THE CRYSTAL STRUCTURE OF METATORBERNITE

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Abstract

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E. S. MAKAROV and K. I. TOBELKO

THE CRYSTAL STRUCTURE OF METATORBERNITE

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Belonging to the large group of uranium micas, metatorbernite $Cu[(UO_2)(PO_4)]_2 \cdot 8H_2O$, according to reference mineralogical data ([1]), has a tetragonal structure with lattice constants $a = 6.96$ kX; $c = 8.62$ kX. According to Donnay–Donnay ([1,2]), the period c is doubled and has the value 17.41 Å, space group $P4_2/n$.

The present investigation was carried out on crystals supplied to us by V. I. Gerasimovskii. The crystals were well-formed plates and in intergrowths had a dark-green color. For the X-ray structural analysis, the crystal most perfect in optical reflections was selected, with linear dimensions of 0.5 mm in length and 0.2 mm in thickness.

A chemical analysis of samples of the crystals under investigation, carried out in our laboratory (I. F. Dolmanova), confirmed the gross formula of metatorbernite, including a content of 8 molecules of water.

From rotation X-ray photographs the following values of the constants of the tetragonal lattice were determined: $a = 6.95 \pm 0.02$ Å; $c = 17.26 \pm 0.06$ Å. Reflections $0kl$ with l odd, requiring a doubling of the cell along the c axis, were clearly visible, but had weak intensity. The pycnometric density of metatorbernite measured by us is 3.79 g/cm^3, which leads to a content of $2.05 \simeq 2$ formula groups $Cu(UO_2)_2(PO_4)_2 \cdot 8H_2O$ in the cell.

Using molybdenum radiation, X-ray goniometric layer-line photographs were obtained on a KFOR camera for the 0th, 1st, 2nd, and 3rd layer lines along the a axis, and for the 0th, 1st, and 2nd along the c axis. From the extinction statistics the space group was unambiguously established as D_{4h}^7—$P4/nmm$.

From projections of interatomic vectors onto the planes (001) and (100), the coordinates of the atoms of uranium, copper, phosphorus, and some oxygen atoms were found in the first approximation. The positions of the uranium and phosphorus atoms generally coincided with the corresponding atoms in the structure of meta-autunite $Ca(UO_2)_2(PO_4)_2 \cdot 8H_2O$ proposed by Beintema ([3]).

On the basis of the coordinates found, the signs of the structural amplitudes were calculated and a projection of the electron density onto the coordinate plane $(0yz)$ was constructed. The synthesis of the electron density was carried

Fig. 1. Projection of the electron density of metatorbernite onto the yz plane, (100)

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out using 109 experimental structural amplitudes of type $0kl$. Corrections for absorption and temperature factor were not introduced.

The resulting electron-density projection is shown in Fig. 1 for the case of placing the origin of coordinates at $2/m$.

Maxima 1 and $1'$ with weights 788 and 780 correspond to the positions of uranium atoms, onto which two oxygen atoms from the PO_4 group are projected. Maxima 2 and $2'$ with weights 234 and 222 correspond to phosphorus atoms. Maxima 3 and $3'$ with weights 222 and 124 correspond to copper atoms. Maximum $3'$ with the smaller weight is false and appears, as we established, because of an insufficient number of experimental amplitudes of type $0kl$ with $l = 2n+1$.

Maxima 4 and $4'$, 5 and $5'$, with weights, respectively, 46 and 66, 56 and 64, refer to the oxygens of uranyl groups elongated parallel to the Z axis. Maxima 6 and 7, with weights 37 and 48, together with two other maxima projecting onto the positions of uranium atoms, refer to oxygen atoms from the tetrahedral environment of phosphorus. The doubled positions of water molecules correspond approximately to maxima 8 and $8'$, with weights 34 and 39.

Fig. 1. Projection of the electron density of metatorbernite onto the yz plane, (100)

From the electron-density projection, the coordinates of all the indicated atoms were determined; they occupy the following regular systems of points in the space group D_{4h}^7—$P4/nmm$:

Atom	Position	Coordinate(s)	Note
2U	in $2(c)$	$z = 0.449$	
2U	in $2(c)$	$z = 0.949$	
$2O_I$	in $2(c)$	$z = 0.353$	Oxygen atoms in uranyl groups
$2O_I$	in $2(c)$	$z = 0.549$	Oxygen atoms in uranyl groups
$2O_I$	in $2(c)$	$z = 0.052$	Oxygen atoms in uranyl groups
$2O_I$	in $2(c)$	$z = 0.857$	Oxygen atoms in uranyl groups
2Cu	in $2(c)$	$z = 0.688$	
2P	in $2(a)$		
2P	in $2(b)$		

Atom	Position	Coordinate(s)	Note
$8O_{II}$	in 8(i)	$x =$ 0.064, $z =$ 0.046	
$8O_{II}$	in 8(i)	$x =$ 0.066, $z =$ 0.543	
$8H_2O$	in 8(j)	$x =$ 0.450, $z =$ 0.170	
$8H_2O$	in 8(j)	$x =$ 0.530, $z =$ 0.320	

The coordinates of the water molecules were refined from geometrical analysis. For the structure found, the reliability factor is $R = 0.25$.

Projections of the structure of metatorbernite onto the planes (100) are presented in Fig. 2, and onto the plane (110), in Fig. 3. The designations of the atoms in Fig. 3 are the same as in Fig. 2. The uranyl oxygens are indicated by bold circles and denoted O_I.

From consideration of the structure it is evident that the doubling of the cell along the z axis is caused by the arrangement of the copper atoms and water molecules. From the projections of the structure it is seen that two uranyl radicals, joined to one another through a copper atom, form linear groups extending along the Z axis, with the following interatomic distances (in Å):

$$O^{1.79}\,U^{1.58}\,O^{2.90}\,Cu^{2.40}\,O^{1.74}\,U^{1.66}\,O.$$

The ions of divalent copper link the layers $[(UO_2)_2(PO_4)_2]^{-2}$, which lie parallel to the plane (001) and consist of PO_4 tetrahedra, whose oxygens, together with the uranyl oxygens, form a distorted octahedron around the uranium atoms. Interatomic distances: P—O_{II} = 1.52 Å; U—O_{II} = 2.18 Å; O_{II}—O_{II} = 3.08 Å; O_I—O_I = 2.72—2.84 Å.

Between the layers there are large voids, in which 16 water molecules per unit cell are accommodated. The water molecules, together with the uranyl oxygens, form a distorted octahedron around the copper atoms, with distances: Cu–H_2O = 2.17 Å; O_1–H_2O = 2.36 Å; O_1–H_2O = 2.50 Å.

Fig. 2. Projection of the metatorbernite structure onto the plane yz, (100)

Fig. 3. Projection of the metatorbernite structure onto the plane (110)

Thus, the crystal-chemical formula of metatorbernite will have the form $Cu^{2+}[(UO_2)_2 \cdot (PO_4)_2]^{2-} \cdot 8H_2O$.

Institute of Geochemistry and Analytical Chemistry
named after V. I. Vernadskii
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.