
STRUCTURE
OF INORGANIC COMPOUNDS

Crystal Structure of β -Uranophane from the Transbaikal Region and Its Relation to the Structure of the α Modification

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Abstract—The crystal structure of β -uranophane was refined ($R = 0.034$, 4898 independent reflections), and its relation to the α modification was established. The modifications of uranophane differ primarily in the orientation of the silicon–oxygen tetrahedra with respect to the plane of the layer formed by Si-tetrahedra and U^{6+} -bipyramids and also in the arrangement of calcium cations between the layers. In the structure of β -uranophane, calcium cations are bound to three oxygen atoms of uranyl groups of the adjacent U–O-polyhedra, whereas Ca atoms in the α modification are bound only to two uranyl oxygen atoms. © 2003 MAIK “Nauka/Interperiodica”.

Two polymorphs of calcium uranyl silicate (α -uranophane and β -uranophane) occur in nature. Both minerals have the stable elemental composition $Ca(UO_2)_2[SiO_3OH] \cdot 5H_2O$ and contain no isomorphous impurities. The paragenetic association was established for many natural specimens of this compound [1], which indicates that these modifications can be formed under similar conditions. This assumption was confirmed experimentally during decrystallization of the common gel [2]. However, the comparison of the solubility curves shows that the β modification is formed in a weakly acidic medium, whereas the α modification, over a wide range of neutral and alkaline solutions, which is reflected in the more widespread occurrence of the α modification in nature. Slight deviations from pH 7 (close to “neutral”) can stimulate the formation of mixed-layered phases and inclusions of the α modification into β -uranophane resulting in crystal imperfection. The structure of α -uranophane was first solved in [3] and refined in [4] within the sp. gr. $P2_1$. Recently, we have refined the structure of α -uranophane within the centrosymmetric sp. gr. $P2_1/b$ [5] on a specimen from the hydrothermal deposit of the Strel'tsovskii ore field (Transbaikal region). In the oxidation zone of this deposit, crystals of α -uranophane occur in association with the second modification (β -uranophane) existing as massive amber–honey-colored formations. From these formations, single-crystal chips were easily separated along perfect-cleavage

planes. Although the structure of β -uranophane had already been established [6], we refined it starting from the atomic coordinates determined earlier. The refinement completely confirmed the structure motif described in [6]. However, we refined the structure to a lower R factor and obtained atomic coordinates with a higher accuracy.

The crystallographic parameters of the mineral and details of X-ray diffraction study are given in Table 1. The atomic coordinates and principal interatomic distances are listed in Table 2 and Table 3, respectively.

Like α -uranophane, the structure of β -uranophane contains U^{6+} -ions coordinated by seven O anions, which form typical pentagonal bipyramids. In these polyhedra, two O atoms, which either occupy lone vertices or are included into Ca-polyhedra, are located at short distances from the central cation and form uranyl groups UO_2 . The five remaining O atoms are located in the equatorial plane. The U^{6+} -bipyramids share edges to form chains along the [100] direction. The adjacent uranium-containing chains are linked into layers parallel to the (001) plane via the Si-tetrahedra sharing the vertices and edges with the U^{6+} -bipyramids. Similar mixed layers of T-tetrahedra and UO_7 -bipyramids were found in 16 structures (half of these structures belong to minerals) [9], and these layers are topologically equivalent to the uranophane layers. In β -uranophane, the layers are linked by the Ca cations along the longest b axis and

Table 1. Crystallographic parameters and characteristics of X-ray diffraction study

Characteristic	Data and conditions
Formula	$\text{Ca}(\text{UO}_2)_2[\text{SiO}_3\text{OH}]_2 \cdot 5\text{H}_2\text{O}$
Unit-cell parameters, Å	
<i>a</i>	13.947
<i>b</i>	15.465
<i>c</i>	6.626
β , deg	91.399
Unit-cell volume <i>V</i> , Å ³	1428.73
Sp. gr.; <i>Z</i>	$P2_1/b$; 4
$\rho_{\text{exp}} - \rho_{\text{calcd}}$, g/cm ³	3.96–4.08, 3.9
Absorption coefficient μ , cm ^{−1}	3.384
Molecular weight	1712.68
Diffractometer	ENRAF–NONIUS
Radiation, wavelength	$\text{MoK}\alpha$, 0.709
Total number of reflections	9227
Number of reflections with, $ F > 3\sigma(F)$	9069
Maximum $\sin \theta/\lambda$	0.806
Ranges of the indices of measured reflections	$-22 < h < 22$; $0 < k < 24$; $-10 < l < 10$
Number of reflections upon averaging equivalent reflections	4898
<i>R</i> -factor upon merging	0.052
Program for structure calculations	AREN [7]
Absorption correction	DIFABS [8]
<i>R</i> -factor upon anisotropic refinement	0.037
Extinction parameter <i>E</i>	0.0000015

Table 2. Atomic coordinates and equivalent thermal parameters

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq} , Å ²
U(1)	0.0192(0)	0.2601(0)	0.2627(0)	1.09(1)
U(2)	0.2315(0)	0.7395(0)	0.4708(0)	0.96(1)
Ca	0.1902(1)	0.4856(1)	0.2826(2)	1.30(2)
Si(1)	0.0187(1)	0.2230(1)	0.7297(2)	0.73(3)
Si(2)	0.2670(1)	0.1945(1)	0.0636(2)	0.56(3)
O(1)	0.2652(3)	0.3523(3)	0.4927(9)	1.00(8)
O(2)	0.9920(5)	0.1491(4)	0.2347(10)	1.62(9)
O(3)	0.7321(4)	0.8741(3)	0.4401(8)	0.90(8)
O(4)	0.0441(5)	0.3724(4)	0.2893(10)	1.7(1)
O(5)	0.1794(4)	0.2234(4)	0.2114(7)	0.98(8)
O(6)	0.8923(4)	0.7639(5)	0.4197(8)	1.37(9)
O(7)	0.3579(4)	0.2045(4)	0.2200(8)	1.23(8)
O(8)	0.5684(4)	0.7492(4)	0.4260(8)	1.30(9)
O(9)	0.9795(4)	0.7189(4)	0.0718(7)	1.12(8)
O(10)	0.7271(4)	0.7468(4)	0.1343(8)	0.99(8)
OH(1)	0.9857(5)	0.8807(5)	0.2099(11)	1.7(1)
OH(2)	0.7414(5)	0.9074(5)	0.0016(11)	1.9(1)
H ₂ O(1)	0.5426(5)	0.9459(6)	0.1656(14)	2.3(1)
H ₂ O(2)	0.3609(8)	0.4906(7)	0.3296(17)	3.1(2)
H ₂ O(3)	0.8044(7)	0.5927(5)	0.0255(12)	2.5(2)
H ₂ O(4)	0.8770(6)	0.4992(5)	0.3770(11)	2.2(1)
H ₂ O(5)	0.1303(8)	0.0064(7)	0.2371(18)	3.5(1)

also by hydrogen bonds between the hydroxy groups and water molecules.

The essential difference between the two uranophane modifications is the orientations of the Si-tetrahedra relative to the layer planes. In the structure of α -uranophane (Fig. 1a), the free vertices of all the Si-tetrahedra located on one side of the uranium-containing chains deviate in the same directions with respect to the layer plane, whereas the free vertices of the Si-tetrahedra located on another side of the uranium-containing chains deviate in the opposite directions. By contrast, the free vertices of the Si-tetrahedra located on each side of the uranium-containing chains in the structure of β -uranophane alternate in their orientations relative to the layer plane (Fig. 1b), which results in doubling of the period along the chain axis ($\sim 7 \text{ Å} \times 2$). These differences can also be described in the context

of the symmetry approach [10, 11] with the aid of zero-dimensional modules. Each module consists of one bipyramid and one tetrahedron; the modules are related by the symmetry elements located on the shared edges of the pentagonal bipyramids and thus form chains. Unlike the structure of β -uranophane, in which the two-fold axes alternate with inversion centers in the chains, in the structure of α -uranophane, the zero-dimensional modules are related by twofold axes.

The difference in the orientation of Si-tetrahedra in two polymorphs is also reflected in the arrangement of the Ca cations between the layers. Although the structure of α -uranophane is centrosymmetric, the Ca atoms statistically occupy only one of two positions related by a center of symmetry (Ca–Ca distance is $\sim 4 \text{ Å}$). By contrast, the Ca atoms in the structure of β -uranophane occupy both positions separated by a distance exceed-

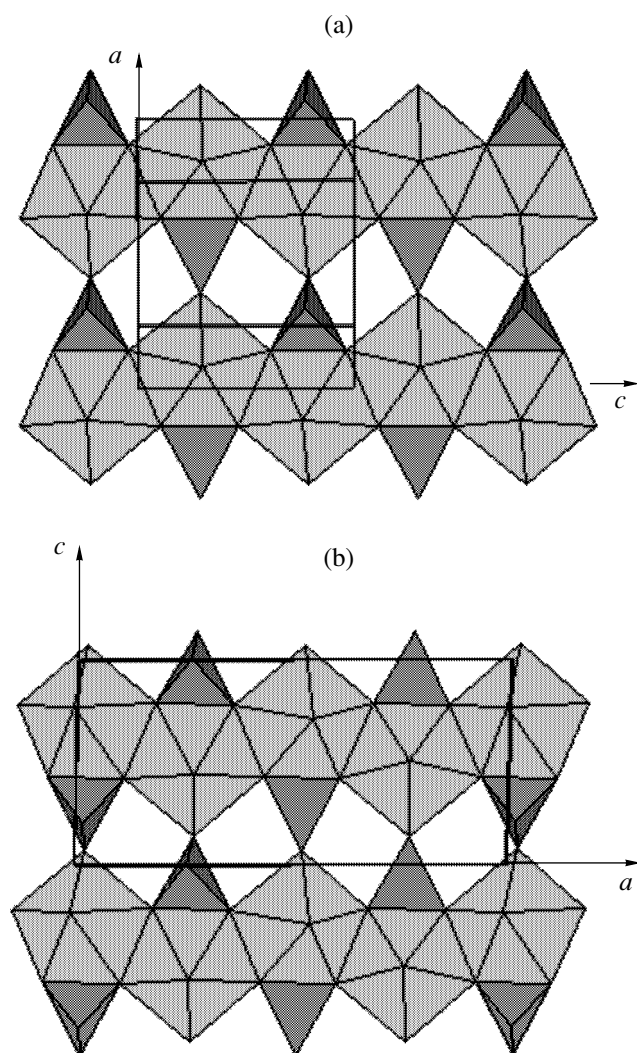


Fig. 1. Layers of UO_7^- and SiO_4 -polyhedra in the structures of (a) α -uranophane and (b) β -uranophane.

ing 6 Å. Because of these displacements, the Ca cations in the structure of α -uranophane are bound to two oxygen atoms of the uranyl groups from two adjacent layers, whereas the calcium cations in the structure of β -uranophane are bound to three oxygen atoms of uranyl groups. Two of these oxygen atoms are involved in coordination of the uranium atoms of one layer, whereas the third oxygen atom is coordinated to the uranium atom from another layer (Figs. 2a and 2b). Correspondingly, the Ca-polyhedra differ in their coordination numbers. In the structures of the α - and β -modifications, the Ca atoms are located in the seven- and eight-vertex polyhedra, respectively. Therefore, it can be assumed that the β modification is characterized by stronger inter layer bonding.

It should be noted that the structure of β -uranophane has two types of OH groups, unlike the structure of α -uranophane containing OH groups of only one type sta-

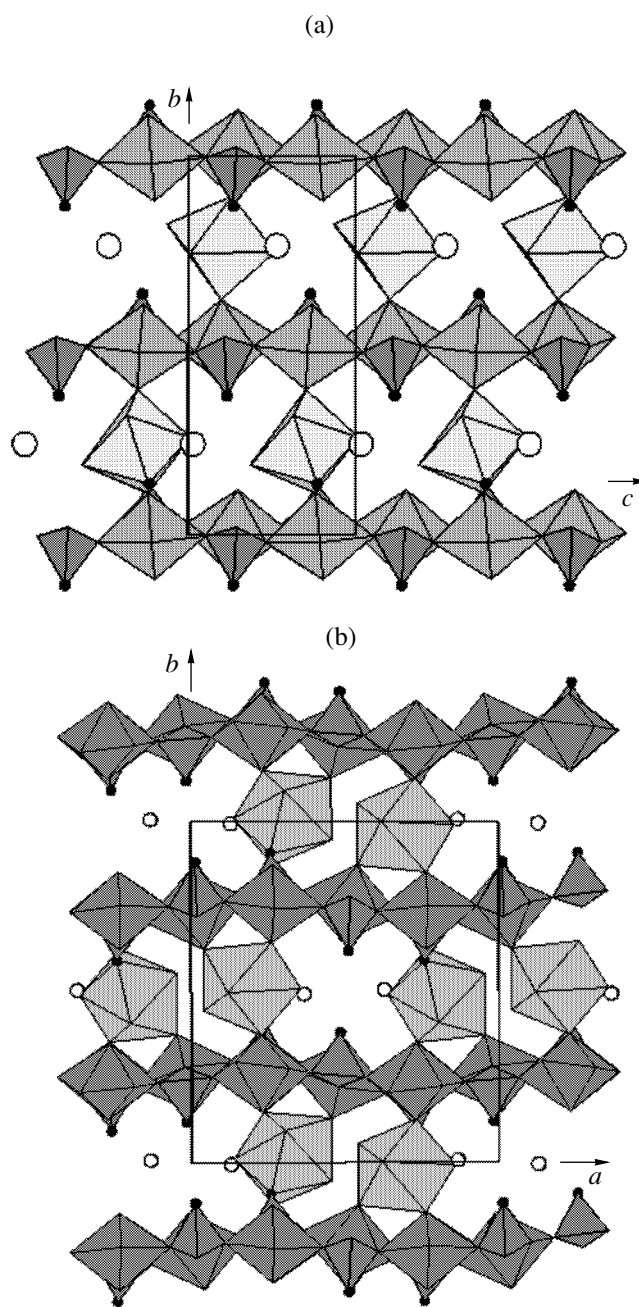


Fig. 2. Structures of (a) α -uranophane projected onto the (100) plane and (b) β -uranophane projected onto the (001) plane. OH groups and free water molecules are indicated by solid and empty circles, respectively.

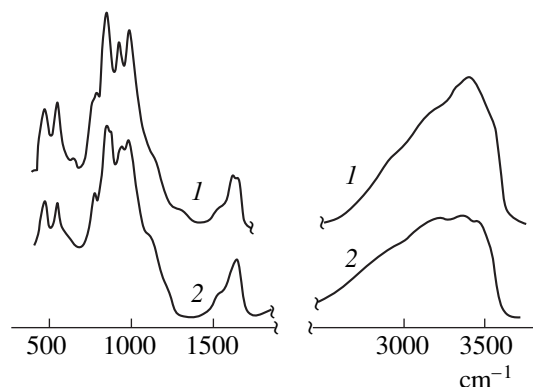
tistically incorporated into the Ca-polyhedra. In the structure of β -uranophane, the OH(2) group is bound to the Ca atom, whereas the OH(1) group is not bound to the Ca atom.

The differences between the structures of the two polymorphs clearly manifest themselves in the IR and luminescence spectra. In the IR spectra of both modifications (Fig. 3) measured by N.V. Chukanov, the bands

Table 3. Interatomic distances, Å

U-seven-vertex polyhedra			
U(1)–O(2)	1.767(7)	U(2)–O(1)	1.761(5)
O(4)	1.778(7)	O(3)	1.769(5)
O(9)	2.240(5)	O(10)	2.238(5)
O(7)	2.325(5)	O(6)	2.276(6)
O(5)	2.337(5)	O(8)	2.292(6)
O(8)	2.429(6)	O(5)	2.432(5)
O(6)	2.442(6)	O(7)	2.483(5)
	$\langle 2.188 \rangle$		$\langle 2.179 \rangle$
Si-tetrahedra			
Si(1)–O(9)	1.593(6)	Si(2)–O(10)	1.599(6)
O(6)	1.620(6)	O(7)	1.625(5)
O(8)	1.626(6)	OH(2)	1.636(8)
OH(1)	1.653(8)	O(5)	1.646(6)
	$\langle 1.623 \rangle$		$\langle 1.627 \rangle$
Ca-eight-vertex polyhedron			
Ca–H ₂ O(3)	2.376(8)		
H ₂ O(2)	2.39(1)		
H ₂ O(1)	2.426(8)		
O(3)	2.471(6)		
H ₂ O(4)	2.475(8)		
OH(2)	2.603(8)		
O(1)	2.685(6)		
O(4)	2.688(8)		
	$\langle 2.514 \rangle$		

at (3450, 3348), (986, 946), and (880, 845) cm^{-1} were attributed to the H₂O molecules, UO₂ groups, and SiO₄-tetrahedra, respectively. However, the $\nu(\text{Si}-\text{O})$ and

**Fig. 3.** IR spectra of (1) α -uranophane and (2) β -uranophane.

$\nu(\text{UO}_2)$ bands in the IR spectrum of the β modification are split, unlike analogous bands in the spectrum of the α modification. In addition, the $\nu(\text{SiO}-\text{H})$ band in the spectrum of the β modification has a higher intensity than the analogous band in the spectrum of α -uranophane.

To summarize, the analysis of the structural relations between α - and β -uranophanes provided the interpretation of the difference in their unit-cell parameters, crystal morphology and properties (in particular, instability of optical characteristics), and the conditions of the formation of these polymorphs.

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