fiercely) for the vacuum cleavage operation. In addition to the variation in condensation rate, the form of deposit in the neighbourhood of mosaic boundaries may also vary, as shown in Fig. 10. It must again be emphasized that the crystallographic orientation in the film of Fig. 10 was very highly developed. The directions of the furrows appeared quite unrelated to the directions of the deposit crystal axes.

Conclusion

By choice of suitable substrate, deposition temperature and rate of deposition it has proved possible to grow films of iron in single orientation. Potassium chloride and potassium iodide are particularly suitable, at 330 °C and at a deposition rate of the order 300 Å.min^{-1}.

The structure of the iron deposit obtained depends on whether or not the substrate has been exposed to air. As has been previously observed, epitaxic growth takes place on vacuum-cleaved surfaces at significantly lower temperatures than for surfaces which have been exposed to air. Whereas a temperature of 320 °C is required for complete orientation of iron on air-cleaved potassium iodide, a temperature of 260 °C suffices for the vacuum-cleaved material. Deposition during the act of cleaving the crystal ensures a minimum of interference from residual gas atoms and exposes the deposit material more strongly to the substrate forces. In contrast, however, to earlier work, a qualitative difference is observed in the decoration effects of the iron nuclei compared with those obtained with gold. Although generally similar decoration effects have been observed as with gold, such decoration was obtained only on surfaces which had not been exposed to air. Strong etch figures developed on air-exposed surfaces under conditions for which no trace of etching was observed on the vacuum-cleaved surface. Although this suggests a powerful effect of the adsorbed air, or probably water and carbon dioxide, on the surface, it is not clear how the initial adsorbed layer can result in etching to the very substantial depths observed.

The mobility of iron atoms on the potassium iodide surface appears to be lower than that generally observed for silver and gold on halide surfaces, leading to decoration patterns of somewhat higher resolution than is possible with the noble metals.

References

Bassett, G. A. (1958). *Phil. Mag.* **3**, 1042.
Brück, L. (1936). *Ann. Phys. Lpz.* **26**, 233.
Collins, L. E. & Heavens, O. S. (1957). *Proc. Phys. Soc.* B, **70**, 265.
Gobeli, G. W. & Allen, F. G. (1960). *Phys. Chem. Solids.* **14**, 23.
Heavens, O. S. (1959). *J. Sci. Instrum.* **36**, 95.
Heavens, O. S., Brown, M. M. & Hinton, V. (1959). *Vacuum,* **9**, 17.
Heavens, O. S., Moss, G. L., Miller, R. F. & Anderson, J. C. (1961). *Proc. Phys. Soc.* **78**, 33.
Honjo, G. (1964). In *Single-Crystal Films.* Ed. Francombe & Sato, Pergamon Press.
Sella, C., Conjeaud, P. & Trillat, J. J. (1958). *Proc. Fourth Intern. Conf. Electron Microscopy, Berlin,* **1**, 508.
Sella, C. & Trillat, J. J. (1964). In *Single-crystal Films.* Ed. Francombe & Sato, Pergamon Press.
Shirai, S. (1937). *Proc. Phys. Math. Soc. Japan,* **19**, 937.
Shirai, S. (1938). *Proc. Phys. Math. Soc. Japan,* **20**, 855.

Acta Cryst. (1966). **20**, 292

The Crystal Structure of High-Pressure UO_3*

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The high pressure modification of uranium trioxide is orthorhombic with $a = 7{\cdot}511 \pm 0{\cdot}009$, $b = 5{\cdot}466 \pm 0{\cdot}008$, and $c = 5{\cdot}224 \pm 0{\cdot}008$ Å. The unit cell contains four formula weights and the space group is $P2_12_12_1$. Each uranium atom is bonded to seven oxygen atoms leading to shared $[UO_7]$ configurations. Two short bonds of 1·80 Å and 1·85 Å are nearly equal and collinear and are identified as uranyl bonds. The five secondary bonds form a puckered pentagonal coordination about the uranyl groups. The formula may thus be written as $(UO_2)O$. Bond distances vary considerably but are consistent with published bond strength–bond length values.

Introduction

Six crystalline forms of UO_3 and one amorphous modification are known. The high pressure type described here is the seventh polymorph to be reported and was produced at a pressure of 30 kilobars and a temperature of 1100 °C. Crystals suitable for structural studies were prepared at pressure and temperature.

Crystallographic data

The symmetry is orthorhombic with

$$a = 7{\cdot}511 \pm 0{\cdot}009 \text{ Å}$$
$$b = 5{\cdot}466 \pm 0{\cdot}008$$
$$c = 5{\cdot}224 \pm 0{\cdot}008$$
$$D_{\text{X-ray}} = 8{\cdot}85 \text{ g.cm}^{-3}$$
$$D_{\text{meas.}} = 8{\cdot}62 \text{ g.cm}^{-3}.$$
$$Z = 4$$

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* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

Reflections $h00$ with h odd are absent, $0k0$ with k odd are absent, and $00l$ with l odd are absent. This leads to space group $P2_12_12_1$ with all atoms in general positions $x, y, z; \frac{1}{2}-x, \bar{y}, \frac{1}{2}+z; \frac{1}{2}+x, \frac{1}{2}-y, \bar{z}; \bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$.

Experimental

Mo $K\bar{\alpha}$ radiation ($\lambda=0{\cdot}71069$ Å) was used in the investigation, and for this wavelength the linear absorption coefficient is 925 cm^{-1}. Crystals of rough spherical shape produced by grinding were found to be satisfactory for intensity measurements. The crystal used in this study had an average diameter of $0{\cdot}070 \pm 0{\cdot}005$ mm.

Data were obtained with a single-crystal orienter mounted on an XRD-5 diffraction unit. Nearly the entire sphere for reflections up to $2\theta=50°$ was investigated and intensities were obtained with the use of balanced filters. The reflections were maximized and intensity values were taken as the difference in readings for the two filters. A total of 1213 reflections was recorded and averaged to give 247 values to be used in a least-squares program. Absorption, Lorentz, and polarization corrections were applied in the usual manner.

Determination of the structure

Uranium positions were determined simply by trial, for the diffraction intensities arise primarily from the uranium atoms. These positions were used in a least-squares refinement in order to help establish an absolute scale for the observed data as well as to obtain better uranium coordinates. The refinement was based on the Busing, Martin & Levy Fortran crystallographic least-squares program.

The averaged observed F_{hkl} and $F_{\bar{h}\bar{k}\bar{l}}$, and the calculated structure factors for uranium, were corrected for the effects of anomalous dispersion using the method described by Zachariasen (1965). The f curves for uranium and oxygen were taken from *International Tables for X-ray Crystallography* (1962), while the anomalous dispersion corrections of $\Delta f'=-9{\cdot}19$ and $\Delta f''=9{\cdot}09$ electrons were obtained from recent values given by Cromer (1965).

The least-squares refinement based on uranium positions alone led to a reliability index R of 0·081 with $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. The uranium contribution was then removed from F_{obs} and a difference Fourier synthesis prepared. Oxygen peaks appeared, and these coordinates, with uranium positions, were used in a least-squares refinement which gave an R index of 0·042 without weighting. However, elimination of five reflections, 200, 201, 401, 011, and 321, which showed poor agreement, reduced R to 0·034. The coordinates obtained from the latter refinement are presented in Table 1. Observed and calculated structure factors are tabulated in Table 2.

Discussion of the structure

The structure is shown in Fig. 1 as projected on the xz plane.

Each uranium atom is bonded to seven oxygen atoms leading to the identification of $[UO_7]$ groups. Each oxygen atom within a group shares with two or three uranium atoms to form an extended network of shared oxygen atoms throughout the structure. Bond distances for the configuration are given in Table 3.

The four oxygen atoms O(1), O(1‴), O(3‴), O(2′), and uranium U(1′) are nearly planar. A least-squares plane through these atoms shows atomic displacements ranging from 0·008 to 0·11 Å along the normals. Atoms O(3″), U(1′), O(3), and O(2″), however, show only negligible displacements along the normals from their corresponding least-squares plane. The two planes defined by these atoms make an angle of 86° with each

Table 2. *Observed and calculated structure factors*

hkℓ	|Fo|	|Fc|	hkℓ	|Fo|	|Fc|	hkℓ	|Fo|	|Fc|
200	167	190	601	92	94	502	77	74
400	50	47	701	42	39	602	160	167
600	144	148	801	57	57	702	16	1
800	149	152	011	199	221	802	122	129
110	98	92	111	171	183	012	47	45
210	167	170	211	118	122	112	129	125
310	173	175	311	79	76	212	141	139
410	177	182	411	57	52	312	145	146
510	126	125	511	89	89	412	149	152
610	72	67	611	123	124	512	101	101
710	15	12	711	115	115	612	86	88
810	45	44	811	108	111	712	47	47
020	26	23	021	41	40	812	55	55
120	200	210	121	121	119	022	30	26
220	24	20	221	80	73	122	215	227
320	86	80	321	216	229	222	89	86
420	6	2	421	32	26	322	47	42
520	151	146	521	156	160	422	85	84
620	16	19	621	48	45	522	93	92
720	177	185	721	22	14	622	41	43
820	17	13	821	22	21	722	133	137
130	94	87	031	151	147	822	22	24
230	121	109	131	173	174	032	62	59
330	179	175	231	87	83	132	105	97
430	130	124	331	65	62	232	102	98
530	128	127	431	47	44	332	149	147
630	50	47	531	89	89	432	108	106
730	15	12	631	87	88	532	106	106
830	29	32	731	119	122	632	70	75
040	243	248	041	21	15	732	31	33
140	44	41	141	49	44	042	163	159
240	135	130	241	148	148	142	44	43
340	14	5	341	44	40	242	114	111
440	31	33	441	174	176	342	79	76
540	25	19	541	37	34	442	36	32
640	120	119	641	73	73	542	62	60
740	24	28	051	154	153	642	125	128
150	46	41	151	84	83	052	30	25
250	119	117	251	90	91	152	75	73
350	90	85	351	46	43	252	103	104
450	141	140	451	37	33	352	77	75
550	69	65	551	47	51	452	116	118
060	38	42	061	28	27	552	59	59
160	122	124	161	63	64	062	40	43
260	29	31	261	43	46	162	119	124
360	40	41	361	129	133	262	52	54
101	70	64	002	203	214	103	131	130
201	193	212	102	45	41	203	150	146
301	48	42	202	160	157	303	46	44
401	213	238	302	109	105	403	159	154
501	32	28	402	41	36	503	74	70

Table 1. *Position parameters and temperature factors*

Atom	x	y	z	B
U	0·06991 ± 0·00013	0·13289 ± 0·00018	0·03502 ± 0·00018	0·40 Å^2
O(1)	0·4947 ± 0·0026	0·1263 ± 0·0040	0·3284 ± 0·0035	1·12
O(2)	0·1604 ± 0·0028	0·3872 ± 0·0045	0·2124 ± 0·0042	1·45
O(3)	0·6735 ± 0·0024	0·6176 ± 0·0040	0·6654 ± 0·0037	0·73

Table 2 (*cont.*)

hkl	|Fo|	|Fc|	hkl	|Fo|	|Fc|
603	72	69	024	13	12
703	97	99	124	119	115
013	138	135	224	113	111
113	122	120	324	38	35
213	131	131	424	128	131
313	99	94	524	59	57
413	80	78	624	51	53
513	93	94	034	124	120
613	98	98	134	74	73
713	82	84	234	93	91
023	147	146	334	89	87
123	75	71	434	59	57
223	85	81	534	81	81
323	160	150	044	100	99
423	34	31	144	57	57
523	115	118	244	66	64
623	83	85	344	110	112
723	17	10	444	29	30
033	93	89	054	68	69
133	120	117	105	148	148
233	110	108	205	69	64
333	73	68	305	50	47
433	84	85	405	71	70
533	85	83	505	76	77
633	75	77	015	66	63
043	24	20	115	75	73
143	99	98	215	79	79
243	109	109	315	107	107
343	40	40	415	98	99
443	121	110	515	78	79
543	59	58	025	149	149
053	109	108	125	35	33
153	69	68	225	85	85
253	83	86	325	69	68
353	77	77	425	30	31
004	137	130	035	49	47
104	74	70	135	67	66
204	83	79	235	82	83
304	144	144	335	79	78
404	31	26	045	21	25
504	109	108	006	49	49
604	92	90	106	69	67
014	131	128	206	23	26
114	100	98	016	95	93
214	106	103	116	96	100
314	88	85			
414	83	81			
514	95	90			
614	67	69			

other. The U(1′)–O(3″) bond direction is nearly normal to the plane of four oxygen atoms, the various bond angles being specified in Table 3.

Bonds U(1′)–O(1) = 1·85 Å, and U(1′)–O(2′) = 1·80 Å form a bond angle near 180° as do bonds U(1′)–O(1‴) = 2·38 Å and U(1′)–O(3‴) = 2·22 Å. The deviations of the bond angles from 180° amount to about 9°. The two short bonds are essentially equal in length and collinear within experimental error and can be considered as uranyl bonds but with lengths slightly longer than observed for a pure uranyl configuration. The remaining five secondary bonds then form a puckered pentagonal configuration about the uranyl group. The formula for the compound may thus be written as $(UO_2)O$.

The first instance of a fivefold coordination about the uranyl group was reported by Zachariasen (1954) for $K_3UO_2F_5$, with fluorine atoms forming a nearly plane pentagon. Evans (1963), in a discussion of uranyl ion coordination, considers the pentagonal configuration to be geometrically stable and has indicated the role that the pentagonal coordination may have in explaining the crystallography of uranyl hydroxides.

The structure is characterized by a wide range of uranium–oxygen bond lengths, ranging from 1·80 to 2·56 Å. The latter value is quite large; however, bond length values up to 2·49 Å are known for uranyl compositions. All oxygen–oxygen distances are normal, and uranium–uranium distances vary from 3·690 ± 0·005 to 4·279 ± 0·005 Å.

Each O(3) atom is bonded to three uranium atoms. On the basis of the bond strength-bond length curve published by Zachariasen & Plettinger (1959) for U^{6+} compositions, this bond strength value of $\frac{2}{3}$ should correspond to a bond length of 2·28 Å. The actual observed bond lengths are 2·22, 2·20 and 2·38 Å. However, if the bond strengths corresponding to the observed bond distances are taken from the published bond strength curve, the total bond strength for the

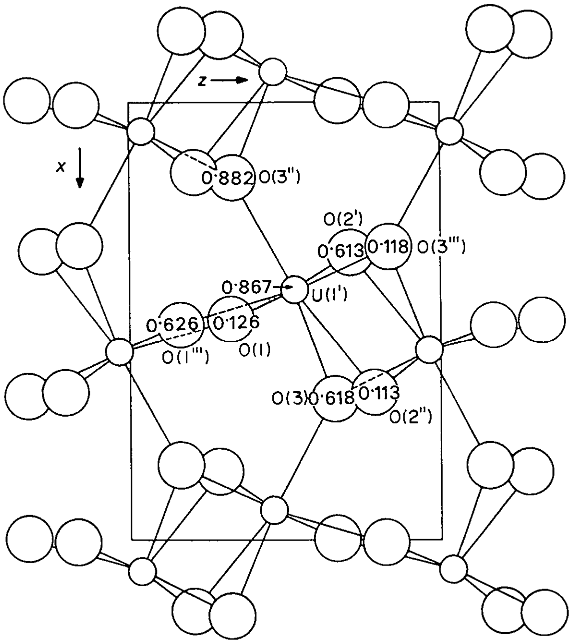

Fig. 1. Structure of UO_3 projected on *xz* plane.

Table 3. *Interatomic distances and bond angles*

U(1′)–O(1)	1·85 ± 0·02 Å	O(1‴)–O(3)	2·87 ± 0·03 Å
U(1′)–O(2′)	1·80 ± 0·02	O(1‴)–O(3″)	2·98 ± 0·03
U(1′)–O(1‴)	2·38 ± 0·02	O(1)–O(3″)	2·76 ± 0·03
U(1′)–O(3‴)	2·22 ± 0·02	O(3‴)–O(3″)	3·10 ± 0·03
U(1′)–O(3″)	2·20 ± 0·02	O(1)–O(3‴)	2·93 ± 0·03
U(1′)–O(3)	2·38 ± 0·02	O(1‴)–O(2′)	3·09 ± 0·03
U(1′)–O(2″)	2·56 ± 0·02	< O(1)–U(1′)–O(1‴)	84 ± 0·2°
O(1)–O(1‴)	2·85 ± 0·02	< O(2′)–U(1′)–O(3‴)	88·9 ± 1
O(2′)–O(3‴)	2·83 ± 0·04	< O(2″)–U(1′)–O(3)	68·5 ± 0·8
O(2″)–O(3)	2·78 ± 0·03	< O(1)–U(1′)–O(3″)	85·5 ± 0·8
O(2′)–O(3″)	2·76 ± 0·03	< O(1‴)–U(1′)–O(3″)	81·3 ± 0·9
O(2″)–O(3‴)	2·52 ± 0·03	< O(3‴)–U(1′)–O(3″)	90 ± 1·0
O(2′)–O(3)	2·52 ± 0·03	< O(2′)–U(1′)–O(3″)	86·8 ± 1·0
O(1)–O(2″)	2·70 ± 0·03		

O(3)–3(U) bond is 2·06. In a similar manner, we find a total bond strength of 1·95 for O(1)–2U and 1·80 for O(2)–2U. For the uranium atom, bond distances vary from 1·80 Å to 2·56 Å, but the total bond strength becomes 5·83 for U–7(O).

The deviations of the total bond strengths from the valences 2 and 6 are probably not significant because of the errors in the coordinate positions. However, it is observed that a number of U–O 'interactions' as low as 3·2 Å are found, and these may contribute to the total bond strength. The accuracy of intensity measurement is not sufficiently high to establish this point.

The temperature factor for O(3) is substantially lower than for the remaining oxygen atoms. This seems reasonable, for the O(3) atom forms three uranium bonds.

References

Cromer, D. T. (1965). *Acta Cryst.* **18**, 17.

Evans, H. T., Jr. (1963). *Science*, **141**, 154.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Zachariasen, W. H. (1954). *Acta Cryst.* **7**, 783.

Zachariasen, W. H. (1965). *Acta Cryst.* **18**, 714.

Zachariasen, W. H. & Plettinger, H. A. (1959). *Acta Cryst.* **12**, 526.

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The Crystal Structure of Calcium Beryllate, $Ca_{12}Be_{17}O_{29}$*

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Calcium beryllate crystallizes in the cubic system with $a_0 = 14{\cdot}023 \pm 0{\cdot}005$ Å. Its crystal structure has been determined by standard three-dimensional Patterson and difference Fourier methods. Refinement of the structure in the acentric space group $F\bar{4}3m$ by iterative structure-factor least-squares calculations gave a final error index $R = 0{\cdot}066$. The ideal composition of the compound was found to be $Ca_{12}Be_{17}O_{29}$ (4 formula weights per unit cell) as a result of this analysis.

The structure is described as composed of rods of close atom packing running parallel to ⟨110⟩ crystal directions and intersecting at 4(*b*) sites of $F\bar{4}3m$. As the rods diverge from the 4(*b*) sites, large (5·4 Å free diameter) holes are left centered at 4(*a*) positions.

Two types of calcium-oxygen coordination are found; one has eight oxygen atoms in the form of a rectangular prism about a calcium atom while the other is a sixfold grouping similar to that reported in cubic rare-earth oxides. Of the 68 beryllium atoms per unit cell, twenty have nearly normal tetrahedral oxygen atom coordinations. Thirty-two beryllium atoms have three close and one long oxygen atom contact; the remaining sixteen have an unusual trigonal oxygen atom coordination.

Introduction

The formation of a compound near 60 mole % BeO in the binary system BeO–CaO was first reported by Ader & Bingle (1956), but a later study of the phase equilibria in this system by Potter & Harris (1962) suggested that the compound might be metastable. The growth of single crystals of calcium beryllate permitted Harris, Potter & Yakel (1962) to determine preliminary crystallographic data for the material.

The purpose of this paper is to present results of an X-ray crystal structure analysis of calcium beryllate.

Experimental

Single crystals of calcium beryllate were obtained by melting in air a powdered mixture of 60 mole % BeO, 40 mole % CaO on the platinum strip of a resistance furnace, and then quenching. The quenched product readily yielded water-clear optically isotropic fragments which were found to be single crystals in most cases. A typical crystal had the general form of an elongated plate with a {110} type plane parallel to the plate face and with a direction between a ⟨110⟩-type and a ⟨111⟩-type direction parallel to the elongated crystal axis.

The diffraction symbol *m*3*mF* . . ., which embraces space groups *F*432, $F\bar{4}3m$, and *Fm*3*m*, was indicated by diffraction data obtained from rotation, Weissenberg, and precession photographs (Cu *Kα* radiation, $\lambda = 1{\cdot}54178$ Å) as well as selected intensity measurements of reflection pairs of the type *hk*0, *kh*0 and *hkl*, *hlk*. An X-ray density of $2{\cdot}64 \pm 0{\cdot}01$ ($g.cm^{-3}$) was computed on the basis of 4 formula weights of $Ca_{12}Be_{17}O_{29}$ per cell – the composition suggested by the results of the structure analysis to be described. The lattice parameter was determined from high-angle reflections on a calibrated zero layer Cu *Kα* Weissenberg film about a [110] lattice direction.

Initial intensity data were collected from a plate-shaped crystal having dimensions $0{\cdot}039 \times 0{\cdot}057 \times 0{\cdot}200$

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