THE CRYSTAL STRUCTURE OF (Cd,In)-RICH CANNIZZARITE FROM KUDRIAVY VOLCANO, ITURUP ISLAND, KURILES, RUSSIA

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Abstract

A (Cd,In)-rich variety of cannizzarite has been found in sublimates from high-temperature fumaroles of the Kudriavy volcano, on Iturup Island, Kurile Archipelago, Russia. An electron-microprobe analysis gave the unit formula (calculated on the basis of 14 anions): $(Pb_{3.54}Cd_{1.06})_{\Sigma4.60}(Bi_{5.45}In_{0.29})_{\Sigma5.74}(S_{13.30}Se_{0.70})_{\Sigma14}$. A single-crystal X-ray-diffraction study indicates a monoclinic symmetry, space group $P2_1/m$, with unit-cell parameters a 15.4172(9), b 4.0582(2), c 20.8071(12) Å, β 98.031(2)°, V 1289.05(12) Å^3, and $Z = 2$. Its crystal structure has been solved and refined to $R_1 = 0.0504$ on the basis of 3158 unique reflections. There are 25 atom positions, corresponding to 11 cations and 14 anions. Among cations, bond-valence calculations allow us to distinguish three Pb sites, two Bi sites, and six mixed sites. Selenium seems to concentrate at two specific S positions of the H layer. In the cannizzarite variable-fit series of the composite layer type, the two H and Q sublattices are here in the ratio 3H : 5Q, like in the synthetic isotypic selenide $Pb_5Bi_6Se_{14}$. The structural features of H and Q layers and the common pseudotranslational sublattices of cations and anions are examined. The distribution of Pb, Bi, Cd and In among the mixed sites is discussed; cadmium and In could not be differentiated. In the final proposal, the Q layer contains the three Pb sites, with two mixed (Pb,Bi) sites; the H layer contains the two Bi sites, one [Pb,Bi,(Cd,In)] site, and three [Bi,(Cd,In)] sites.

Keywords: sulfosalt, cannizzarite, cadmium, indium, crystal structure, pseudotranslational sublattices, Kudriavy volcano, Iturup Island, Kurile Archipelago, Russia.

Introduction

The mineral cannizzarite, a rare Pb–Bi sulfosalt, discovered in 1925 as a product of fumarole exhalations at the crater La Fossa, on the island of Vulcano, Aeolian Islands, Italy (Zambonini *et al*. 1924), was considered to be discredited for a quarter of century. Then it was rehabilitated as a mineral species on the basis of synthesis and X-ray-diffraction data (Graham *et al*. 1953). This first X-ray study revealed two noncommensurate monoclinic sublattices that differ in one unit-cell parameter.

This noncommensurability was confirmed by solving the crystal structure of cannizzarite (Matzat 1979). The structure consists of two types of regularly alternating layers. One is the Q layer with a pseudo-tetragonal subcell, whereas the other is the double-octahedron H layer with a pseudohexagonal subcell (Makovicky & Hyde 1981). The general formulas of these layers are M_2S_2 and M_4S_6, respectively, where M is Pb and Bi. In the intralayer **c** direction of noncommensurability, m c_H may match n c_Q according to the vernier principle (semi-commensurate structure). In this case, a large true cell can be defined, corresponding to a homologous member mH : nQ of the cannizzarite variable-fit series. According to Matzat (1979), Makovicky (1981), Mozgova (1985), Organova (1989) and Borodaev *et al*. (2000), 3H : 5Q, 7H : 12Q and 27H : 46Q have been predicted, although other H : Q matches

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are possible (Makovicky & Hyde 1992). The 3H : 5Q and 7H : 12Q homologues are considered as potential terminal members of the cannizzarite series, with structural formulas $Pb_5Bi_6S_{14}$ and $Pb_{12}Bi_{14}S_{33}$, respectively. The crystal structure of the 7H : 12Q homologue from Vulcano was recently studied in detail by Topa *et al.* (2010).

A novel (Cd,In)-rich variety of cannizzarite was discovered by one of us (I.V.C.) in the sublimate samples taken in 2001 from high-temperature fumaroles of the Kudriavy volcano, on Iturup Island, Kurile Archipelago, in Russia. We report here the results of a crystal-structure study, and compare these with previous results.

EXPERIMENTAL

Mineralogical description

High-temperature sublimates from Kudriavy volcano present a complex assemblage of minerals, among which several In- and Cd-bearing sulfides and sulfosalts have been found (Chaplygin 2009). Indium is a main component in abramovite (Yudovskaya *et al.* 2007, 2008), and cadmium is present in wurtzite, greenockite and kudriavite (Chaplygin *et al.* 2005), whereas these two metals are associated in cadmoindite (Chaplygin *et al.* 2004, 2007). Bismuth and lead, present independently as bismuthinite, guanajuatite and ikunolite, and galena, respectively, are also associated in various sulfosalts: abramovite, cannizzarite, cosalite, kudriavite and lillianite.

Our sample of cannizzarite contains these four cations. It is present as needle-like crystals ($0.42 \times 0.02 \times 0.01$ mm), associated with kudriavite, greenockite and pyrite.

Chemical data

Chemical analyses were done with a Camebax SX–50 electron microprobe (Moscow State University) at an accelerating voltage of 20 kV and a beam current of 30 nA. The beam diameter was ~2 μm. The standards (analytical lines) are PbS (Pb$M\alpha$), Bi$_2$S$_3$ (Bi$M\alpha$), Sb$_2$S$_3$ (S$K\alpha$), CdSe (Se$L\alpha$), CdIn$_2$S$_4$ (Cd$L\alpha$, In$L\alpha$), SnS (Sn$L\alpha$), Pb$_5$(VO$_4$)$_3$Cl (Cl$K\alpha$), BiTeI (I$L\beta$). Two electron-microprobe analyses were made [an1/an2 (average), in wt.%]: Pb 28.25/29.18 (28.72); Bi 44.31/44.98 (44.65); S 16.44/17.20 (16.82); Cd 4.70/4.68 (4.69); In 1.49/1.78 (1.64); Se 2.61/1.55 (2.08); I 0.04/0.05(0.04); sum 97.84/99.42 (98.63). Tin and Cl were also sought, but were not detected.

On the basis of 14 anions, a chemical analysis (average) gave the unit formula (Pb$_{3.54}$Cd$_{1.06}$)$_{\Sigma4.60}$(Bi$_{5.45}$In$_{0.29}$)$_{\Sigma5.74}$(S$_{13.30}$Se$_{0.70}$)$_{\Sigma14}$ (with Z = 2). There is a significant deficit of cations (total = 10.34 atoms), commonly encountered in analyses of such a compound, suggesting some analytical artifact.

CRYSTALLOGRAPHY

X-ray single-crystal study

A diffraction pattern of suitable quality was obtained for only one among a large number of selected crystals. Diffraction data were collected at 293 K from a crystal of $0.42 \times 0.02 \times 0.01$ mm by a standard technique (a 4K CCD-equipped Bruker Nonius X8Apex diffractometer, Mo$K\alpha$ radiation, graphite monochromator, ϕ-scan) (Bruker 2004). Table 1 lists crystallographic characteristics, and results of the diffraction experiment are presented in Table 2. A list of structure factors and a cif file are available from the Depository of Unpublished Data on the Mineralogical Association of Canada website [document Cannizzarite 3H:5Q CM50_387].

The unit-cell parameters of our sample agree well with the scheme developed for the structure of the cannizzarite homologous series (Matzat 1979, Topa *et al.* 2010). The *a* parameter corresponds to the stacking of one H layer with one Q layer. The intralayer *c* parameter corresponds to the shortest *c* value of the cannizzarite series, with sublattice parameters c_H and c_Q equal to 6.94 and 4.16 Å, respectively. It corresponds

TABLE 1. CRYSTAL DATA FOR 3H : 5Q CANNIZZARITE: EXPERIMENTAL AND REFINEMENT DETAILS

Crystal data			
Crystal system	Monoclinic	Space group	$P2_1/m$
a (Å)	15.4172(9)	D_{calc} (g/cm^3)	6.793
b (Å)	4.0582(2)	No. of reflections	3662
c (Å)	20.8071(12)	for cell parameters	
β (°)	98.031(2)	μ (mm^{-1})	67.515
V (Å^3)	1289.05(12)	Crystal shape	needle-like
Z	2	Crystal color	black
Data collection			
T_{min}	0.0143	T_{max}	0.5517
No. of measured reflections		11107	
No. of independent reflections		4256	
No. of observed reflections		3158 for $F_o > 4\sigma(F_o)$	
Criterion for observed reflections		$I > 2\sigma(I)$	
R_{int}, R_{sigma}		0.0368, 0.0454	
θ$_{max}$ (°)		30.53	
Range of *h*, *k*, *l*		$-21 \le h \le 22, -3 \le k \le 5, -29 \le l \le 29$	
Refinement			
R_1		0.0504	
wR_2		0.1199	
$S(GooF)$		0.976	
No. of reflections used		3158	
No. of parameters refined		160	
Weighting scheme		$w = 1/[\sigma^2(F_o^2) + (0.0284P)^2 + 110.2947P]$, where $P = (F_o^2 + 2F_c^2)/3$	
$\Delta\rho_{max}$ (e/ Å^3)		5.274	
$\Delta\rho_{min}$ (e/ Å^3)		-6.234	
Extinction coefficient		0.000142(10)	
Computer programs			
Structure solution		*SIR*2004 (Burla *et al.* 2005)	
Structure refinement		*SHELXL*97 (Sheldrick 1997)	

to the simplest match of multiples of 7.03 and 4.13 Å described by Matzat (1979), *i.e.,* the 3H : 5Q match first observed by Organova (1989). Its unit-cell content is thus $[3 \times (M_4S_6)] + [5 \times (M_2S_2)] = M_{22}S_{28}$, ideally $Pb_{10}Bi_{12}S_{28}$ (= $2\ Pb_5Bi_6S_{14}$), with only Pb^{2+} and Bi^{3+} as cations.

Crystal-structure refinement

The structure was solved by direct methods (Burla *et al.* 2005) and refined by the full-matrix least-squares method for F^2 in anisotropic approximation using the SHELX97 package of programs (Sheldrick 1997). The coordinates and displacements parameters (isotropic and anisotropic) of atoms are reported in Table 2, and *M*–S distances, in Table 3. A slight decrease in *R* takes place by substituting minor selenium for sulfur at the S7 and S6 sites, which have the highest isotropic displacement parameters.

Owing to their close *Z* number, partitioning of Pb and Bi among *M* positions is not possible on the sole basis of electron-density measurement with X-ray diffraction data. An alternative was recently proposed by Zhang *et al.* (2005) through the crystal-structure study of $Pb_5Bi_6Se_{14}$, using resonant scattering at very high-energy *K*-edges. Another approach to such a partitioning can be proposed taking into account the larger

size of the Pb^{2+} cation relatively to the Bi^{3+} cation. On the basis of *M*–S distances in Table 3, bond-valence calculations (Brese & O'Keeffe 1991), taking *M* either as Pb or Bi (which have the same bond-valence parameter if bound with S), allow one to obtain for each *M* position its bond-valence sum (BVS).

Among the 11 *M* positions, three (nos. 2, 5 and 6) have a BVS close to 2, with coordination number VII (*M*6) or VIII (*M*2 and *M*5), and can be considered as pure Pb positions. All other *M* positions, with octahedral coordination, have BVS values significantly greater than 2, from 2.38 (*M*1) up to 2.83. The two positions with BVS = 2.83 (*M*3 and *M*7) can be considered as pure Bi positions. Other positions have mixed occupancy with Bi, Pb, Cd and In. Their occupancy could not be resolved directly, despite a significant proportion in the structural formula of lighter (and smaller) Cd and In atoms. A distribution model is proposed below on the basis of a crystal-chemical discussion.

Crystal-structure description

Figure 1 shows the projection of the crystal structure of the (Cd,In)-rich cannizzarite along the **b** axis, showing its layered semicommensurate organization. In Figure 2, we compare the unit cells of cannizzarite for the two matches, 7H : 12Q and 3H : 5Q (bold lines), on

TABLE 2. FINAL COORDINATES AND ANISOTROPIC DISPLACEMENT PARAMETERS OF ATOMS IN 3H : 5Q CANNIZZARITE
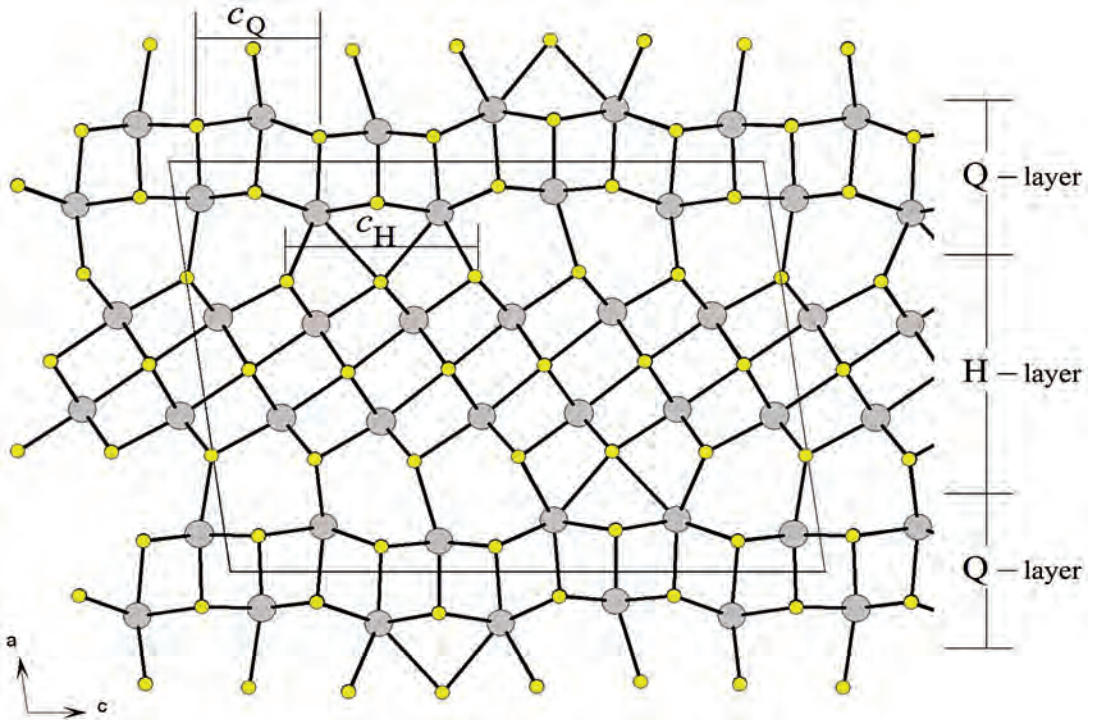
Atom	x	y	z	b.v.s.*	site-occupancy factor	U_{eq}	U_{11}	U_{22}	U_{33}	U_{13}
M(1)	0.6212(1)	-0.25	0.5380(1)	2.38	0.792(2)Pb + 0.208(2)In	0.017(1)	0.020(1)	0.016(1)	0.015(1)	0.004(1)
M(2)	-0.1259(1)	-0.25	0.2360(1)	1.91	Pb	0.029(1)	0.036(1)	0.023(1)	0.028(1)	0.003(1)
M(3)	0.6037(1)	-0.25	0.2070(1)	2.83	Bi	0.024(1)	0.026(1)	0.025(1)	0.022(1)	0.004(1)
M(4)	0.0730(1)	0.25	0.3587(1)	2.74	0.837(2)Bi + 0.163(2)Cd	0.019(1)	0.023(1)	0.018(1)	0.018(1)	0.004(1)
M(5)	-0.1247(1)	-0.25	0.4422(1)	1.94	Pb	0.030(1)	0.040(1)	0.024(1)	0.028(1)	0.009(1)
M(6)	0.1094(1)	-0.75	0.1680(1)	1.80	Pb	0.029(1)	0.035(1)	0.022(1)	0.032(1)	0.010(1)
M(7)	0.6125(1)	0.25	0.3725(1)	2.83	Bi	0.022(1)	0.024(1)	0.022(1)	0.018(1)	0.003(1)
M(8)	0.3758(1)	0.25	0.1244(1)	2.61	Bi	0.026(1)	0.028(1)	0.025(1)	0.025(1)	0.005(1)
M(9)	0.3809(1)	-0.25	-0.0442(1)	2.71	0.761(2)Bi + 0.239(2)Cd	0.019(1)	0.021(1)	0.018(1)	0.019(1)	0.005(1)
M(10)	0.3667(1)	0.75	0.2914(1)	2.67	0.779(2)Bi + 0.221(2)Cd	0.016(1)	0.017(1)	0.015(1)	0.016(1)	0.003(1)
M(11)	0.0901(1)	0.25	-0.0429(1)	2.67	0.811(2)Bi + 0.189(2)Cd	0.018(1)	0.023(1)	0.015(1)	0.017(1)	0.004(1)
S(1)	0.7197(1)	0.25	0.4865(1)	1.82	S	0.012(1)	0.012(1)	0.009(1)	0.014(1)	0.004(1)
S(2)	0.4867(1)	0.25	0.2482(1)	2.07	S	0.019(1)	0.020(1)	0.019(1)	0.018(1)	0.004(1)
S(3)	0.0871(1)	-0.25	0.0570(1)	1.92	S	0.014(1)	0.019(1)	0.011(1)	0.011(1)	0.003(1)
S(4)	0.2840(1)	0.25	-0.0017(1)	2.01	S	0.021(1)	0.018(1)	0.017(1)	0.030(1)	0.008(1)
S(5)	0.7077(1)	-0.75	0.1687(1)	1.87	S	0.009(1)	0.008(1)	0.009(1)	0.008(1)	0.000(1)
S(6)	0.7059(1)	-0.25	0.3264(1)	2.00	0.828(5)S + 0.172(5)Se	0.022(1)	0.025(1)	0.021(1)	0.021(1)	0.005(1)
S(7)	0.2699(1)	0.25	0.3375(1)	1.72	0.711(6)S + 0.289(6)Se	0.030(1)	0.021(1)	0.024(1)	0.048(1)	0.015(1)
S(8)	0.2750(1)	0.75	0.1711(1)	1.82	S	0.014(1)	0.012(1)	0.013(1)	0.015(1)	0.001(1)
S(9)	0.0606(1)	-0.25	0.4518(1)	1.91	S	0.014(1)	0.019(1)	0.012(1)	0.011(1)	-0.001(1)
S(10)	0.0595(1)	-0.25	0.2598(1)	1.95	S	0.014(1)	0.020(1)	0.013(1)	0.007(1)	0.002(1)
S(11)	0.4957(1)	-0.25	0.4182(1)	1.96	S	0.018(1)	0.022(1)	0.015(1)	0.018(1)	0.006(1)
S(12)	0.4940(1)	-0.25	0.0832(1)	2.06	S	0.019(1)	0.022(1)	0.017(1)	0.019(1)	0.006(1)
S(13)	-0.1006(1)	0.25	0.3408(1)	2.03	S	0.013(1)	0.018(1)	0.010(1)	0.012(1)	0.006(1)
S(14)	-0.0743(1)	-0.75	0.1380(1)	1.95	S	0.016(1)	0.023(1)	0.010(1)	0.017(1)	0.008(1)

$U_{12} = 0$, $U_{13} = 0$ by symmetry. * b.v.s.: bond-valence sum (Brese & O'Keeffe 1991). The formula derived from the crystal-structure determination is $Bi_{5.94}Cd_{1.06}In_{0.28}Pb_{3.72}S_{13.48}Se_{0.52}$.

TABLE 3.   INTERATOMIC DISTANCES (Å) IN 3H : 5Q CANNIZZARITE

M(1)–S(1)	2.834(2)	M(4)–S(10) #4	2.877(1)	M(8)–S(8) #1	2.811(2)
M(1)–S(1) #1	2.834(2)	M(4)–S(7)	3.129(2)	M(8)–S(8)	2.811(2)
M(1)–S(7) #2	2.884(2)	M(5)–S(9)	2.835(2)	M(8)–S(2)	2.885(2)
M(1)–S(11)	2.933(2)	M(5)–S(13) #1	2.988(2)	M(8)–S(12) #4	2.934(2)
M(1)–S(11) #2	2.941(2)	M(5)–S(13)	2.988(2)	M(8)–S(12)	2.934(2)
M(1)–S(11) #3	2.941(2)	M(5)–S(9) #7	3.057(2)	M(9)–S(4)	2.738(2)
M(2)–S(10)	2.833(2)	M(5)–S(9) #8	3.057(2)	M(9)–S(4) #1	2.738(2)
M(2)–S(13)	2.965(2)	M(5)–S(1) #5	3.367(2)	M(9)–S(5) #7	2.755(2)
M(2)–S(13) #1	2.965(2)	M(5)–S(1) #9	3.367(2)	M(9)–S(12)	2.962(2)
M(2)–S(14)	3.059(2)	M(5)–S(6) #5	3.298(2)	M(9)–S(12) #8	2.989(2)
M(2)–S(14) #4	3.059(2)	M(6)–S(14)	2.814(2)	M(9)–S(12) #7	2.989(2)
M(2)–S(6) #8	3.408(2)	M(6)–S(10)	2.961(2)	M(10)–S(8)	2.697(2)
M(2)–S(5) #5	3.413(1)	M(6)–S(10) #1	2.961(2)	M(10)–S(7) #4	2.768(1)
M(2)–S(5) #6	3.413(1)	M(6)–S(3)	3.056(2)	M(10)–S(7)	2.768(1)
M(3)–S(6)	2.750(2)	M(6)–S(3) #1	3.056(2)	M(10)–S(2) #4	2.969(2)
M(3)–S(5) #4	2.771(1)	M(6)–S(8) #1	3.254(2)	M(10)–S(2)	2.969(2)
M(3)–S(5)	2.771(1)	M(6)–S (8) #10	3.254(2)	M(10)–S(11) #4	3.075(2)
M(3)–S(12)	2.877(2)	M(7)–S(1)	2.695(2)	M(11)–S(3) #9	2.707(2)
M(3)–S(2) #1	2.923(2)	M(7)–S(6)	2.739(1)	M(11)–S(14) #10	2.821(2)
M(3)–S(2)	2.923(2)	M(7)–S(6) #4	2.739(1)	M(11)–S(14) #9	2.821(2)
M(4)–S(13)	2.650(2)	M(7)–S(11)	2.957(2)	M(11)–S(3) #4	2.910(2)
M(4)–S(9) #4	2.830(2)	M(7)–S(11) #4	2.957(2)	M(11)–S(3)	2.910(2)
M(4)–S(9)	2.830(2)	M(7)–S(2)	3.008(2)	M(11)–S(4)	2.993(2)
M(4)–S(10)	2.877(1)	M(8)–S(4)	2.802(2)		

Symmetry transformations used to generate equivalent atoms: #1 x, y – 1, z;   #2 –x + 1, –y, –z + 1;
#3 –x + 1,–y – 1,–z + 1; #4 x, y + 1, z; #5 –x, –y, –z + 1; #6 –x, –y – 1,–z + 1; #7 –x + 1,–y – 1,–z;
#8 –x + 1, –y, –z; #9 –x, –y, –z; #10 –x, –y – 1, –z.

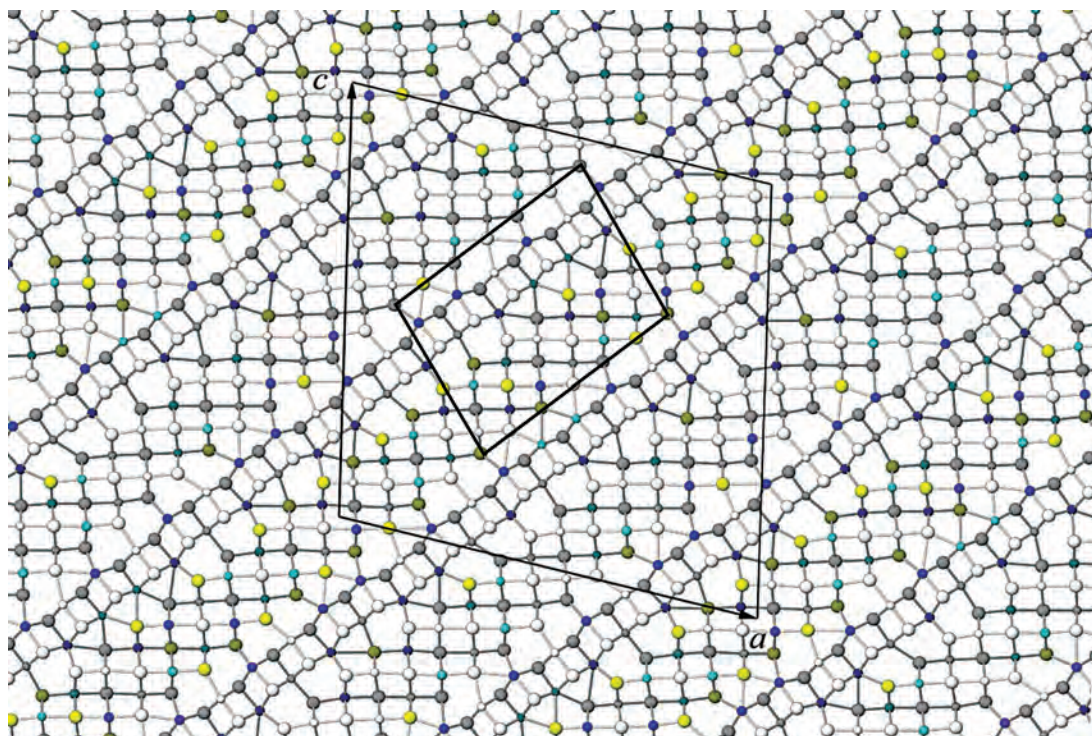Fig. 1.   Projection of the 3H : 5Q cannizzarite on the **x–z** plane.

FIG. 2. Projection on the **x–z** plane of the unit cells of 7H : 15Q (Topa *et al*. 2010) and 3H : 5Q (bold lines) cannizzarite homologues.

the basis of the structural scheme of Topa *et al*. (2010). In the central, more regular H layer, sulfur-bearing octahedra cross the mirror plane *m*, which coincides with the {110} plane of the PbS structure type. The *m* plane is the sole remainder of the cubic symmetry of PbS. This is also true for the so-called tetragonal Q layer intermediate between the H layers.

CRYSTALLOGRAPHIC ANALYSIS

A diffraction pattern of the cannizzarite sample studied does not exhibit pronounced reflections from the two discrete sublattices; therefore, this may be considered as a sign of their ideal conjugation within the unified translational lattice. Therein lies a distinction of our structure with respect to the structure of the 7H : 12Q cannizzarite, with its *a* and *c* parameters of about 40 Å, where such a conjugation has not met with success (Topa *et al*. 2010).

Special attention must be given to structure-describing factors that define the long-range order in the atomic arrangement. Assuming that the latter is provided by ordering the atoms with the systems of parallel equidistant planes (Borisov 1992, Borisov *et al*. 1998, 2002), let us analyze the close-packed crystallographic planes both for all atoms, and for cations and anions separately. Data from Table 4 calculated with the CASS–PAN package of programs (Borisov *et al*. 1998) show that for all atoms, there are no planes that differ radically in density of filling, except for the (020) mirror planes. As for cations in the d_{hkl} range with distances compared to the intercation distances, one can consider the translational sublattice formed by the (400), ($\bar{2}$06), and (020) planes. Figure 3 shows the cation sites of the cannizzarite structure in projection on the **x–z** plane and the intersection traces of it with the families of (400) and ($\bar{2}$06) planes and the derivative (206) planes. Most of the cation sites are located near the sublattice nodes, and only in two horizontal rows of the Q layer are there five cations per six nodes without a distinctly marked vacancy. An important point to note is that the ($\bar{2}$06) and (206) planes passing through the crystal accommodate the cation sites of all H layers and a part of the cations of the Q layers (6 of 10 for the unit cell). Thus, in the structure, there is a pseudotranslational cation sublattice with 48 nodes in the unit cell. The number of nodes is determined by the determinant of the indices (400), ($\bar{2}$06), and (020) planes (Borisov *et al*. 1998). As

along the **b** parameter (~4 Å), the neighboring nodes are separated by $d_{020} \approx 2$ Å, the cations occupy those nodes in alternation with vacancies and, hence, of the available 24 nodes, only 18 are filled.

A similar situation holds with the anion sites. In the anion sublattice, we consider the (500) plane instead of (400). As seen in Figure 4, the translational sublattice of the intersection nodes of the (500), ($\bar{2}$06), and

TABLE 4. RELATIVE* DENSITIES OF FILLING OF THE CRYSTALLOGRAPHIC PLANES BY ALL ATOMS OF THE CANNIZZARITE STRUCTURE (ρ_0), BY CATIONS ALONE (ρ_K), AND BY ANIONS (ρ_a)

h	k	l	d_{hkl}	ρ_0	h	k	l	d_{hkl}	ρ_K	h	k	l	d_{hkl}	ρ_a
$\bar{3}$	1	3	2.98	0.57	4	0	0	3.82	0.87	1	1	3	3.35	0.60
2	0	6	2.98	0.57	1	1	3	3.35	0.59	$\bar{2}$	0	6	3.31	0.63
$\bar{6}$	0	6	2.19	0.50	$\bar{2}$	0	6	3.31	0.60	5	0	0	3.05	0.79
0	2	0	2.03	1.00	$\bar{3}$	1	3	2.98	0.53	$\bar{3}$	1	3	2.98	0.60
1	1	9	2.01	0.59	2	0	6	2.98	0.50	2	0	6	2.98	0.62
					5	1	3	2.22	0.70	0	2	0	2.03	1.00
					$\bar{6}$	0	6	2.196	0.58					
					0	2	0	2.03	1.00					
					$\bar{1}$	1	9	2.01	0.57					

* Normalized with respect to 1.

(020) families of planes (the determinant 60) specifies the sites of 20 atoms among 28 to accommodate more regular anion sites of the H layers within the crystal.

We leave aside the atomic ordering with other families of close-filled crystallographic planes, though all their actions create the crystalline state. Nonetheless, the cation and anion pseudotranslational sublattices discussed above, conjugated within the large "lozenge-like" unit cell, may be considered as the main structure-describing factors of the cannizzarite structure. A similar situation was observed in the structures of other complex and simple sulfides (Borisov *et al.* 1998, 2011).

CRYSTAL-CHEMICAL DISCUSSION

The crystal structure of this cannizzarite from Kudriavy is isotypic (*i.e.*, with the same 3H : 5Q match) with that of a synthetic selenide, ~$Pb_5Bi_6Se_{14}$ (Zhang *et al.* 2005). In Table 5, we compare their unit cell and subcell data. There is quite an isotropic expansion of about 3.5% of the unit cell of the selenide relative to the sulfide. Comparison with the 7H : 12Q derivative (Topa *et al.* 2010) indicates a slight contraction of the stacking periodicity (15.266 *versus* 15.319 Å). But whereas there is a contraction of the a_H subparameter (–1.7%), the a_Q
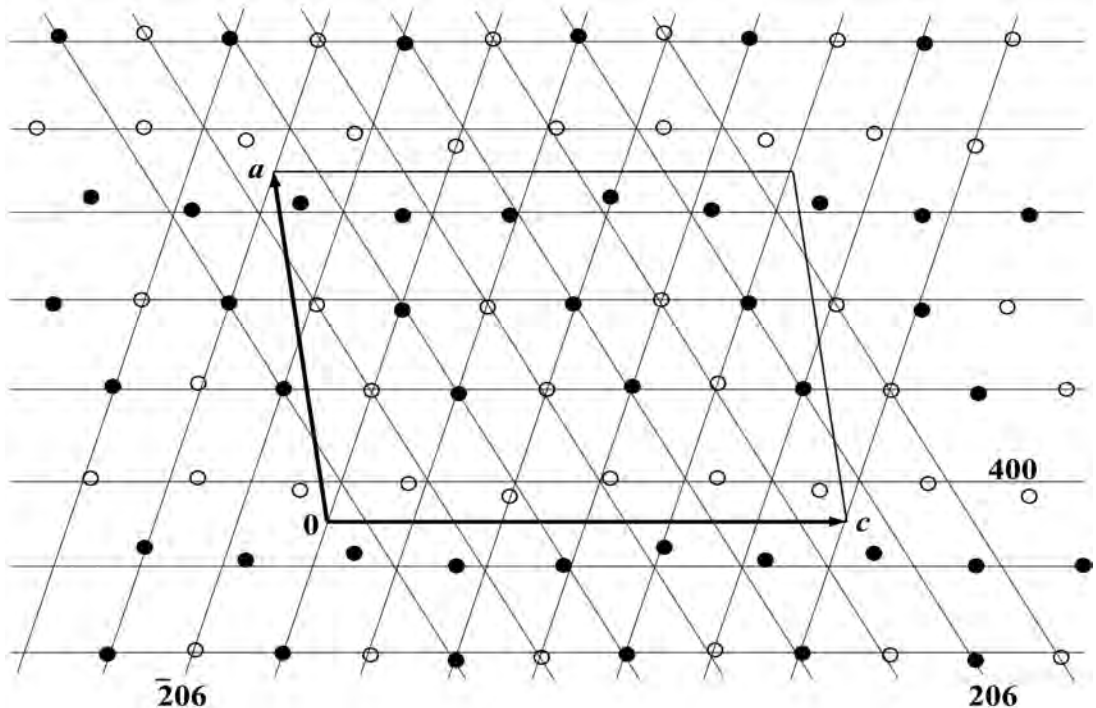

FIG. 3.   Projection of cation sites of the 3H : 5Q cannizzarite on the **x–z** plane (open circles *y* = ¼, black circles *y* = ¾) and sublattice nodes for the (400), ($\bar{2}$06), and (020) planes.
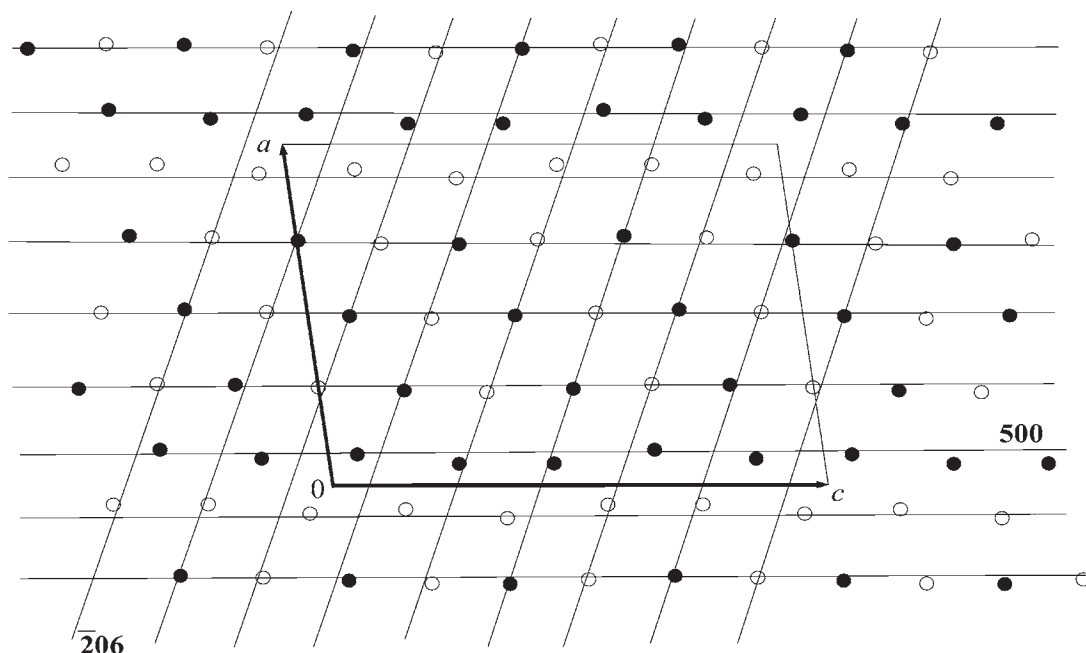
FIG. 4.   Projection of anion sites of the 3H : 5Q cannizzarite on the **x–z** plane (open circles $y = \frac{1}{4}$, black circles $y = \frac{3}{4}$) and sublattice nodes for the (500), ($\overline{2}$06), and (020) planes.

TABLE 5. COMPARISON OF UNIT-CELL DATA FOR CANNIZZARITE HOMOLOGUES

	7H : 12Q [1]	(Cd,In)-(3H : 5Q) [2]	Se-(3H : 5Q) [3]
Se/(S + Se)*	0.079	0.058	1
a (Å)	38.86	15.4172	16.0096
b (Å)	4.090	4.0582	4.20148
c (Å)	39.83	20.8071	21.5689
β (°)	102.30	98.031	97.537
V (Å³)	6188	1289.05	1438.28
(sub-)stacking periodicity (Å)	15.319	15.266	15.871
c_H (Å)	7.054	6.936	7.190
c_Q (Å)	4.115	4.161	4.314
$S_H = c_H.b$ (Å²)	28.85	28.15	30.21
$S_Q = c_Q.b$ (Å²)	16.83	16.89	18.13
V_H	442.0	429.7	479.4
V_Q	257.8	257.8	287.7

* According to EPMA results. [1] Topa *et al.* (2010). [2] This study. [3] Zhang *et al.* (2005).

subparameter increases (+1.1%). Finally, the values of V_Q are identical, whereas V_H of the 3H : 5Q variant is about 3% less than that of the 7H : 12Q one. The Pb2, Pb5 and Pb6 positions of cannizzarite belong to the Q layer, and correspond to Pb5, Pb3 and Pb2 of the selenide, respectively. In the 7H : 12Q structure from

Vulcano (Topa *et al.* 2010), one can also observe a 3H : 5Q fragment in which the Pb6, Pb8 and Pb2 positions correspond respectively to the Pb2, Pb5 and Pb6 positions of cannizzarite from Kudriavy.

In our variant of cannizzarite, Se-enriched sulfur positions (S6 and S7) are located at the margin of the H layer, connected with $M2$ and $M5$, and $M4$ of the Q layer. This is in accordance with the Se distribution in the 7H : 12Q structure of Topa *et al.* (2010). It confirms the hypothesis of selective Se partitioning in the H layer (of the tetradymite type) proposed in the cannizzarite–wittite series by Mozgova *et al.* (1992).

The most delicate question refers to the filling of mixed M positions, especially the distribution of the light metals Cd and In. Abramovite, $Pb_2SnInBiS_7$, also discovered at Kudriavy (Yudovskaya *et al.* 2008), can be taken into account for this question. Abramovite is a non-commensurate sulfide of the cylindrite type, *i.e.,* where a diatomic Q layer alternates with a single octahedral H layer. Although its crystal structure has not been resolved, its simplified formula can be written $(Pb_2BiS_3) \bullet (SnInS_2)$, where Q = (Pb_2BiS_3) and H = $(SnInS_2)$. On this basis, one can consider that in 3H : 5Q cannizzarite from Kudriavy, mixed M positions of the Q layer contain only Pb and Bi, whereas Cd and In are concentrated exclusively in the H layer. This choice is also justified by the significant contraction of c_H relative

to c_Q between the 3H : 5Q and 7H : 12Q variants (see Table 5 and the remark above). Although Cd and In have been located at distinct positions in the crystal structure of kudriavite (Balić-Žunić & Makovicky 2007), they have not been distinguished here.

On the basis of 11 cations, the selected electron-microprobe data can be simplified as $Pb_{3.8}(Cd_{1.1}In_{0.3})_{\Sigma 1.4}Bi_{5.8}S_{14}$ (1). On the basis of BVS values, the two mixed positions $M4$ and $M11$ in the Q layer have been filled by $(Pb_{0.2}Bi_{0.8})$ and $(Pb_{0.4}Bi_{0.6})$, respectively. The proposed formula for the Q layer is thus $Pb_{3.6}Bi_{1.4}S_5$; its subtraction from (1) gives the formula of the H layer: $Pb_{0.2}(Cd_{1.1}In_{0.3})_{1.4}Bi_{4.4}S_9$. As two pure Bi positions have been considered in this H layer, the four remaining M positions correspond to $Pb_{0.2}(Cd_{1.1}In_{0.3})_{\Sigma 1.4}Bi_{2.4}$. The Pb atom (0.2 at.) has been located at $M1$, which corresponds to the largest octahedron (with the lowest BVS), whereas (Cd,In) has been distributed in quite equal amounts among the four positions. The proposed distribution is $M1 = (Pb_{0.2}(Cd,In)_{0.3}Bi_{0.5})$, $M8 = [(Cd,In)_{0.4}Bi_{0.6}]$, $M9 = [(Cd,In)_{0.3}Bi_{0.7}]$ and $M10 = [(Cd,In)_{0.4}Bi_{0.6}]$. All these site-occupancy factors of mixed M positions are reported in Table 3.

Conclusions

We report here the discovery of a cannizzarite variant with the ratio 3H : 5Q. Its crystal structure was investigated *via* X-ray diffraction and refined satisfactorily. There are 25 atom positions, corresponding to 11 cations and 14 anions. Among cations, bond-valence calculations allow us to discriminate three Pb sites, two Bi sites, and six mixed sites. Selenium seems to concentrate at two specific S positions of the H layer. In the cannizzarite variable-fit series of the composite layered type, the two H and Q sublattices are here in the 3H : 5Q ratio, like in the synthetic isotypic synthetic selenide $Pb_5Bi_6Se_{14}$. We have examined structural features of H and Q layers and the common cation and anion pseudo-translational sublattices. We have discussed the distribution of Pb, Bi, Cd and In among mixed sites. Cadmium and In could not be differentiated. In the final proposal, the Q layer contains the three Pb sites, with two mixed (Pb,Bi) sites; the H layer contains the two Bi sites, one [Pb,Bi,(Cd,In)] site and three [Bi,(Cd,In)] sites.

Acknowledgements

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