

Crystal Structure of Urusovite $\text{Cu}[\text{AlAsO}_5]$: a New Type of a Tetrahedral Aluminoarsenate Polyanion

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Abstract—The crystal structure of the new mineral urusovite $\text{Cu}[\text{AlAsO}_5]$ has been determined (monoclinic system, sp. gr. $P2_1/c$, $a = 7.335(1) \text{ \AA}$, $b = 10.255(1) \text{ \AA}$, $c = 5.599(1) \text{ \AA}$, $\beta = 99.79(1)^\circ$, $V = 415.0(1) \text{ \AA}^3$, $Z = 4$). The structure is solved by direct methods and refined to $R = 0.048$ ($wR = 0.103$). The structure is built by open-branched $\{uB, \frac{2}{\infty}\}[\text{AlAsO}_5]^{2-}$ layers parallel to the (100) plane. The layers consist of two-link chains of ${}^1_{\infty}[\text{Al}_2\text{O}_6]$ tetrahedra, which are parallel to the z -axis and are connected through the $[\text{AsO}_4]$ -groups. The sharing-edges $[\text{CuO}_5]$ tetragonal pyramids link the aluminoarsenate layers to form a three-dimensional framework. The established layer is the second example of a tetrahedral aluminoarsenate polyanion. © 2000 MAIK “Nauka/Interperiodica”.

INTRODUCTION

Polyanions consisting of various tetrahedra belong to one of the most abundant types of mixed anionic radicals [1]. However, aluminoarsenate structures formed by condensation of the $[\text{Al}^{+3}\text{O}_4]$ and $[\text{As}^{+5}\text{O}_4]$ -tetrahedra are very rarely observed in compounds of this type. The well-known and, apparently, the only representative of this group is the exhalative mineral alarsite AlAsO_4 [2], recently discovered in fumaroles of the Bol'shoi Tolbachinskiĭ fissure eruption (BTFE, the Kamchatka peninsula). Alarsite belongs to the structural-type of berlinite, AlPO_4 . This mineral is a close analogue of quartz and has a framework structure built by vertex-sharing $[\text{Al}^{+3}\text{O}_4]$ and $[\text{As}^{+5}\text{O}_4]$ tetrahedra [3–5]. In this work, we report the results of the crystal structure determination of the new mineral urusovite $\text{Cu}[\text{AlAsO}_5]$ discovered in fumaroles of BTFE and named after the well-known scientist working in the field of crystal chemistry, Corresponding Member of the Russian Academy of Sciences V.S. Urusov. (Urusovite was recognized as a new mineral type by the Commission on New Minerals and Mineral Names of the International Mineralogical Association on March 5, 1999).

EXPERIMENTAL

Urusovite crystals, $\text{Cu}[\text{AlAsO}_5]$, chosen for our study were elongated transparent pale-green plates with vitreous luster. X-ray study by the Laue and Weissenberg methods showed that the crystals are monoclinic, the sp. gr. $P2_1/c$. The detailed description of data collection and the results of determination of the unit-

cell parameters and structure refinement are given in Table 1.

The structure was solved by direct methods. The positions of the copper and arsenic atoms were determined. The remaining atoms were located using successive approximations of difference Fourier syntheses. The initial processing of X-ray intensities and the choice of the structural model were performed using the AREN program package [6]. The structure was refined by the least-squares method to the R factor of 0.048 ($wR = 0.103$) by the SHELXL93 program package [7]. The absorption corrections were introduced using the DIFABS program [8].

The atomic coordinates and thermal parameters are listed in Table 2. The local valence balance calculated by the method suggested by Brown [9, 10] (the bond valences were calculated with the use of parameters taken from [10]) is given in Table 3.

RESULTS AND DISCUSSION

All atoms in the crystal structure of urusovite $\text{Cu}[\text{AlAsO}_5]$ occupy the general positions. The calculation of the local valence balance (Table 3) demonstrated that the sum of the valence bond stresses at each atom is equal (within the admissible error) to the formal valences corresponding to the chemical formula of the compound.

One crystallographically independent copper atom is coordinated by five oxygen atoms, forming a tetragonal pyramid. Four oxygen atoms located in the base of the pyramid are at distances of 1.960–1.975 Å from the copped atom, whereas the oxygen atom occupying the

Table 1. Crystallochemical characteristics of urusovite and the details of X-ray data collection and structure refinement

Chemical formula	Cu[AlAsO ₅]
System	Monoclinic
Sp. gr., <i>Z</i>	<i>P</i> 2 ₁ / <i>c</i> , 4
Unit-cell parameters	<i>a</i> = 7.335(1) Å <i>b</i> = 10.255(1) Å <i>c</i> = 5.599(1) Å β = 99.79(1)° <i>V</i> = 415.0(1) Å ³
<i>d</i> _{calc} , g/cm ³	3.93
Radiation	MoK α (λ = 0.71069 Å)
Diffraction, scanning mode	Syntex <i>P</i> 2 ₁ ; ω -2 θ
Number of independent reflections	1333
Number of observed reflections	1134 [<i>I</i> > 2 σ (<i>I</i>)]
Ranges of indices	-13 ≤ <i>h</i> ≤ 12; 0 ≤ <i>k</i> ≤ 18; 0 ≤ <i>l</i> ≤ 10
2 θ _{min} -2 θ _{max}	2.8-40.0
μ , mm ⁻¹	13.292
<i>R</i> (<i>F</i>)	0.048
<i>wR</i> (<i>F</i>)	0.103
<i>S</i>	0.977
Weighting scheme	$w = 1/[\sigma^2(F_0^2) + (0.0606P)^2]$, where $P = (F_0^2 + 2F_c^2)/3$
$\delta\rho_{\min}$, $\delta\rho_{\max}$	-1.305 ≤ $\delta\rho$ ≤ 1.417 eÅ ⁻³

Table 2. Atomic coordinates and thermal parameters (Å²) in the crystal structure of urusovite

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} [*]	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} [*]
Cu	0.4618(1)	0.14033(8)	0.9095(1)	0.0102(2)	O(2)	0.9041(7)	0.1996(5)	0.3745(8)	0.0123(9)
Al	0.1455(3)	0.1770(2)	0.4355(4)	0.0080(4)	O(3)	0.5707(7)	0.1946(5)	0.5470(9)	0.0110(9)
As	0.7257(1)	0.10839(6)	0.4261(1)	0.0082(1)	O(4)	0.2354(7)	0.2223(5)	0.7328(8)	0.0101(9)
O(1)	0.6231(8)	0.0407(4)	0.1596(8)	0.013(1)	O(5)	0.1984(8)	0.0136(5)	0.3844(9)	0.013(1)

$$* U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij} a_i^* a_j^* a_i a_j.$$

Table 3. Local valence balance in the crystal structure of urusovite according to [9, 10]

	O(1)	O(2)	O(3)	O(4)	O(5)	Σ		
Cu	0.47	0.45	0.45	0.15	0.45	1.97		
Al		0.74			0.78	0.77	0.75	3.04
As	1.19	1.29	1.30				1.29	5.07
Σ	2.11	2.03	1.90	2.00	2.04			

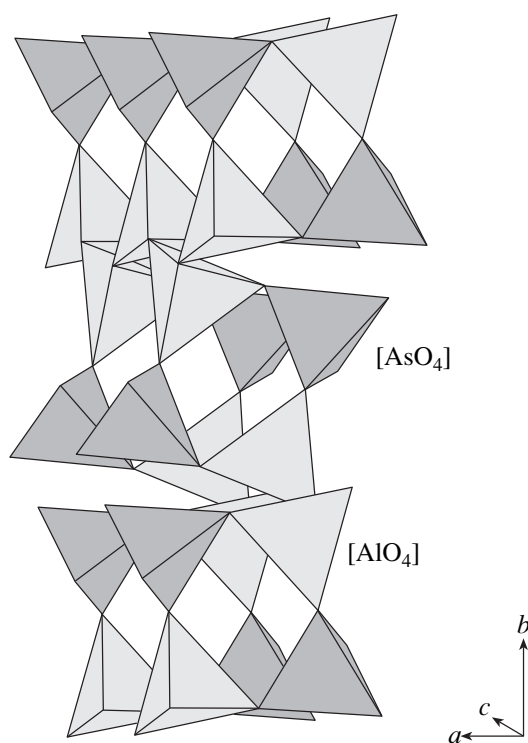


Fig. 1. Open-branched $\{uB_{\infty}^2\}$ $[\text{AlAsO}_5]^{2-}$ layer of tetrahedra in the urusovite structure (side view).

vertex is located at a distance of 2.370 Å. This coordination of the copper atom is typical of oxygen compounds [11, 12].

The coordination polyhedra of the aluminum and arsenic atoms are tetrahedra formed by oxygen atoms with the following average bond lengths and bond angles: Al–O, 1.751 Å; O–Al–O 109.5°; As–O 1.679 Å; and O–As–O 109.4°.

The crystal structure of urusovite consists of the ${}^2_{\infty}[\text{AlAsO}_5]^{2-}$ tetrahedral layers parallel to the (100) plane (Fig. 1). The layers are built by two-link tetrahedral ${}^1_{\infty}[\text{Al}_2\text{O}_6]$ chains parallel the z -axis and linked to the $[\text{AsO}_4]$ groups through the bridging O(2) and O(5) vertices. Two oxygen atoms (O(1) and O(3)) of the arsenate groups are terminal. In the ${}^1_{\infty}[\text{Al}_2\text{O}_6]$ chains, the $[\text{AlO}_4]$ -tetrahedra are linked together via the O(4) atoms. Within the framework of the silicate classification developed by Liebau [13], the mixed aluminosilicate tetrahedral layer thus formed can be described as an open-branched layer. The major structural unit of this layer is a two-membered aluminate chain branching because of attachment of arsenate “branches.” A similar structure of the aluminosilicate layer ${}^2_{\infty}[\text{Si}_3\text{AlO}_{10}]$ was also observed in prehnite [14, 15]. This layer consists of two-link aluminosilicate

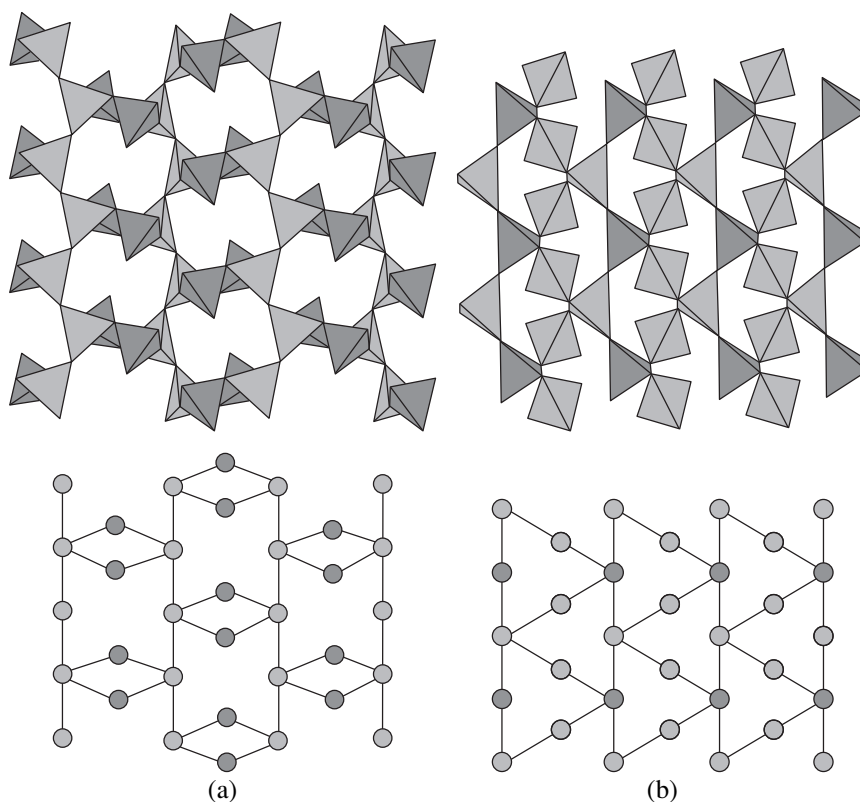


Fig. 2. Structure of the open-branched $\{uB_{\infty}^2\}$ $[\text{AlAsO}_5]^{2-}$ layers of tetrahedra in (a) urusovite and (b) prehnite and the corresponding topological diagrams (tetrahedra are indicated by circles).

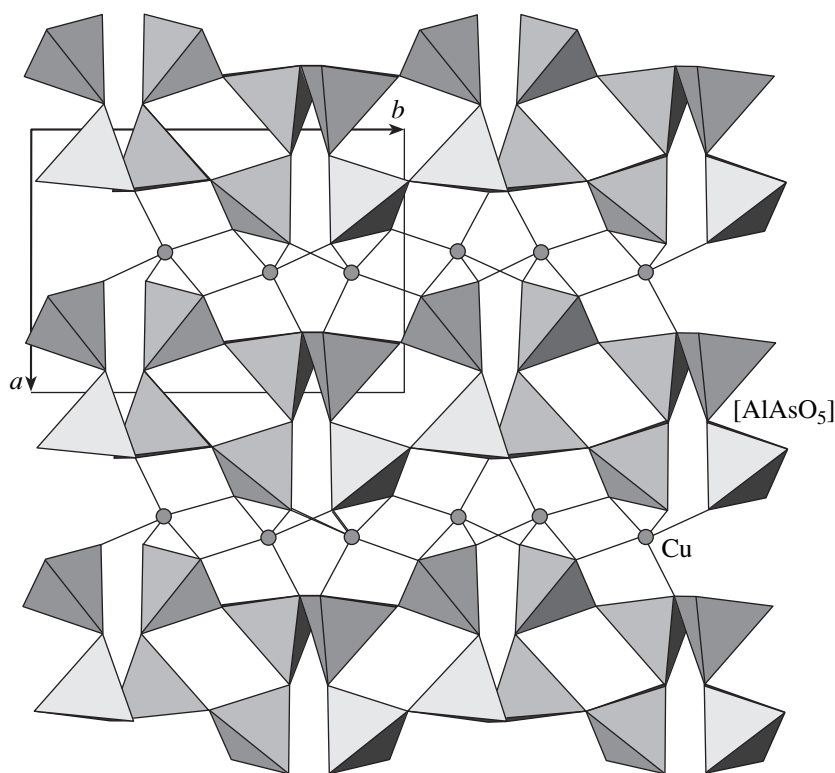


Fig. 3. Crystal structure of urusovite projected onto the xy plane.

chains connected via single $[\text{SiO}_4]$ -tetrahedra playing the role of “branches.” However, the topology of the structure of the layered polyanion in prehnite is essentially different from that of the mineral under study. The structures of the layers of the minerals under consideration and their topological diagrams are shown in Fig. 2. The aluminosilicate layer in prehnite can be represented as a layer consisting of six-membered rings, whereas the aluminosilicate layer in urusovite consists of four- and eight-membered rings. In the latter case, the four-membered rings are not directly linked to each other, i.e., they share no tetrahedra. No analogous tetrahedral layers were revealed in the known crystal structures, which indicates that we observed a new type of tetrahedral layers in the mineral under consideration.

As is seen from Table 3, the bridging O(2) and O(5) atoms, “connecting” the aluminate and arsenate tetrahedra, are completely valence-saturated, whereas the O(1), O(3), and O(4) coordinated with the copper atoms are not. The tetragonal $[\text{CuO}_5]$ -pyramids are linked in pairs by shared O(1)–O(1) edges (Fig. 3). These pairs are responsible for linking of aluminosilicate layers into a three-dimensional structure. The O(1)–Cu–O(1) bond angle resting on the shared O(1)–O(1) edge is shortened to 77.4° .

As was mentioned above, the crystal structure of urusovite is the second example of the tetrahedral polyanion formed by condensation of the $[\text{AsO}_4]$ and $[\text{AlO}_4]$ tetrahedra. Note that the change of trivalent alu-

minum by a divalent cation results a substantially wider variety of mixed anions. As an example, we refer to a series of compounds with the $[\text{ZnO}_4]$ - and $[\text{AsO}_4]$ -tetrahedra, which are linked by bridging vertices into layered and framework structures [16–20].

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