refinement (program SHELXL, Sheldrick 1997b), remaining atom-positions were deduced from difference-Fourier syntheses by selecting from among the strongest maxima at appropriate distances.

The structure of makovickyite was refined (program SHELXL, Sheldrick 1997b) using atom positions published by Mumme (1990) as the starting input. Refinement data are given in Table 2; fractional coordinates, isotropic and anisotropic displacement parameters of the atoms are listed in Tables 3 and 4, and selected *Me*–S bond distances are presented in Table 5. Selected geometrical parameters, calculated with the program IVTON (Balić-Žunić & Vicković 1996), related to individual coordination-polyhedra, are given in Table 6. The structures refined are presented in Figures 1 to 4, including the site labeling. The tables of structure factors may be obtained from the Depository of Unpublished Data, MAC web site [document Cupromakovickyite CM46_515].

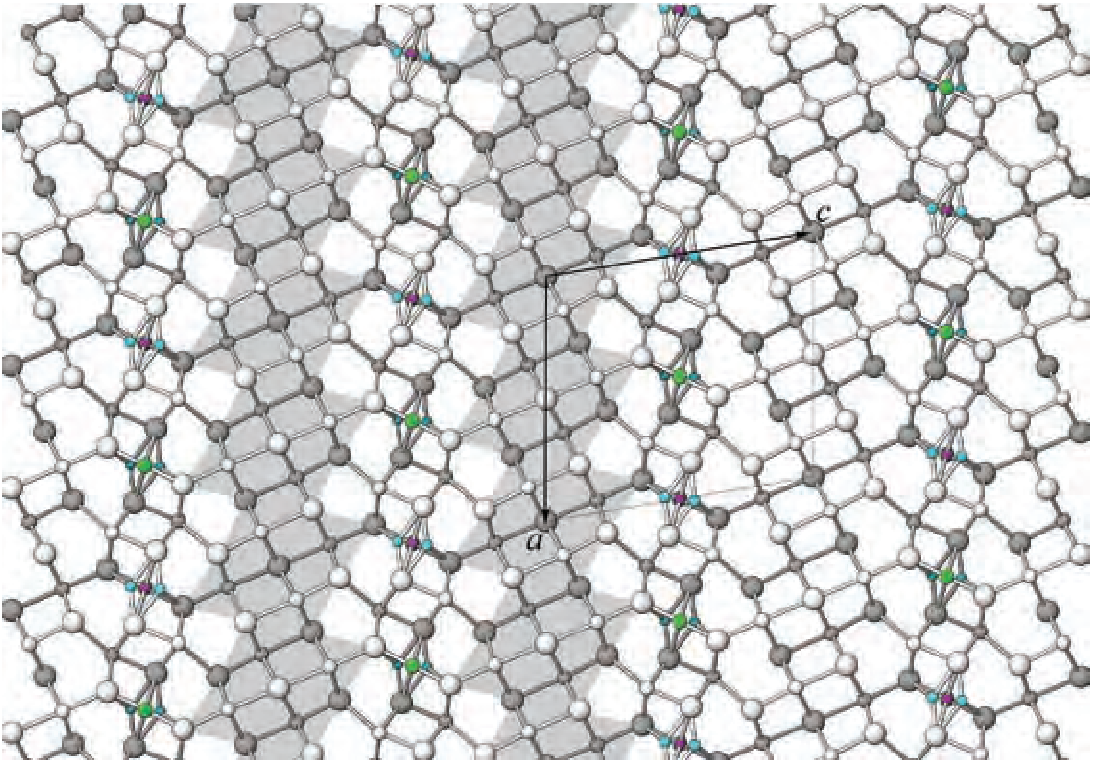

FIG. 1. The crystal structure of makovickyite in projection on (010), with atoms at $y = 0$ (white) and at 0.5 (grey shading), respectively. In the order of decreasing size, circles represent S, Ag (green), Bi, and Cu (cyan and magenta). The thin layer (unshaded) between two thick layers (grey shading) is illustrated.

TABLE 2. SINGLE-CRYSTAL X-RAY DIFFRACTION: EXPERIMENTAL AND REFINEMENT DETAILS

	makovickyite Felbertal	cupromakovickyite Băiţa Bihor
Crystal data		
Chemical formula	$Cu_{2.25}Ag_{1.56}(Pb_{0.27}Cd_{0.13})_{\Sigma 0.4}Bi_{10.48}S_{18}$	$Cu_{7.79}Ag_{2.40}Pb_{2.95}Bi_{18.55}S_{36}$
Formula weight	3090.86	6222.70
Cell setting	Monoclinic	Monoclinic
Space group	*C*2/*m*	*C*2/*m*
a (Å)	13.239(3)	13.405(8)
b (Å)	4.0547(7)	4.016(3)
c (Å)	14.667(3)	29.949(19)
β (°)	99.397(4)	99.989(16)
V (Å^3)	776.7(3)	1587.8(17)
Z	1	1
D_x (mg m^{-3})	6.608	6.689
No. of reflections for cell param.	732	3119
μ (mm^{-1})	63.173	63.422
Crystal morphology	irregular	irregular
Crystal size (mm)	0.03 × 0.03 × 0.04	0.03 × 0.035 × 0.07
Crystal color	black	black
Data collection		
T_{min}	0.0119	0.0506
T_{max}	0.0567	0.2881
Measured reflections	3954	8133
Independent reflections	1320	2680
Observed reflections	1122	1997
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	7.41%	13.09%
θ_{max} (°)	30.52	30.53
Range of h,k,l	$-17 < h < 18$ $-5 < k < 5$ $-20 < l < 20$	$-17 < h < 18$ $-5 < k < 5$ $-42 < l < 42$
Refinement		
Refinement on F_o^2 $R[F_o > 4\sigma(F_o)]$	4.36%	5.36%
wR (F_o^2)	10.79%	14.31%
S(GooF)	1.056	1.048
Reflections used in refinement	1320	2680
No. of parameters refined	66	110
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0676P)^2 + 2.2094P]$	$w = 1/[\sigma^2(F_o^2) + (0.0731P)^2 + 13.0888P]$
	where $P = (F_o^2 + 2F_c^2)/3$	
$(\Delta/\sigma)_{max}$	0.004	0.007
$\Delta\rho_{max}$ (e/Å^3)	2.614	4.83
$\Delta\rho_{min}$ (e/Å^3)	-4.758	-3.27
Extinction method	none	0.00031(4)
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	
Computer programs		
Structure solution	*SHELXS97* (Sheldrick 1997a)	
Structure refinement	*SHELXL97* (Sheldrick 1997b)	

COMPARISON OF THE STRUCTURES OF MAKOVICKYITE AND CUPROMAKOVICKYITE

The Cu-bearing makovickyite exhibits all the typical features of a pavonite homologue. It is composed of alternating thicker layers of octahedra (the "incremental layers" of the pavonite homologous series) and a thinner, one-octahedron-thick, configurationally constant layer (Makovicky 1997). The incremental layer is four octahedra thick (shaded layer in Fig. 1). Its marginal Bi2 octahedron is a pure Bi position, whereas the internal Bi1 site was refined as 0.8 Bi + 0.2 Ag. The isolated columns of octahedra in the thin layer (Fig. 1) have a set of partially occupied cation sites: about 0.28 Ag in the octahedron centers (Table 3, Figs. 2, 5), 2 × 0.384 Cu in the flattened tetrahedral coordination, situated in the upper and lower parts of these octahedra (site Cu1), and 2 × 0.147 Cu in the tetrahedra situated between the tips of adjacent octahedra (site Cu2) (Table 3, Figs. 2, 5). This makes 1.342 univalent cations for each octahedron of the thin layer. The structural formula is $Cu_{2.12}Ag_{1.36}Bi_{11.2}S_{18}$, and the small amount of Pb and Cd derived from electron-microprobe data cannot be localized either in thin or thick layer. The ideal chemical formula of makovickyite, $Ag_3Bi_{11}S_{18}$, can be rewritten $[Ag_2Bi_4S_7]^{\text{thin layer}}\ [AgBi_7S_{11}]^{\text{thick layer}}$ and compared with the rewritten structural formula $[Cu^{i}_{0.588}(Cu^{s}_{1.536}Ag_{0.56})_{\Sigma\ 2.096}Bi_4\ S_7]^{\text{thin layer}}\ [Ag_{0.8}Bi_{7.2}\ S_{11}]^{\text{thick layer}}$ and empirical formula (Table 1). A part of Cu, Cu^s (Cu1) substitutes for Ag, and the rest of Cu, Cu^i (Cu2), is interstitial.

Lead in cupromakovickyite occurs in an unorthodox way: instead of replacing Bi in the incremental layer as observed, *e.g.*, in the structure of benjaminite (N = 7 of the pavonite homologous series, Makovicky *et al.* 1977, Makovicky & Mumme 1979), lead substitutes for one of the Bi atoms in the paired Bi polyhedra of the thin layer. This substitution leads to: 1) a coordination typical for Pb, *i.e.*, a slightly asymmetric bicapped trigonal prism, and 2) a fairly unusual combination of a typical Bi5 pyramid of a pavonite type (Table 5), paired with a lillianite-like configuration of the Pb atom (Fig. 3). This leads to the unique scheme of occupancy described above for the column of foreshortened ("flat") octahedra in the thin layer (Figs. 3, 4), which differs from the scheme observed in makovickyite. The asymmetric tetrahedrally coordinated, fully occupied Cu1 site in the tetrahedral voids (S7–2 × S8–S9) between the tips (represented by S8 atoms) of the octahedra, is oriented toward the pavonite-like side of the thin layer, *i.e.*, toward Bi5. The somewhat asymmetric flat-tetrahedral Cu2 site is oriented sideways inside the vacant octahedron of the thin layer. In makovickyite, it is split along [010], *i.e.*, along the axis of the column of octahedra.

There are two types of incremental layers in cupromakovickyite, those situated between two adjacent rows of Bi5 (a pavonite-like module) and those between the adjacent rows of prismatic Pb sites (a lillianite-like module) (Fig. 3). They differ only slightly, essentially in the Ag–Bi pattern of substitution. The former, with the Bi2 and Bi3 position, have the Ag substitution scheme identical to that in makovickyite, whereas the latter have 0.16–0.17 Ag substituting for both the marginal Bi4 and the central Bi1 sites. The distribution of longer and shorter Bi bonds is very similar in the two layers (Table 5); it also is close to the situation in makovickyite.

Details of coordination

Sites Bi3 in makovickyite and Bi5 in cupromakovickyite belong to the thin layers of the pavonite-like structure. Atom Bi3 has a coordination typical for Cu-rich pavonite homologues (Makovicky *et al.* 1977, Makovicky 1997), with the bonds in the bases of its square coordination pyramid of about equal length, obviously an adjustment to the adjacent flattened octahedron with Ag and Cu sites. This is not the case for Bi5, where a typical asymmetric coordination occurs (Table 5). The trigonal prismatic coordination of lead is somewhat asymmetric, partly perhaps owing to the requirement of the prevailing pavonite-like structure motif, and partly to a certain percentage of Bi in this position, as indicated by the chemical data, as well as by the shortest bond-length and anisotropic displacement-parameters.

Marginal Bi sites of the incremental layers, Bi2 in makovickyite, and Bi2 and (Bi,Ag)4 in cupromako-

TABLE 3. STRUCTURE DATA FOR Cu-BEARING MAKOVICKYITE FROM FELBERTAL

Atom	*a/x*	*b/y*	*c/z*	sof	U_{11}	U_{22}	U_{33}	U_{13}	U_{eq}
Bi1	0.15070(4)	0.0	0.06591(4)	0.800(4)	0.0248(3)	0.0273(4)	0.0285(4)	0.0038(2)	0.0270(2)
Ag1	0.15070(4)	0.0	0.06591(4)	0.200(4)					
Bi2	0.44756(4)	0.0	0.19061(4)		0.0287(3)	0.0292(3)	0.0252(3)	0.0041(2)	0.0277(2)
Bi3	0.24868(4)	0.0	0.62393(4)		0.0342(3)	0.0325(3)	0.0240(3)	0.0025(2)	0.0311(2)
Ag	0.5	0.0	0.5	0.280(8)	0.10(1)	0.048(11)	0.10(1)	0.07(1)	0.092(8)
Cu1	0.5	0.189(7)	0.5	0.384(28)	0.020(3)	0.14(2)	0.043(4)	0.0002(24)	0.068(7)
Cu2	-0.0168(13)	0.0	0.4448(19)	0.147(12)	0.032(8)	0.09(2)	0.09(2)	0.006(8)	0.070(9)
S1	0.5	0.0	0		0.028(2)	0.028(2)	0.017(2)	0.0008(16)	0.0246(9)
S2	0.09017(23)	0.0	0.22856(25)		0.023(1)	0.030(2)	0.024(2)	0.0008(11)	0.0261(7)
S3	0.14326(22)	0.0	0.45866(23)		0.022(1)	0.027(2)	0.018(2)	0.0006(11)	0.0229(6)
S4	0.20751(24)	0.0	0.87555(31)		0.024(1)	0.024(2)	0.047(3)	0.0032(14)	0.0327(9)
S5	0.39748(27)	0.0	0.35899(27)		0.033(2)	0.026(2)	0.029(2)	0.014(1)	0.0283(7)

sof: site-occupancy factor.

TABLE 4. STRUCTURE DATA FOR CUPROMAKOVICKYITE FROM BĂIŢA BIHOR

Atom	*a/x*	*b/y*	*c/z*	sof	U_{11}	U_{22}	U_{33}	U_{13}	U_{eq}
Bi1	0.34910(7)	0	0.46675(3)	0.834(6)	0.0187(5)	0.0222(5)	0.0218(5)	0.0020(3)	0.0211(3)
Ag1	0.34910(7)	0	0.46675(3)	0.166(6)					
Bi2	0.44698(6)	0.5	0.09518(3)		0.0197(4)	0.0209(4)	0.0133(4)	0.0033(3)	0.0179(2)
Bi3	0.64982(7)	0	0.03264(3)	0.812(6)	0.0179(6)	0.0215(5)	0.0254(5)	0.0028(4)	0.0217(3)
Ag3	0.64982(7)	0	0.03264(3)	0.188(6)					
Bi4	0.55023(7)	0.5	0.40700(3)	0.834(4)	0.0207(5)	0.0232(5)	0.0170(5)	0.0029(4)	0.0204(3)
Ag4	0.55023(7)	0.5	0.40700(3)	0.166(4)					
Bi5	0.23915(6)	0	0.19489(4)		0.0154(4)	0.0266(4)	0.0179(4)	-0.0029(3)	0.0207(2)
Pb	0.74078(8)	0	0.32562(4)		0.0354(6)	0.0229(5)	0.0393(6)	0.0131(4)	0.0317(3)
Cu1	-0.01975(23)	0.5	0.21158(12)		0.017(1)	0.033(1)	0.040(2)	-0.005(1)	0.0310(7)
Cu2	0.45067(23)	0.5	0.27437(12)		0.021(1)	0.022(1)	0.040(2)	-0.006(1)	0.0288(7)
S1	0.5	0.5	0		0.023(4)	0.023(3)	0.015(3)	-0.0004(28)	0.021(1)
S2	0.40887(40)	0	0.38753(18)		0.014(2)	0.020(2)	0.017(2)	-0.0009(18)	0.018(1)
S3	0.29366(45)	0	0.06067(22)		0.021(3)	0.019(2)	0.035(3)	0.0003(24)	0.025(1)
S4	0.20840(41)	0.5	0.43626(21)		0.013(2)	0.016(2)	0.038(3)	0.005(2)	0.024(1)
S5	0.59356(40)	0	0.11343(17)		0.017(2)	0.013(2)	0.015(2)	-0.011(2)	0.016(1)
S6	0.5	0.5	0.5		0.025(4)	0.021(3)	0.019(4)	-0.003(3)	0.023(2)
S7	0.14852(36)	0.5	0.23335(16)		0.008(2)	0.017(2)	0.015(2)	0.002(2)	0.0134(8)
S8	0.40537(41)	0.5	0.17803(17)		0.019(3)	0.018(2)	0.0152)	0.008(2)	0.0168(9)
S9	0.36457(36)	0	0.27147(15)		0.012(2)	0.015(2)	0.010(2)	0.002(2)	0.0123(8)
S10	0.59796(38)	0.5	0.32498(17)		0.013(2)	0.019(2)	0.015(2)	0.004(2)	0.0153(9)

sof: site-occupancy factor.

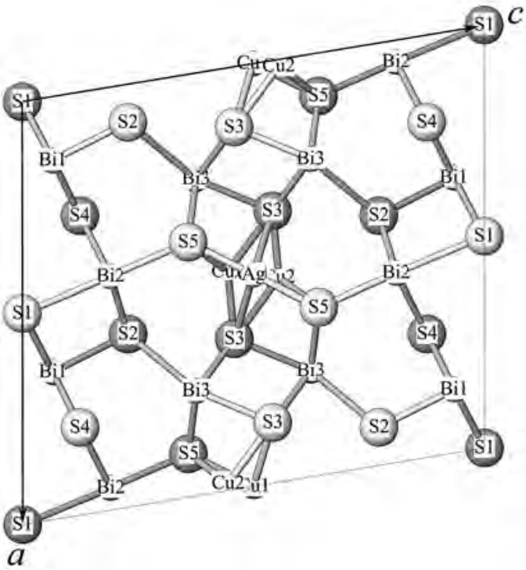

FIG. 2. Site labeling for the structure of makovickyite.

TABLE 5. SELECTED CATION–LIGAND DISTANCES (IN Å) FOR MAKOVICKYITE AND CUPROMAKOVICKYITE

					Makovickyite						
Bi1-	S2	2.638(4)	Bi2-	S5	2.660(5)						
	S4	2.801(2)		S2	2.765(2)						
	S4	2.801(2)		S2	2.765(2)						
	S1	2.897(1)		S4	2.935(2)						
	S1	2.897(1)		S4	2.935(2)						
	S4	3.008(4)		S1	2.989(1)						
Bi3-	S3	2.591(3)	Ag-	S5	2.281(4)	Cu1-	S5	2.406(10)	Cu2-	S3	2.095(17)
	S5	2.842(3)		S5	2.281(4)		S5	2.406(10)		S3	2.363(24)
	S5	2.842(3)		S3	2.907(2)		S3	2.435(15)		S5	2.554(14)
	S3	2.862(2)		S3	2.907(2)		S3	2.435(15)		S5	2.554(14)
	S3	2.862(2)		S3	2.907(2)						
	S2	3.440(3)		S3	2.907 2)						
	S2	3.440(3)									
					Cupromakovickyite						
Bi1-	S2	2.633(6)	Bi2-	S8	2.636(6)	Bi3-	S5	2.656(6)	Bi4-	S10	2.644(6)
	S4	2.797(4)		S5	2.797(4)		S3	2.810(5)		S2	2.753(4)
	S4	2.797(4)		S5	2.797(4)		S3	2.810(5)		S2	2.753(4)
	S6	2.901(1)		S3	2.930(5)		S1	2.888(1)		S4	2.941(4)
	S6	2.901(1)		S3	2.930(5)		S1	2.888(1)		S4	2.941(4)
	S4	3.131(7)		S1	3.055(2)		S3	3.020(7)		S6	2.977(2)
Bi5-	S9	2.598(5)	Pb-	S10	2.772(4)	Cu1-	S7	2.237(6)	Cu2-	S10	2.271(6)
	S7	2.706(4)		S10	2.772(4)		S8	2.387(3)		S9	2.310(3)
	S7	2.706(4)		S7	2.825(5)		S8	2.387(3)		S9	2.310(3)
	S8	3.105(5)		S9	3.217(4)		S9	2.566(6)		S8	2.844(6)
	S8	3.105(5)		S9	3.217(4)						
	S5	3.484(4)		S2	3.332(4)						
	S5	3.484(4)		S2	3.332(4)						
				S4	3.417(7)						

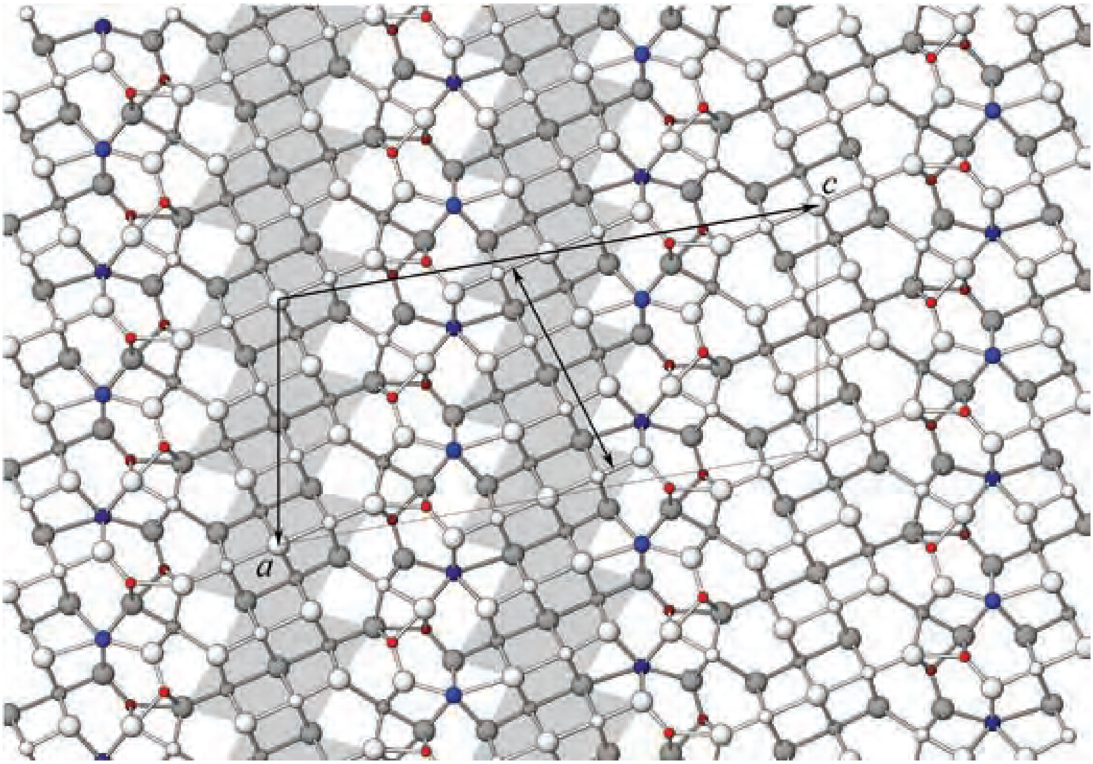

FIG. 3. The crystal structure of cupromakovickyite in projection on (010). Red circles: fully occupied Cu positions, blue circles: Pb. For remaining legend, see Figure 1.

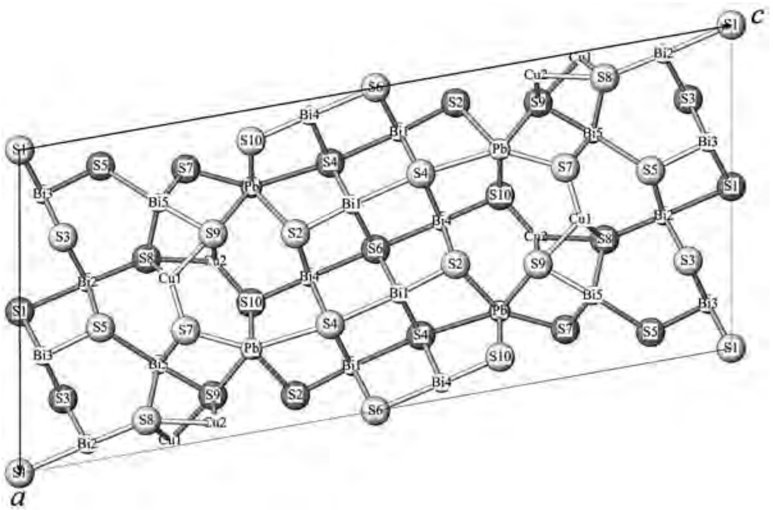

FIG. 4. Site labeling for the structure of cupromakovickyite.

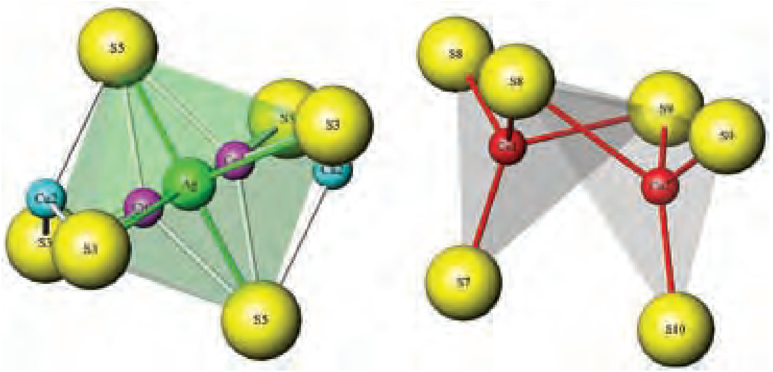

FIG. 5. Ag and Cu coordination polyhedra in the crystal structure of makovickyite and cupromakovickyite.

vickyite, all display nearly identical (3 + 2 + 1) bond asymmetry connected with their marginal position. The shortest *versus* longest difference appears a bit dampened in the (Bi,Ag)4 site, apparently owing to the presence of Ag. The inner Bi sites of these layers, Bi1 and Bi1, Bi3, in the above order of compounds, are less asymmetric in those bonds that are diagonal to (010) of the lattice of makovickyite, but seem more asymmetric in the ratio of outwardly : inwardly oriented bonds (distances) (Table 5). This is related to the presence of slightly inflated lone-electron-pair micelles in the incremental layers. They are delimited on their margins by the short Bi1–S2 bonds and are placed diagonally *en échelon* in these layers.

The coordination polyhedra observed for the monovalent cations in *makovickyite* are a compromise obtained by averaging of several different, competing and, in the crystal-structure determination, overlapping types of coordination polyhedra. Silver in the incremental layers could not be refined as a separate atom, and was therefore placed in one site with the predominant bismuth, exercising only weak influence on the Bi coordination polyhedron. The Ag site in the isolated octahedral site of makovickyite is linearly coordinated (2 × 2.281 Å and 4 × 2.907 Å); the distances observed come, however, from the predominantly Cu-occupied column of octahedra. The influence of silver, observed on the characteristics of flattened tetrahedral coordina-

TABLE 6. POLYHEDRON CHARACTERISTICS FOR THE REFINED STRUCTURE OF MAKOVICKYITE AND CUPROMAKOVICKYITE

Atom	Sphere radius (Å)	Volume distorsion (%)	Volume-based eccentricity	Volume-based sphericity	Sphere volume (Å^3)	Polyhedron volume (Å^3)
			Makovickyite			
Bi1	2.843	0.0036	0.1917	0.9832	96.235	30.523
Bi2	2.838	0.0009	0.2028	0.9904	95.701	30.435
Bi3	3.024	0.1849	0.4316	0.9511	115.808	35.718
Ag	2.698	0.0338	0	0.6404	82.297	25.311
Cu1	2.417	0.1273	0.0429	1	59.18	6.328
Cu2	2.359	0.0608	0.3801	1	54.987	6.328
			Cupromakovickyite			
Bi1	2.866	0.0078	0.2467	0.9882	98.61	31.145
Bi2	2.852	0.001	0.223	0.9967	97.173	30.899
Bi3	2.847	0.0024	0.1861	0.9926	96.643	30.689
Bi4	2.834	0.0023	0.2135	0.9826	95.332	30.274
Bi5	3.073	0.166	0.4976	0.9583	121.613	38.381
Pb	3.108	0.0352	0.3434	0.8971	125.794	52.61
Cu1	2.376	0.0402	0.2271	1	56.2	6.609
Cu2	2.438	0.1467	0.473	1	60.736	6.349

Distortion parameters are defined in Balić-Žunić & Makovicky (1996) and Makovicky & Balić-Žunić (1998).

tion of Cu1, manifests itself as the extension of the observed Cu–S distances. The combined influence of dominantly Ag and Cu1 sites on the refined average positions of the S3 and S5 atoms results in a distorted bond-distance scheme of the minority Cu2 position (Tables 3, 4). The Cu–Ag positions observed are apparently a result of "freezing" of an array of monovalent cations of the isolated columns of octahedra that were mobile at the temperature of formation. The sulfur positions in the thin layers of *cupromakovickyite* are less susceptible to the influence of cation substitution; the primary factor influencing them is a partial occupancy of the Pb site by bismuth. Thus, both Cu sites in the columns of octahedra have a close-to-regular (3+1) coordination (Table 5).

The Cu1–Cu2 configuration in the octahedra and tetrahedra of the columns of octahedra in *cupromakovickyite* is identical to that observed in such columns in $Cu_4Bi_4S_9$ (Takéuchi & Ozawa 1975, Bente & Kupčík 1984) and in $Cu_4Bi_4Se_9$ (Makovicky *et al.* 2002). This configuration assures short Cu–Cu contacts (2.825 Å) and might represent an ion-conduction path at the temperatures of mineral formation.

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