The Synthesis and Crystal Structure of α-Ca$_3$UO$_6$

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Single crystals of α-Ca$_3$UO$_6$ were grown from a UO$_3$–CaCl$_2$–CaO melt by the slow cooling method from 950°C. The crystal structure was determined by means of X-ray diffraction with $R = 0.032$ and $R_w = 0.019$. The structure of α-Ca$_3$UO$_6$ is of Mg$_3$TeO$_6$ type. α-Ca$_3$UO$_6$ is rhombohedral with $a = 6.729$ (1) Å, $\alpha = 90.30$ (1)°, $Z = 2$, $D_c = 4.955$ g/cm^3, $D_m = 4.79$ g/cm^3, space group $R\bar{3}$. Uranium and calcium atoms are six-coordinated. At 1200°C rhombohedral α-Ca$_3$UO$_6$ irreversibly transforms to monoclinic β-Ca$_3$UO$_6$.

Introduction

Ca$_3$UO$_6$ crystallizes in two crystal modifications. The monoclinic form (*1*) with lattice parameters $a = 5.728$ Å, $b = 5.958$ Å, $c = 8.301$ Å, and $\beta = 90.57°$ has two formula units in the unit cell, $D_c = 5.33$ g/cm^3, space group $P2_1$. Structural investigation showed that Ca$_3$UO$_6$ has a perovskite superstructure with the formula Ca$_2$(Ca,U)O$_6$ (*1*). The monoclinic form is stable up to 1400°C (*2*).

The other form of Ca$_3$UO$_6$ was synthesised by Brisi (*3*) from a mixture of Ca(NO$_3$)$_2$ and UO$_2$(NO$_3$)$_2$ at temperatures from 900 to 1100°C in air. This was called the metastable form m-Ca$_3$UO$_6$, as temperatures higher than 1100°C produce the monoclinic form of Ca$_3$UO$_6$. Only characteristic d_{hkl} values and intensities for m-Ca$_3$UO$_6$ were given in this work (*3*). In the present work the metastable form of Ca$_3$UO$_6$ is labeled α-Ca$_3$UO$_6$ and the monoclinic form β-Ca$_3$UO$_6$.

Preparation of the single crystals, the crystal structure, and some thermochemical properties of α-Ca$_3$UO$_6$ are reported in this paper.

Experimental

Crystals of α-Ca$_3$UO$_6$ were grown by the method of slow cooling of the melt. Starting materials were U$_3$O$_8$ (nuclear grade), CaO (Ventron 99.95%), and CaCl$_2$ (Kemika, p.a.).

α-Ca$_3$UO$_6$ crystals were observed when growing Ca$_2$UO$_5$ crystals from the melt CaCl$_2$–CaO–UO$_3$. Besides orange crystals of Ca$_2$UO$_5$, yellow crystals of α-Ca$_3$UO$_6$ were produced. The best conditions for its growth were 70 mole% CaCl$_2$, 10 mole% CaO, and 20 mole% U$_3$O$_8$. The mixture was usually heated in air in a covered Pt crucible, with a volume of 20 cm^3, with a heating rate of 600°C/hr up to 950°C. The sample was held at this temperature for 24 hr. The mixture was then cooled down to 700°C at a cooling rate of 12°C/hr and the furnace was turned off. Single crystals of α-Ca$_3$UO$_6$ up

to 1 mm in diameter with hexagonal habit and Ca$_2$UO$_5$ were leached out from the mixture with cold water. The different crystals were sorted out.

Differential thermal and thermogravimetric analysis of the crystals were made on Netzsch equipment, model STA 429, in a Pt-Holder in air. The heating and cooling rate was 300°C/hr. The sample weight was 150 mg, and the accuracy of the measured weight changes was 0.1 mg.

The density was measured by displacement of hexane in an evacuated pycnometer. Measuring precision was ±0.05 g/cm^3.

α-Ca$_3$UO$_6$ crystallizes in the rhombohedral space group $R\bar{3}$ (No. 148) with cell dimensions $a = 6.729$ (1) Å and $\alpha = 91.30$ (1)°, $Z = 2$, $M = 454.26$, $V = 304.45$, $F(000) = 400$.

Cell dimensions were determined by least-squares refinement, using the θ values of 90 reflections in the range $12° < \theta < 19°$ measured with MoKα_1 (graphite monochromator $\lambda = 0.70926$ Å, $T = 293(1)$ K) radiation on a CAD-4 Enraf Nonius diffractometer.

Three-dimensional diffractometer data were collected on the same diffractometer. The experimental conditions were MoKα radiation (graphite monochromator $\lambda = 0.71069$ Å), $D_m = 4.79(5)$ g/cm^3, $D_c = 4.955$ g/cm^3 crystal size 0.28 × 0.32 × 0.38 mm, ω-2θ, 2$\theta \le 70°$, 2θ scan width (°) = 0.7 + 0.2 tan aperture (mm) = 2.4 + 0.9 tan θ, maximum scan time = 40 sec, background $\frac{1}{4}$ of the scan time at each of the scan limits, intensity control after every 120 reflections with 303, 332, and 400 reflections. There was a 1.7% intensity decrease during the data collection, and a complete sphere of 6639 reflections was measured. An exact absorption correction was made (linear absorption coefficient = 277.14 cm^{-1}, 13 crystal faces, 10 × 10 × 10 grid points) with minimum and maximum values of transmission of 0.007 and 0.05, respectively. Equivalent reflections were averaged (R_{int} =

4.5%) to give 1259 unique reflections, of which 17 were considered to be unobserved with $I \le 3\sigma(I)$.

The structure was solved by the heavy-atom method. A Patterson function suggested placing U atoms at the 1 (a) and 1 (b) positions. The positions of the other atoms were found from a Fourier synthesis. The full-matrix least-squares refinement with anisotropic thermal parameters reduced R and R_w values to 0.032 and 0.019. The empirical weighting function $W = W_f \times W_s$ where

$$W_f(|F_o| < 36.0) = (|F_o|/36.0)^{2.1}$$

$$W_f(|F_o| > 50.0) = (50.0/|F_o|)^{2.5}$$

$$W_f(36.0 < |F_o| < 50.0) = 1.0$$

and

$$W_s(\sin \theta < 0.4) = (\sin \theta/0.4)^2$$

$$W_s(\sin \theta > 0.5) = (0.5/\sin \theta)^2$$

$$W_s(0.4 > \sin \theta < 0.5) = 1.0$$

was applied to keep $\Sigma w|F|^2$ uniform over the ranges of (sin θ/λ) and $|F_o|$. The ratio of maximum least-squares shift to error in the final refinement cycle was 0.5 (extinction) and the average shift to error ratio was 0.02. The data (m) to variable (n) ratio was 38 with $S = (|\Sigma w(|F_o| - |F_c|)^2/(m - n)|^{\frac{1}{2}})$ equal to 0.64.

An isotropic extinction correction (4) was taken into account (2.67). Atomic scattering and dispersion factors (5, 6) for neutral atoms U, Ca, and O were used. All calculations were carried out on the DEC System-10 computer at the University Computer Center in Ljubljana, with the X-RAY 76 system of crystallographic programs (7).

Results and Discussion

When the structure of α-Ca$_3$UO$_6$ was determined an isostructural compound, Mg$_3$TeO$_6$ was already known (8). As found

TABLE I

FINAL FRACTIONAL COORDINATES ($\times 10^5$) AND
EQUIVALENT ISOTROPIC TEMPERATURE FACTOR
($\times 10^5$)

	x	y	z	U_{eq}
Ca	25087(7)	6039(7)	55664(7)	648(15)
(Mg)	(24850)	(6320)	(55360)	
U(1)	00000(0)	00000(0)	00000(0)	298(6)
(Te(1))	(00000)	(00000)	(00000)	
U(2)	50000(0)	50000(0)	50000(0)	292(6)
(Te(2))	(50000)	(50000)	(50000)	
O(1)	41310(35)	54186(35)	20610(34)	847(72)
(O(1))	(45560)	(59010)	(19920)	
O(2)	6530(33)	92572(35)	29244(35)	846(73)
(O(2))	(6930)	(92770)	(29970)	

by those authors (9), the compound belongs to a new structure type. it is isostructural with the series of tellurates and antimonates of the type M_3XO_6 (where $X = Te^{6+}$ or Sb^{5+}) (9, 10) and with Ho_3ScO_6, Y_3ScO_6, and Dy_3ScO_6 (12). Final fractional coordinates with Ueq (11), for our compound are given in Table I. The coordinates for the corresponding atoms of Mg_3TeO_6 (8), are given in parentheses as proof that the compounds are isostructural.

The structure of α-Ca_3UO_6 is formed from UO_6 and CaO_6 octahedra; see Fig. 1. The octahedra $U(1)O_6$ and $U(2)O_6$ are regular, as can be seen from the interatomic distances (Table II). CaO_6 octahedra are very distorted, as shown from the Ca–O interatomic distances, which vary form 2.306 to 2.492 Å, and from the angles. Each UO_6 octahedron shares edges with six CaO_6 octahedra, but none with other UO_6 octahedra. Each CaO_6 octahedron is linked by its edges to two UO_6 octahedra, and by four edges with other CaO_6 octahedra.

All oxygen atoms are surrounded by one uranium atom and three calcium atoms, in the form of a distorted tetrahedron.

In Table III the U–O bond distances in some known Ca-uranates are collected (13). In the $CaUO_4$ structure, a uranium atom has the coordination number 8 (14). Two oxygen atoms are at a distance of 1.963 Å and form a O–U–O bond. Ca has coordina-
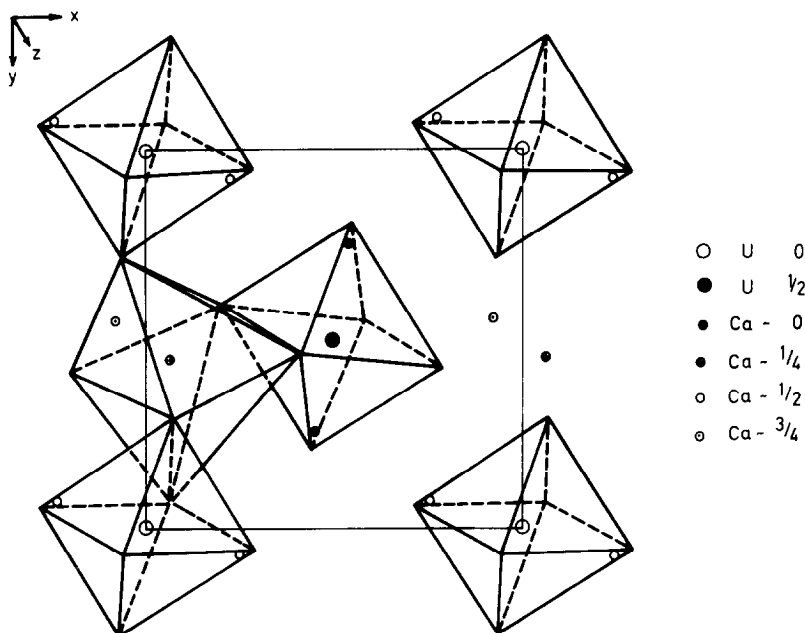

FIG. 1. Projection of atoms down [001] plane.

TABLE II

SELECTED INTERATOMIC DISTANCES (Å) AND BOND
ANGLES (°) IN α-Ca₃UO₆

U(1)–O(2^i)	2.0810(24)Å	×6
O(2)^i–U(1)–O(2)^{iv})	180.0(1)°	×3
O(2)^i–U(1)–O(2)^{iii})	95.68(9)°	×6
O(2)^i–U(1)–O(2)^{ii})	84.32(9)°	×6
U(2)–O(1)^i	2.0767(23)Å	×6
O(1)^i–U(2)–O(1)^{iv})	180.0(1)°	×3
O(1)^i–U(2)–O(1)^{iii})	85.66(9)	×6
O(1)^i–U(2)–O(1)^{ii})	94.34(9)	×6
Ca–O(2^i)	2.3056(23)	×1
Ca–O(1^v)	2.3064(24)	×1
Ca–O(2^{iv})	2.3810(23)	×1
Ca–O(1^{ii})	2.4021(24)	×1
Ca–O(1^{iii})	2.4032(24)	×1
Ca–O(2^{iii})	2.4923(24)	×1
O(2)^i–Ca–O(2^{iv})	82.75(8)°	×1
O(2)–Ca–O(1^{iii})	105.26(8)°	×1
O(2)^{iv}–Ca–O(1^{iii})	81.71(8)°	×1
O(1)^{iii}–Ca–O(1^{ii})	71.97(8)°	×1
O(1)^{ii}–Ca–O(1^v)	81.67(8)°	×1

Note: Symmetry code:

	x	y	z
i	x	y	z
ii	y	z	x
iii	z	x	y
iv	$\bar{x}$	$\bar{y}$	$\bar{z}$
v	$\bar{y}$	$\bar{z}$	$\bar{x}$
vi	$\bar{z}$	$\bar{x}$	$\bar{y}$

tion number 5, and the average bond length is 2.45 Å.

In the structure of Ca_2UO_5, the uranium atom is six-coordinated. Distorted uranium octahedra share opposite corners and form infinite chains of UO_5 units. The coordination number of Ca is 7.

Uranium atoms and one third of the Ca atoms in β-Ca_3UO_6 are six-coordinated (*1*). Distorted octahedra share corners to form a net. The average Ca–O distance is 2.31 Å. The rest of the Ca atoms have a coordination number of 12.

Comparing the U–O bond length in α-Ca_3UO_6 with the bond length in other Ca-uranates it can be seen that it is comparable

to the average U–O bond lengths for six-coordinated uranium in Ca_2UO_5 and β-Ca_3UO_6. The average Ca–O bond length in α-Ca_3UO_6 is 2.38 Å, which is longer than the average distance of the six-coordinated Ca atoms in β-Ca_3UO_6, namely 2.31 Å.

As can be seen from the theoretical densities of β-Ca_3UO_6 (D_c = 5.33 g/cm³) and α-Ca_3UO_6 (D_x = 4.955 g/cm³), the stack of atoms is denser in β-Ca_3UO_6. TG analysis of α-Ca_3UO_6 showed the compound to be stoichiometric regarding oxygen up to 1400°C. DTA showed a strong endothermic peak at 1200°C, which was not detected on cooling. By X-ray analysis it was proved that α-Ca_3UO_6 irreversibly transforms in air to the monoclinic form β-Ca_3UO_6. This agrees with the results of Brisi (*3*), who did not find α-Ca_3UO_6 at temperatures higher than 1100°C.

According to the third Pauling rule, presence of shared edges or faces of coordination polyhedra decreases the stability of structure. In α-Ca_3UO_6 structure each UO_6 octahedron shares edges with CaO_6 octahedra, while in β-Ca_3UO_6 all octahedra share their vertexes. Minimal interatomic distance between Ca atoms in α-Ca_3UO_6 is 4,08 Å, i.e., essentially less than 4,81 Å

TABLE III

BOND DISTANCES U–O IN SOME Ca-uranates (*13*)

Compound	Atom(1)–atom(2)	Distance	
CaUO₄	U–O(1)	1.963(2)Å	×2
	U–O(2)	2.298(1)	×6
Ca₂UO₅	U(1)–O(2)	2.022(7)	×2
	U(1)–O(4)	2.027(7)	×2
	U(1)–O(5)	2.247(9)	×2
	U(2)–O(1)	2.128(8)	×2
	U(2)–O(3)	1.953(8)	×2
	U(2)–O(5)	2.206(9)	×2
β-Ca₃UO₆	U–O(1)	2.102(30)	×1
	U–O(2)	2.034(27)	×1
	U–O(3)	2.023(32)	×1
	U–O(4)	2.112(28)	×1
	U–O(5)	2.026(28)	×1
	U–O(6)	2.181(33)	×1

which is the corresponding distance in β-Ca_3UO_6. On the other side the U–U distance in both structures is approximately equal. Perhaps the less stable structure of α-Ca_3UO_6 can be explained on the basis of cation–cation interactions which after O'Keeffe et al. (16) play a much larger role in determining the structure as it was believed to be up to now.

Acknowledgments

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