Original paper

Single-crystal structure refinement of bukovite, (Cu₃Fe)∑₄Tl₂Se₄

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Single-crystal X-ray diffraction study of bukovite, ideally $(Cu_3Fe)_{\Sigma4}Tl_2Se_4$, was performed using a specimen from the Ústaleč uranium deposit, 15 km west of Horažďovice, SW Bohemia, Czech Republic. In the studied specimens, bukovite occurs in calcite gangue with uraninite associated with bytízite, chaméanite, clausthalite, hakite-(Hg) and umangite. Electron microprobe analysis gave (in wt. % – average of 20 spot analyses): Cu 19.90, Tl 41.21, Fe 5.55, S 0.31, Se 31.60, total 98.57. On the basis of 10 atoms per formula unit, the empirical formula of bukovite is $(Cu_{3.06}Fe_{0.97})_{\Sigma4.03}$ $Tl_{1.97}(Se_{3.91}S_{0.09})_{\Sigma4.00}$ ($Z = 1$). Unit-cell parameters are $a = 3.9694(8)$, $c = 13.694(3)$ Å, $V = 215.77(10)$ Å³, space group $I4/mmm$. The crystal structure was refined by single-crystal X-ray diffraction data to $R_1 = 0.0264$ for 92 unique reflections with $F_o > 4\sigma(F_o)$ and 10 refined parameters. The crystal structure of bukovite can be described as formed by single mackinawite-like {001} layers of edge-sharing (Cu,Fe)-centered tetrahedra, with Tl atoms hosted in eight-fold cubic coordinated sites intercalated between these tetrahedral layers. The role of Fe is discussed and the chemical formula $(Cu_3Fe)_{\Sigma4}Tl_2Se_4$ is proposed.

1. Introduction

Bukovite was first described by Johan and Kvaček (1971) from Bukov, Rožná, Czech Republic, in carbonate veins associated with other selenide minerals; additional findings at Petrovice and Předbořice were cited by these authors. Electron microprobe data suggested the ideal formula $Cu_{3+x}Tl_2FeSe_{4-x}$, with $x \sim 0.28$. Unit-cell parameters are $a = 3.976(5)$, $c = 13.70$ Å, $V = 217(1)$ Å³. Weissenberg photographs indicated an *I*-centered tetragonal lattice, with possible space group *I*-4*m*2, *I*-42*m*, *I*4*mm*, *I*422, and *I*4/*mmm*. Owing to the low quality of the available crystals, further diffraction data cannot be collected at that time.

Zemann (1973) proposed a crystal structure model for bukovite on the basis of the structure determination of synthetic phase Cu_2TlS_2 by Avilov et al. (1971), having a tetragonal unit-cell with parameters $a = 3.80$, $c = 13.77$ Å, and space group *I*4/*mmm*. On the basis of this structural model, Zemann (1973) calculated the X-ray powder diffraction pattern and compared it to that experimentally observed for bukovite. Some years later, Kovalenker et al. (1976, 1977) described the natural analogue of the species studied by Avilov et al. (1971) and named it thalcusite, ideally $Cu_{3-x}Tl_2Fe_{1+x}S_4$. Makovicky et al. (1980) reexamined bukovite from its type locality and proposed the empirical chemical formula $Tl_{1.966}Pb_{0.004}Cu_{3.160}Fe_{0.982}$

$Ag_{0.002}Se_{3.860}$, ideally $Tl_2Cu_{3+x}FeSe_{4-x}$, with $x = 0.14$, confirming the Cu excess and Se deficit suggested by Johan and Kvaček (1971). Finally, Dobrovolskaya et al. (1981) described the K-analogue of thalcusite, murunskite, ideally $Cu_3K_2FeS_4$, from the Murunsky alkaline complex, eastern Siberia, Russia; Pekov et al. (2009) solved the crystal structure of this mineral using a specimen from the Khibiny massif, Kola Peninsula, Russia.

During the examination of a chaméanite-bearing sample from the Ústaleč uranium deposit, bukovite was identified and notwithstanding its intimate intergrowth with chaméanite, single-crystal X-ray diffraction data were collected, allowing the refinement of its crystal structure. In this short paper, this new crystal structure and chemical data on bukovite are reported and discussed.

2. Experimental

The studied sample was collected at the small Ústaleč uranium deposit, located 15 km west of Horažďovice, SW Bohemia, Czech Republic. This deposit belongs to the Horažďovice uranium district; the hydrothermal uranium mineralization is structurally controlled by the regional Horažďovice fault zone trending WNW–ESE. The deposit is hosted in metamorphic rocks of the Varied Group of the Moldanubian complex, at contact with the
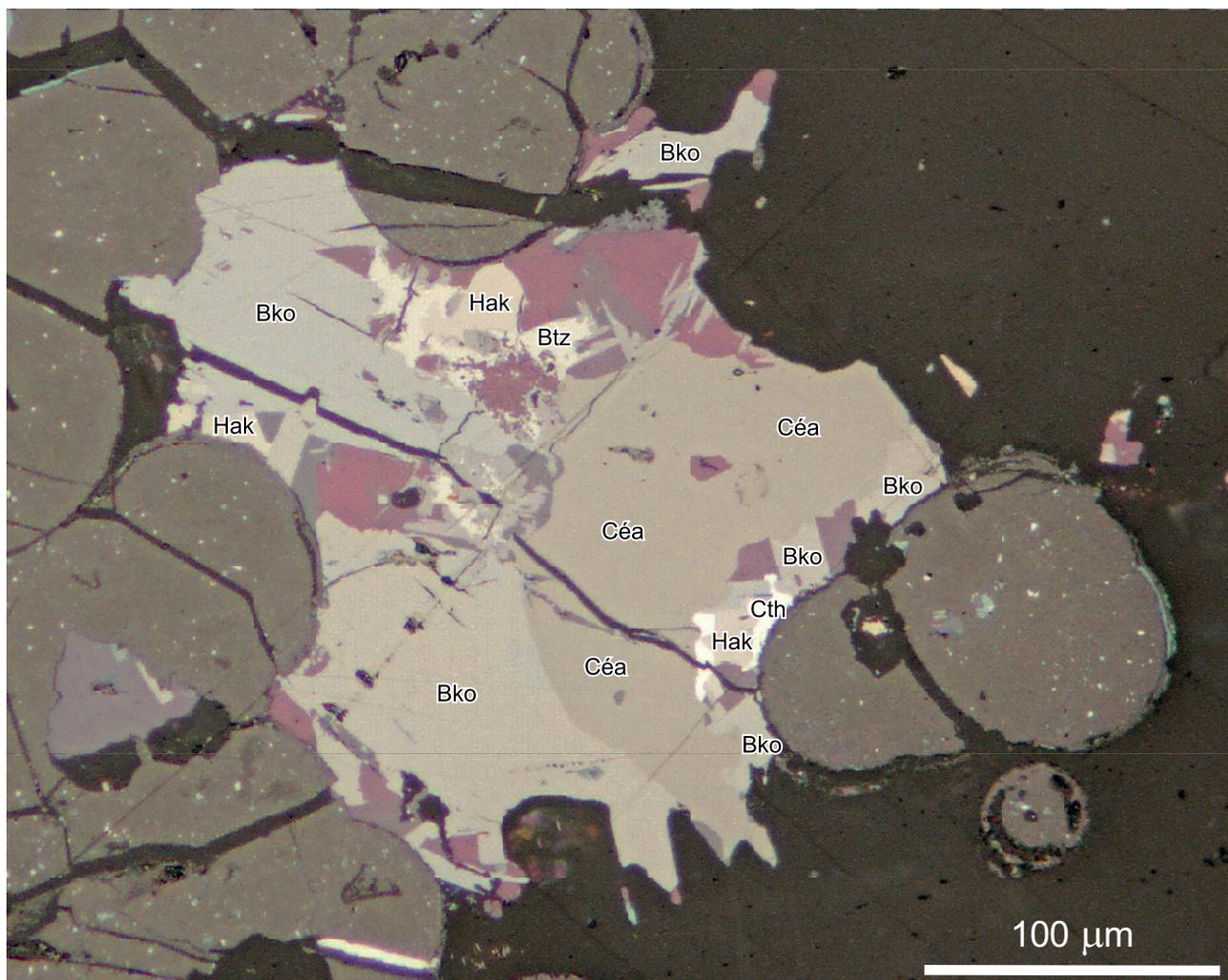
Fig. 1. Association of bukovite (Bko), with chaméanite (Céa), hakite-(Hg) (Hak), bytízite (Btz), clausthalite (Cth) and umangite (reddish purple/grayish blue) in calcite gangue with spherical aggregates of uraninite (brownish gray). Reflected light microscope (plane polarized light). Mineral symbols after Warr (2021).

Chanovice apophysis of the Central Bohemian Plutonic Complex (Litochleb et al. 1999). Selenide minerals are formed during the late-stage evolution of the ore deposit, and are younger than the uranium mineralization. At Ústaleč, the following selenide minerals are described: athabascaite, berzelianite, bukovite, chaméanite, clausthalite, crookesite, eskebornite, eucairite, ferroselite, "hakite", "giraudite", klockmannite, stibioústalečite, and umangite (Litochleb et al. 1999; Sejkora et al. 2022).

In the studied samples, bukovite forms anhedral to tabular grains up to 150 μm in length in calcite gangue with abundant spherical aggregates of uraninite (Fig. 1) in association with bytízite, chaméanite, clausthalite, hakite-(Hg) and umangite. In reflected light, bukovite is gray, pleochroic (bluish to creamy tints); anisotropy under crossed polars is medium.

Quantitative chemical analysis of bukovite was carried on using a Cameca SX 100 electron microprobe (National Museum of Prague, Czech Republic) and the following analytical conditions: wavelength dispersive spectroscopy mode, accelerating voltage 25 kV, beam current 20 nA, beam diameter 0.7 μm. The following standards and

Tab. 1 Chemical data for bukovite from Ústaleč.

element	wt.%	range (n = 20)	e.s.d.
Cu	19.90	19.28 – 21.25	0.64
Tl	41.21	38.77 – 41.85	0.83
Fe	5.55	5.29 – 5.68	0.09
S	0.31	0.00 – 0.80	0.21
Se	31.60	30.65 – 32.40	0.42
Total	98.57	97.54 – 99.90	0.51
	apfu	range	e.s.d.
Cu	3.06	2.99 – 3.23	0.07
Tl	1.97	1.82 – 2.02	0.05
Fe	0.97	0.91 – 1.00	0.02
S	0.09	0.00 – 0.24	0.06
Se	3.91	3.75 – 3.99	0.07

X-ray lines were used to minimize line overlap: chalcopyrite (CuK_α, SK_α), pyrite (FeK_α), PbSe (SeL_α) and Tl(Br,I) (TlL_α). Peak counting times were 20 s for all elements and one half of the peak time for each background. Other elements, such as Ag, As, Au, Bi, Cd, Co, Ga, Ge, Hg, Mo, Ni, Pb, Sb, Sn, Te and Zn were found to be below the detection limits (0.02–0.10 wt. %). Matrix correction by PAP software (Pouchou and Pichoir 1985) was applied to the data. Electron microprobe data of bukovite are given in Tab. 1.

Single-crystal X-ray diffraction intensity data were collected using a Bruker D8 Venture diffractometer (50 kV, 1.4 mA) equipped with an air-cooled Photon III detector, and microfocus $MoK\alpha$ radiation (C.I.S.U.P., University of Pisa, Italy). The detector-to-crystal distance was set to 38 mm. Data were collected using φ and ω scan modes, in 0.5° slices, with an exposure time of 30 s per frame. A total of 756 frames were collected. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm (Bruker 2022). Data were corrected for Lorentz-polarization, absorption, and background. Unit-cell parameters, refined on the basis of the XYZ centroids of 461 reflections above 20 σI with $5.949 < 2\theta < 54.81°$, are $a = 3.9694(8)$, $c = 13.694(3)$ Å, $V = 215.77(10)$ Å^3, space group $I4/mmm$. The crystal structure of bukovite was refined using *Shelxl*-2018 (Sheldrick 2015) starting from the atomic coordinates of murunskite (Pekov et al. 2009). The following neutral scattering curves, taken from the *International Tables for Crystallography* (Wilson 1992), were used: Tl at the A site, Cu *vs*. Fe at the M site, Se *vs*. S at the X site. The Cu : Fe atomic ratio at the Cu site was fixed on the basis of electron microprobe data. The anisotropic structural model for all atoms converged to $R_1 = 0.0264$ for 92 unique reflections with $F_o > 4\sigma(F_o)$ and 10 refined parameters. Table 2 gives details of data collection and refinement, whereas fractional atomic coordinates and displacement parameters, as well as selected bond distances, are given in Tabs 3 and 4, respectively.

Tab. 2 Summary of crystal data and parameters describing data collection and refinement for bukovite.

Crystal data	
Crystal size (mm)	$0.045 \times 0.040 \times 0.025$
Space group	$I4/mmm$
a (Å)	3.9694(8)
c (Å)	13.694(3)
V (Å^3)	215.77(10)
Z	2
Data collection and refinement	
Radiation, wavelength (Å)	Mo $K\alpha$, $\lambda = 0.71073$
Temperature (K)	293(2)
$2\theta_{max}$ (°)	55.83
Measured reflections	861
Unique reflections	106
Reflections with $F_o > 4\sigma(F_o)$	92
R_{int}	0.0366
$R\sigma$	0.0175
Range of h, k, l	$-5 \leq h \leq 3$, $-4 \leq k \leq 5$, $-18 \leq l \leq 18$
R_1 [$F_o > 4\sigma(F_o)$]	0.0264
R_1 (all data)	0.0312
wR_2 (on F_o^2)	0.0735
Goof	1.188
Number of least-squares parameters	10
Maximum and minimum residual peak (e Å^{-3})	+1.47 [at 0.87 Å from A] −1.00 [at 1.78 Å from A]

Tab. 3 Sites, site occupancy, fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for bukovite.

Site	Site occupancy	x/a	y/b	z/c	U_{eq}
A	$Tl_{1.00}$	0	0	0	0.0364(5)
M	$Cu_{0.75}Fe_{0.25}$	0	½	¼	0.0254(6)
X	$Se_{0.988(17)}S_{0.012(17)}$	0	0	0.35786(15)	0.0215(7)

The Crystallographic Information File (CIF) is available as Supplementary Material.

3. Results and discussion

3.1. General features

Electron microprobe data of bukovite point to the chemical formula, based on 10 atoms per formula unit (*apfu*), $(Cu_{3.06}Fe_{0.97})_{\Sigma4.03}Tl_{1.97}(Se_{3.91}S_{0.09})_{\Sigma4.00}$ ($Z = 1$). Whereas Makovicky et al. (1980) discussed the "Cu–Se substitution" proposed by Johan and Kvaček (1971) and mentioned the possible role of correction artifacts, new data do not support such a substitution. No significant Cu excess as well as (Se + S) deficit can be observed (Fig. 2a).

Tab. 4 Selected bond distances (in Å) for bukovite.

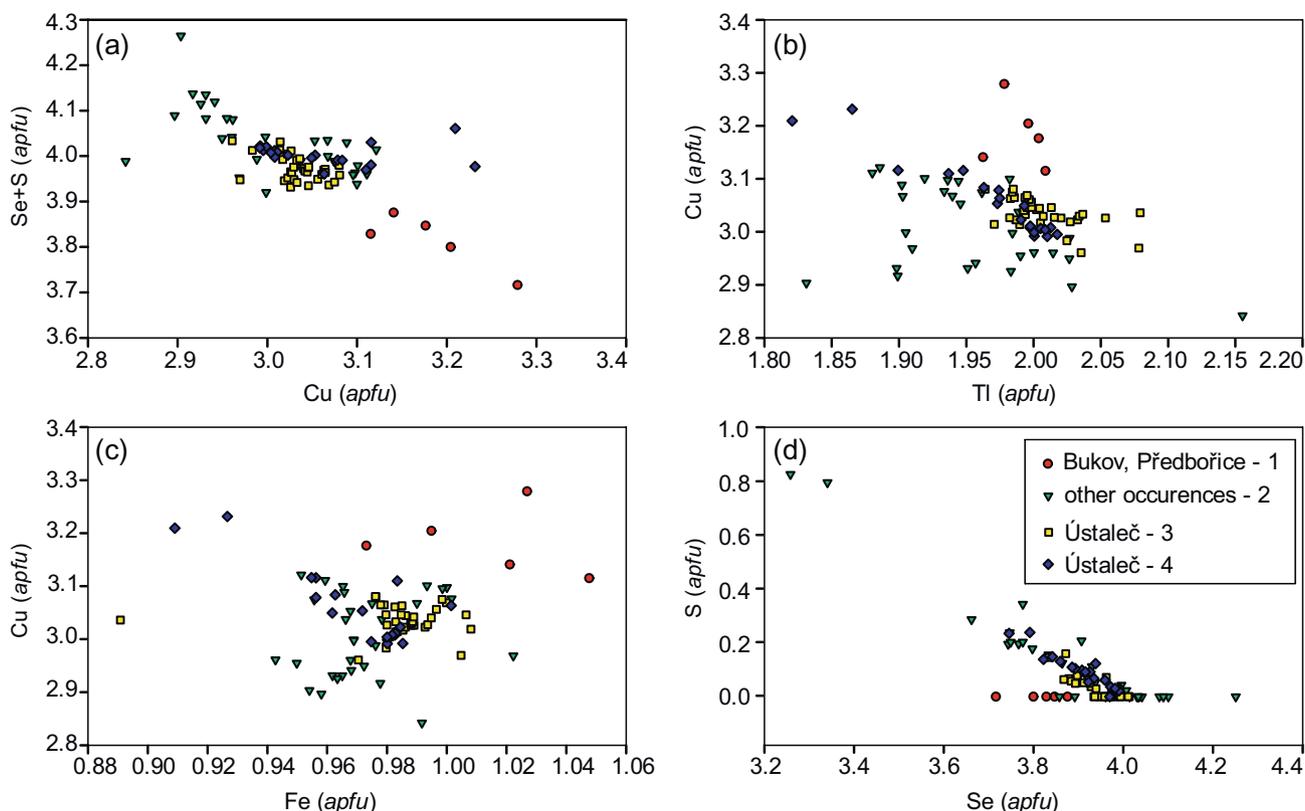| A	$- X \times 8$	3.4157(13)
M	$- X \times 4$	2.4740(13)

Fig. 2. Chemical relations in bukovite; **a** – samples from Bukov and Předbořice (Johan and Kvaček 1971; Makovicky et al. 1980); **b** – samples from Tuminico (Paar et al. 2002), Černý Důl (Kopecký et al. 2010), Zálesí (Sejkora et al. 2014) and Příbram (Škácha et al. 2017); **c** – samples from Ústaleč (this paper); **d** – sample from Ústaleč used for SC-XRD (this paper).

Figure 2 shows chemical relations in bukovite from Ústaleč and other occurrences. No evident relations between Cu/(Se + S), Cu/Tl and Cu/Fe *apfu* can be observed (Fig. 2a–c); the shown chemical range of contents probably reflects rather analytical uncertainties. Finally, a negative correlation between Se and S is evident (Fig. 2d), in agreement with the existence of the S-isotope of bukovite, thalcusite. Indeed, bukovite has isotypic relationship with this mineral, as well as with murunskite.

In agreement with previous authors (e.g., Makovicky et al. 1980; Makovicky 2006), its crystal structure can be described as formed by single mackinawite-like {001} layers of edge-sharing (Cu,Fe)-centered tetrahedra, with Tl atoms hosted in eight-fold cubic coordinated sites intercalated between these tetrahedral layers (Fig. 3). Copper and Fe are statistically distributed at the *M* site, with a Cu/Fe atomic ratio of 3. *M–X* bond distance of 2.474 Å and short *M–M* bonds, i.e., 2.8068(6) Å, occur. Bond-valence sum (BVS) at the *M* site, calculated using the bond-parameters of Brese and O'Keeffe (1991), is 1.47 valence units (*vu*), agreeing with the expected value of 1.50 *vu*, obtained assuming the occurrence of 0.75 Cu^+ and 0.25 Fe^{3+} at the *M* site. Thallium is hosted at the *A* site, and forms eight equivalent Tl–Se bond distances at 3.416 Å. The BVS at the *A* site is 1.16 *vu*, in agree-

ment with the occupancy by Tl^+. The monovalent nature of Cu and Tl in this kind of compound is in keeping with previous results reported by Berger (1989) for synthetic Cu_2TlS_2 (*Z* = 2), for which both crystal structure and X-ray photoelectron spectroscopy supported the presence of Cu^+ and Tl^+; the 3+ valence state of Fe was suggested by crystal structure data and electron transport data reported by Berger and Van Bruggen (1985). Finally, Se is bonded to 4 *M* and 4 *A* atoms, in eight-fold coordination; its BVS is 2.05 *vu*, in accord with the presence of Se^{2-} at the *X* site.

3.2. The role of Fe in bukovite and related phases

The system Tl–Fe–Cu–X (X = S, Se) has been investigated by several authors. Berger and Van Bruggen (1984) showed that synthetic Cu_2TlSe_2 (*Z* = 2) has metallic properties, owing to the occurrence of one valence-band (VB) hole per formula unit; this situation can be formally described by the formula $Cu^+_2Tl^+Se^{3/2-}_2$; this notation does not necessarily imply an ionic type of bond. Similar results were reported by Berger (1989) for synthetic Cu_2TlS_2, that was studied in a metastable state. In both compounds, the occurrence of a VB hole induces an attraction between X atoms and causes a distortion of the CuX_4 tetrahedra in
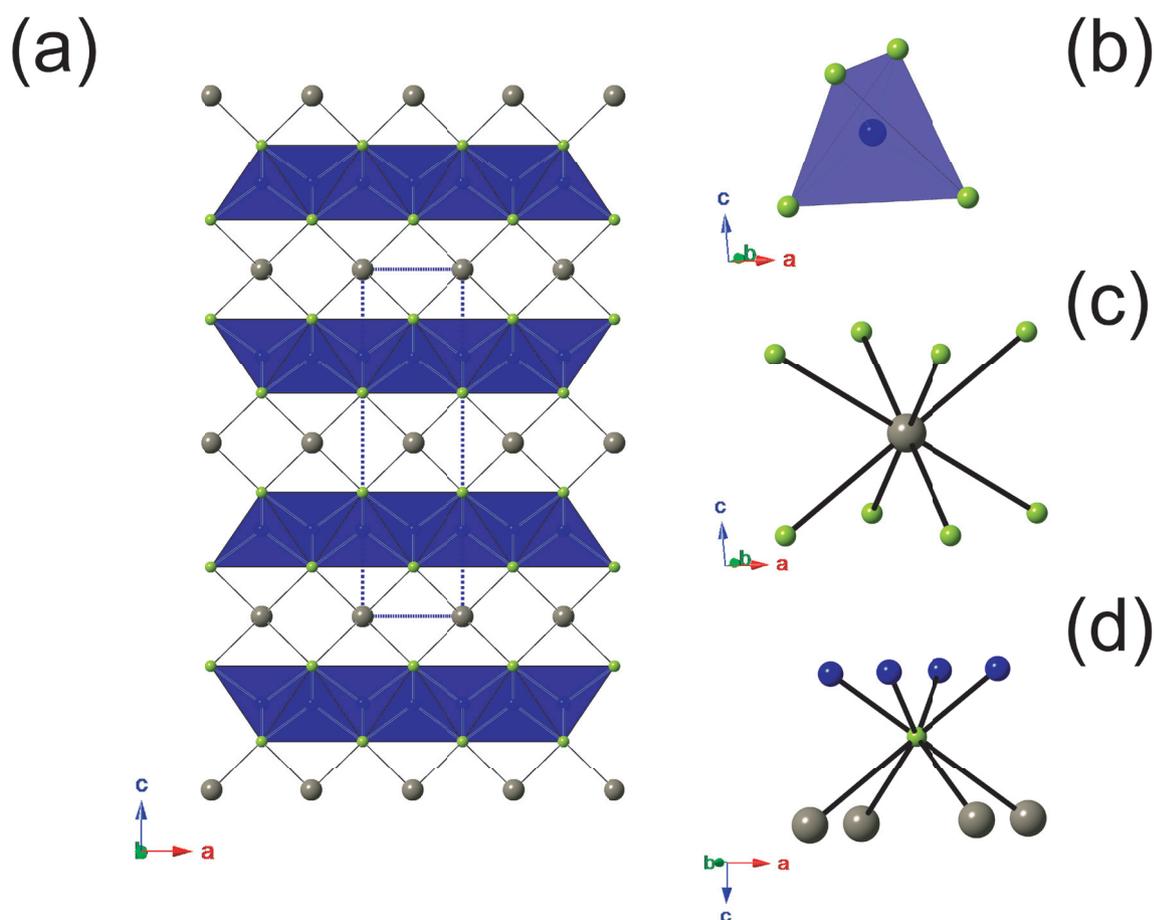
Fig. 3. Crystal structure of bukovite **(a)**, as seen down **b**, and the coordination polyhedra of (Cu,Fe) (*M* site) **(b)**, Tl (*A* site) **(c)**, and Se (*X* site) **(d)**. *M* site are shown as blue polyhedra in **(a)** and **(b)**; *A*, *M*, and *X* sites as grey, blue, and green circles.

the **c** direction; when the VB hole is filled, through the addition of trivalent metals (e.g., Fe^{3+}, Al^{3+}, or Ga^{3+}) the tetrahedra can relax and become more regular.

Berger and Van Bruggen (1985) investigated the system Cu_2TlSe_2–$Cu_{1.5}TlFe_{0.5}Se_2$, confirming the change in the electrical properties from those of a metal to that of a semiconductor (previously observed by Brun et al. 1979) following the partial replacement of Cu by Fe. According to them, the formula $(Cu^+_{1.5}Fe^{3+}_{0.5})Tl^+Se^{2-}_2$ can be written.

In natural specimens of bukovite, about one Fe *apfu* is always present (Fig. 2c). For instance, Makovicky et al. (1980) stressed that bukovite from Bukov contains ca. one Fe *apfu*, whereas associated crookesite and sabatierite do not take up this transition element in their crystal structure. The same occurs for isotypic compounds thalcusite, having chemical composition $Cu_{2.79}Tl_{2.01}Fe_{1.28}S_4$ and $Cu_{2.51}Tl_{2.03}Fe_{1.37}S_4$ (Kovalenker et al. 1977), and murunskite, having Fe contents ranging between 0.95 and 1.51 *apfu* (Pekov et al. 2009). Usually, high Fe contents are coupled with *A*-site vacancy and this relation should be further investigated. For instance, it could suggest the

substitution mechanism $A^+ + Cu^+ = \square + Fe^{2+}$. The presence of Fe^{2+} could be in accord with Berger and Van Bruggen (1985), who suggested that when more Fe than that corresponding to 1 *apfu* (on the basis of 4 Se atoms) is added to these compounds a partial replacement of Fe^{3+} by Fe^{2+} probably takes place. Still higher Fe contents, close to the formula $Cu_2Fe_2Tl_2Se_4$, revealed the occurrence of Fe^{2+} only, as shown by Mössbauer spectroscopy (Berger and Van Bruggen 1985). These valence changes from Fe^{3+} to Fe^{2+}, passing through mixed Fe^{2+}/Fe^{3+} compositions, remind to the behavior of Fe in tetrahedrite-group minerals (e.g., Makovicky et al. 1990, 2003).

4. Conclusion

The refinement of the crystal structure of bukovite confirms its isotypic relation with murunskite and thalcusite. Moreover, the mixed *M* site can be considered as a case of valency-imposed double site-occupancy (Hatert and Burke 2008). Consequently, the chemical formula given

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in the official IMA-CNMNC List of Mineral Names, $Cu_4Tl_2Se_4$, should be revised in $(Cu_3Fe)_{\Sigma4}Tl_2Se_4$.

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