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New data on betekhtinite: refinement of crystal structure and revision of chemical formula

S.V. Krivovichev [a,*], V.N. Yakovenchuk [b]

[a] *Department of Crystallography, Institute of Earth Sciences, Saint-Petersburg State University, Universitetskaya nab. 7/9, Saint-Petersburg, 199034, Russia*
[b] *Nanomaterials Research Centre, Kola Science Centre, ul. Fersmana 14, Apatity, Murmansk Region, 184200, Russia*

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Abstract

The crystal structure of betekhtinite from Dzhezkazgan copper ore deposit, Kazakhstan, has been refined to R_1 = 0.047 for 1321 unique observed reflections. The mineral is orthorhombic, *Immm*, *a* = 3.9047(6), *b* = 14.796(2), *c* = 22.731(3) Å, and *V* = 1313.3(3) Å^3. Structure refinement revealed five additional partially occupied Cu sites compared to the previous structural study. The structure contains one Pb and thirteen Cu sites. The coordination of the Pb site is sevenfold. Coordination geometries of the Cu sites are variable: The Cu1, Cu2, Cu3 Cu6, Cu7, Cu8, and Cu9 sites are tetrahedrally coordinated, whereas Cu4, Cu5, Cu10, Cu11, and Cu13 have a triangular coordination. The Cu12 site is coordinated by two S atoms to form a CuS_2 dumbell. The crystal structure of betekhtinite is based upon complex Pb–Cu sulfide rods running parallel to the *a* axis. The rods have a rhombus-like cross sections with lateral dimensions of *ca*. 11 × 16 Å^2. The core of the rod is composed from the CuS_4 tetrahedra and may be considered a module extracted from the archetype structure of fluorite, CaF_2. The tetrahedral columns are further incrustated by the $Cu4S_3$ and $Cu5S_3$ triangles and Pb atoms to form the $[Pb_2Cu_{16}S_{15}]$ rods, which are linked to each other along the *b* axis via S6 atoms. The low-occupied Cu sites are located in between the rods. The structural formula determined on the basis of the crystal-structure refinement can be written as $Pb_2Cu_{22.18}Fe_{1.04}S_{15}$, which is in good agreement with the chemical analyses of betekhtinite and disagrees notably with the formula $Pb_2(Cu,Fe)_{21}S_{15}$ suggested by Dornberger-Schiff and Höhne. The general crystal chemical formula of betekhtinite can be written as $Pb_2(Cu,Fe)_{22–24}S_{15}$. Information-based structural complexity parameters for betekhtinite are: I_G = 3.696 bits/atom and $I_{G,total}$ = 144.131 bits/cell. Decomposition of betekhtinite into a mixture of galena (PbS; I_G = 1.000 bits/atom; $I_{G,total}$ = 2.000 bits/cell) and chalcocite (Cu_2S; I_G = 1.500 bits/atom; $I_{G,total}$ = 12.000 bits/cell) at temperatures above 150 °C is associated with the loss of structural complexity and the rise of configurational entropy of the system.

Keywords: betekhtinite; crystal structure; sulfide; copper; Dzhezkazgan; Kazakhstan

Introduction

Betekhtinite, a complex Cu–Pb sulfide, was first described by Schüller and Wohlmann (1955) from the Mansfeld copper-bearing shales at Eisleben, Saxony-Anhalt. The mineral was named in honor of Anatolii Georgievich Betekhtin (1897–1962), Soviet–Russian mineralogist and petrologist. Initially, the chemical formula of betekhtinite from Mansfeld was reported as $Pb(Cu, Fe)_{11}S_6$ or $(Pb, Fe)Cu_{10}S_6$. The crystal structure of the mineral was solved by Dornberger-Schiff and Höhne (1959), who refined it to the *R* values of 0.165 for 220 0*kl* reflections and 0.20 for 190 1*kl* reflections. Their study revealed the presence in the structure of betekhtinite of one Pb site and eight Cu sites, of which three sites, Cu6, Cu7 and Cu8, were reported to have partial occupancies of 50, 50 and 33%, respectively. It was found that all copper atoms, except Cu4 and Cu5, have tetrahedral coordination by S atoms, whereas Cu4 and Cu5 sites are coordinated by three S atoms each to form planar CuS_3 triangles. On the basis of the crystal-structure refinement, Dornberger-Schiff and Höhne (1959) corrected the chemical formula of betekhtinite to be $Pb_2(Cu,Fe)_{21}S_{15}$. Later chemical analyses of the Mansfeld samples provided by Schüller and Höhne (1960) were found to be in agreement with the results of the crystal-structure study.

Satpaeva (1959) and Mukanov et al. (1960) reported betekhtinite from copper ores in Dzhezkazgan, Kazakhstan. In this locality, the mineral occurs as subparallel intergrowths of well-crystallized black needles with metallic luster. The chemical composition and physical properties of betekhtinite from Dzhezkazgan were in good agreement with those

* Corresponding author.
E-mail address: s.krivovichev@spbu.ru (Sergey V. Krivovichev)

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Table 1. Cation content of betekhtinite (in atoms per formula unit = apfu) from different mineral deposits

Locality	Pb	Cu	Fe	Ag	Si	Zn	Reference
Mansfeld, Germany	2.00	22.49	1.15	–	–	–	(Schüller and Höhne, 1960)
Yoshino, Japan	2.02	22.67	1.06	–	–	–	(Imai and Ogawa, 1976)
Lyell, Tasmania	1.95	21.68	1.13	–	–	–	(Markham and Ottemann, 1968)
Radka, Bulgaria	1.98	21.64	0.98	0.02	–	–	(Kouzmanov, 2004)
Radka, Bulgaria	2.01	21.71	0.68	–	–	–	(Tsonev et al., 1970)
Bulancak, Turkey	2.11	22.73	1.05	–	–	–	(Akinci, 1970)
Dzhezkazgan, Kazakhstan	2.01	22.11	1.20	0.17	–	–	(Mukanov et al., 1960)
Dzhezkazgan, Kazakhstan	1.97	22.41	1.02	–	0.02	0.01	RRUFF (Lafuente et al., 2015)

provided by Schüller and Wohlmann (1955) for the sample from the Mansfeld shales. Later betekhtinite was reported from many localities worldwide, including Mt. Lyell, Tasmania (Markham and Ottemann, 1968), Urup deposit, Northern Caucasus, Russia (Kachalovskaya and Khromova, 1970), Radka deposit, Bulgaria (Kouzmanov, 2004; Tsonev et al., 1970), La Leona copper mine, Argentina (Honnorez-Guerstei,n 1971), Tsumeb, Namibia (Geier and Ottemann, 1973), Bulancak, Turkey (Akinci, 1976), Odenwald, Germany (Fettel, 1978), etc. Imai and Ogawa (1976) described betekhtinite from the Yoshino mine, Yamagata Prefecture, Japan and provided for the mineral the possible chemical formulas $Pb_{2.02}(Cu_{22.67}Fe_{1.06})S_{15}$ and $Pb_{0.94}(Cu_{10.58}Fe_{0.49})S_7$, calculated on the basis of S = 15 and S = 7, respectively. They noticed that the first formula is different from the ideal formula $Pb_2(Cu,Fe)_{21}S_{15}$ suggested for betekhtinite by Dornberger-Schiff and Höhne (1959) in the higher amount of divalent cations, Cu+Fe, which exceeds the value of 21 apfu (= atoms per formula unit) established on the basis of the crystal-structure determination. Their observation is well supported by various empirical chemical formulae of betekhtinite collected in Table 1, including the most comprehensive analysis of the Dzhezkazgan sample given in the RRUFF online database (Lafuente et al., 2015). Imai and Ogawa (1976) pointed out that, in order to resolve the issue, the crystal structure of betekhtinite has to be refined. Herein we report on the results of the crystal-structure refinement of betekhtinite, which appears to be in agreement with the available chemical data (Table 1) and allows for the revision of its chemical formula.

Experimental

Single crystal of betekhtinite from Dzhezkazgan selected for data collection was mounted on a glass fiber with epoxy for the single crystal X-ray diffraction analysis. More than a hemisphere of the X-ray diffraction data were collected with the frame width of 0.5° in ω, and 20 s spent counting for each frame using a Bruker APEX CCD diffractometer operated with MoK_α radiation at 50 kV and 40 mA. The data were integrated and corrected for absorption using a multiscan type model using the Bruker programs *APEX* and *SADABS*. The unit-cell parameters and space group of betekhtinite (Table 2) were found to be in a good agreement with those reported by Dornberger-Schiff and Höhne (1959). As an initial model of the structure, the coordinates determined by Dornberger-Schiff and Höhne (1959) were used and the refinement converged to $R_1 \sim 0.11$. The SHELX package was used for all structure calculations (Sheldrick, 2008). Inspection of the Fourier difference electron-density maps revealed the presence of five additional low-occupied Cu sites located in between the Pb–Cu–sulfide rods (see below). Their introduction into the refinement and simultaneous refinement of the occupancies of

Table 2. Crystal data, data collection and structure refinement parameters for betekhtinite

Crystal data	
Temperature	293 K
Radiation, wavelength	MoK_α, 0.71073 Å
Crystal system	orthorhombic
Space group	*Immm*
Unit-cell dimensions *a*, *b*, *c* (Å)	3.9047(6), 14.796(2), 22.731(3)
Unit-cell volume (Å^3)	1313.3(3)
Z	2
Calculated density (g/cm^3)	5.975
Absorption coefficient (mm^{-1})	32.027
Crystal size (mm^3)	0.06 × 0.12 × 0.22
Data collection	
θ range	1.64°–35.84°
h, *k*, *l* ranges	–6 → 6, –21 → 24, –37 → 37
Total reflections collected	11159
Unique reflections (R_{int})	1752 (0.033)
Unique reflections $F > 4\sigma(F)$	1321
Structure refinement	
Refinement method	Full-matrix least-squares on F^2
Weighting coefficients *a*, *b*	0.0760, 41.3949
Data/restraints/parameters	1752/0/123
R_1 [$F > 4\sigma(F)$], wR^2 [$F > 4\sigma(F)$]	0.047, 0.072
R_1 all, wR^2 all	0.118, 0.138
Goodness-of-fit on F^2	0.926
Largest diff. peak and hole, *e* Å^{-3}	2.625, –4.019