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X-RAY STUDIES OF SYNTHETIC COFFINITE, THORITE AND URANOTHORITES*

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ABSTRACT

X-ray data are presented for synthetic coffinite, thorite, and several uranothorites. The cell constants obtained for coffinite are $a=6.981\pm0.004$ kX, $c=6.250\pm0.005$ kX; for thorite $a=7.128\pm0.004$ kX, $c=6.314\pm0.003$ kX. Intermediate constants determined for several uranothorites indicate a continuous solid solution between $USiO_4$ and $ThSiO_4$. Coffinite and thorite are isostructural with zircon; the space group is D_{4h}^{19}—$I_4/a\ md$. The oxygen positions for coffinite are $u=0.180\pm0.010$, $v=0.347\pm0.010$ and for thorite $u=0.166\pm0.010$ $v=0.347\pm0.010$. No changes were observed either in line intensities or in cell constants when (OH) was removed from the hydrothermal preparations.

The mineral coffinite, described as a uranous silicate with hydroxyl substitution, was identified on the basis of the similarity of its *x*-ray powder pattern to that of zircon ($ZrSiO_4$) or thorite ($ThSiO_4$) (Stieff, Stern and Sherwood, 1956). Pabst (1951) obtained single crystal patterns of a New Zealand detrital uranothorite (11.5 wt% UO_2) and determined the space group to be the same as given for zircon. A similar assignment was made by Bonatti and Gallitelli (1951) on detrital thorite crystals from Nettuno Rome.

Although coffinite is isostructural with zircon and thorite, the naturally occurring mineral is reported to exist as the hydroxyl substituted form of $USiO_4$ (Stieff, Stern and Sherwood, 1956). This consideration is based on the low silicon content which appears in the analyses of the mineral. However, our observations on a synthetic product (Hoekstra and Fuchs, 1956) indicate that neither cell dimensions nor line intensities appear to be modified when water is removed, suggesting therefore that the synthesized product may be $USiO_4$ without hydroxyl substitution. Infrared examination of heated samples made in this laboratory clearly indicate that water has been expelled (Hoekstra and Fuchs, to be published).

In addition to coffinite, we have synthesized thorite and some uranothorites. The thorite can be prepared by a hydrothermal process or from the melt (Fuchs, 1958). The latter process yields water-free samples, and again it does not seem possible to distinguish between hydroxyl-containing and hydroxyl-free samples on the basis of *x*-ray powder patterns.

Powder data for the synthesized coffinite and thorite are presented in Table I. Cell dimensions and *x*-ray densities for these samples are given

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

TABLE I. *X*-RAY DATA FOR COFFINITE AND THORITE. $CuK\alpha_{1,2}=1.5386$ kX

Coffinite

hkl	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	I_o	I_c
101	0.02758	0.02759	197	214
200	.04917	.04912	203	227
211	.07636	.07653	96	105
112	.08540	.08538	196	184
220	.09784	.09792	53	58
202	.1097	.1098	9	5
301	.1252	.1252	62	54
103	.1489	.1490	60	38
321	.1737	.1739	69	58
312	.1827	.1829	144	141
400 213	.1964	.1953 .1977 } .1965	66	67
411	.2227	.2226	32	25
004 420 303	.2437	.2429 .2440 .2464 } .2444	53	53
402	—	.2559	0	<1
332	.2802	.2802	47	37
204	.2913	.2916	48	30
323	.2948	.2951	10	12
422	—	.3045	0	<1
501 431	0.3200	0.3199	34	29
224 413	.3405 .3433	.3402 .3437	47	45
314	—	.3646	0	<1
521	.3684	.3685	15	10
512	.3777	.3774	36	38
440 105	.3906	.3898 .3914 } .3906	18	14
404 600 215 503 433	.4390	.4375 .4383 .4400 .4409 .4409 } .4395	56	52
611	.4649	.4655	13	9
532	.4753	.4745	37	30
424 620 305 523	.4870	.4860 .4868 .4886 .4894 } .4877	60	59
602	—	.4988	0	<1

Thorite

hkl	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	I_o	I_c
101	0.02669	0.02666	174	208
200	.04711	.04712	210	249
211	.07348	.07357	99	111
112	.08287	.08299	162	188
220	.09376	.09376	63	68
202	.1065	.1064	6	4
301	.1202	.1202	63	57
103	.1456	.1456	42	40
321	.1672	.1669	67	63
312	.1765	.1764	135	140
400	.1870	.1870	40	34
213	.1924	.1922	33	39
411	.2138	.2134	25	24
420	.2335	.2335	39	35
004 303	.2383	.2378 .2388 } .2383	18	19
402	—	.2462	0	<1
332	.2695	.2694	38	39
204 323	.2847	.2843 .2854 } .2849	36	41
422	—	.2926	0	0
501 431	0.3066	0.3064	27	30
224 413	.3315	.3309 .3318 } .3314	36	43
521	.3534	.3529	10	11
314	—	.3541	0	<1
512	.3627	.3624	38	39
440	.3732	.3728	8	8
105	.3829	.3828	5	5
600	.4193	.4193	12	11
404 433 503	.4245	.4239 .4248 .4248 } .4245	26	29
215	.4292	.4293	14	12
611	.4466	.4457	11	9
532	.4557	.4553	27	31
620	.4657	.4658	17	16
424 523	.4705	.4703 .4713 } .4708	33	42
602	—	.4785	0	0
541	.4928	.4922	7	7

TABLE 1. (*continued*)

Coffinite

hkl	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	I_o	I_c
541	.5145	.5141	9	7
325	.5380	.5372	10	8
622	—	.5474	0	<1
514	—	.5589	0	<1
631	.5628	.5626	14	10
116	.5697	.5701	20	14
415, 613	.5866	.5858, .5865 } .5862	17	18
206	—	.5944	0	<1
701	.6122	.6111	6	4
444, 640, 543	.6340	.6317, .6324, .6350 } .6330	29	34
534	—	.6560	0	<1
721	.6601	.6596	14	9
316, 552, 712	.6684	.6672, .6685, .6685 } .6681	56	56
604, 505, 435, 633	.6827	.6802, .6829, .6829, .6836 } .6828	28	27
642	—	.6928	0	<1
624, 525, 703	.7304	.7287, .7314, .7320 } .7307	32	39
406	—	.7400	0	<1
107, 651	.7564	.7548, .7567 } .7558	10	10
336, 732	.7660	.7643, .7656 } .7650	33	38
800, 723	.7803	.7779, .7806 } .7792	14	15
426	—	.7885	0	<1
217, 811, 741 α_1	.0837	.8025, .8036, .8036 } .8033	21	18
217, 811, 741 α_2	.8068	.8053, .8075, .8075 } .8068		
820, 615	.8281	.8265, .8285 } .8275	17	21

Thorite

hkl	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	I_o	I_c
325	.5227	.5224	7	7
622	—	.5245	0	<1
631	.5395	.5388	9	10
514	—	.5398	0	0
116	.5573	.5576	10	14
613	.5649	.5644	9	10
415	.5682	.5690	7	9
206	—	.5809	0	<1
701	.5863	.5854	3	3
640	.6051	.6055	12	13
444, 543	.6099	.6094, .6103 } .6099	15	21
721	.6323	.6320	5	6
534	—	.6329	0	<1
552, 712 α_1	.6411	.6408	20	22
552, 712 α_2	.6424	.6439		
316α_1	.6501	.6501	14	14
604, 633 α_1	.6566	.6559, .6568 } .6564	13	10
505, 435 α_1	.6607	.6614	10	7
642	—	.6641	0	<1
624α_1	.7023	.7024 }	28	27
703		.7034 }		
624α_2	.7059	.7055 }		
525α_1	.7090	.7080	6	6
406	—	.7206	0	<1
651α_1, 107	.7247	.7243, .7272 } .7257	8	7
732α_1	.7336	.7339	15	17
732α_2	.7375	.7374		
336, 800 α_1	.7444	.7431, .7443 } .7437	10	11
723α_1	.7493	.7498	8	5
426	—	.7671	0	0
811, 741 α_1	.7715	.7708	8	9
811, 741 α_2	.7746	.7746		
217α_1	.7847	.7846	6	6
820α_1	.7915	.7908	8	8

TABLE 1. (*continued*)

Coffinite

hkl	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	I_o	I_c
802	—	.8385	0	<1
714	—	.8502	0	<1
307	.8517	.8518	8	5
516α_1	.8610	.8501 }	36	38
516α_2	.8646	.8639 }		
644, 660, 545, 653	.8769	.8744, .8751, .8771, .8778 } .8761	Observed intensities not resolved.	
822	—	.8871		
327, 831	.9018	.9004, .9024 } .9014		
635, 743, 813	.9258	.9257, .9264, .9264 } .9262		
734	—	.9474		
417	.9480	.9490		
536, 752	.9585	.9586, .9600 } .9593		
840	.9729	.9723		
705	—	.9743		
606	—	.9831		

Thorite

hkl	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	I_o	I_c
820α_2	.7951	.7948		
615α_1	.8021	.8010	5	5
802	—	.8046	0	<1
307		.8319	0	4
516, 660 α_1	.8363	.8361, .8374 } .8368		
714		.8189		
516, 660 α_2	.8421	.8393, .8415 } .8404	Observed intensities not resolved.	
644, 653 α_1	.8421	.8420, .8429 } .8424		
644, 653 α_2	.8467	.8457, .8468 } .8463		
545α_1	.8467	.8475		
822	—	.8501		
545α_2	.8525	.8510		
831α_1	.8641	.8638		
831α_2	.8682	.8680		
327α_1	.8773	.8777		
327α_2	.8815	.8807		
743, 813 α_1	.8893	.8894		
743, 813 α_2	.8939	.8935		
635α_1	.8939	.8946		
734	—	.9120		
752α_1	.9202	.9199		
752α_2, 417α_1	.9247	.9243, .9242		
536, 840 α_1	.9292	.9292, .9304 } .9298	Observed intensities not resolved.	
536, 840 α_2	.9345	.9328, .9350 } .9339		
705α_1	.9402	.9405		
008α_1	.9485	.9489		
606	—	.9535		
901α_1	.9574	.9569		
901α_2	.9622	.9616		
804, 833 α_1	.9818	.9815, .9824 } .9820		
804, 833 α_2	.9870	.9860, .9871 } .9866		

TABLE II. CELL DIMENSIONS AND DENSITIES OF COFFINITE, THORITE AND URANOTHORITES

Material	a	c	a/c	ρ gm./cm.^{3} calc.
$USiO_4$*	6.981±.004 kX	6.250±.005 kX	1.1170	7.15±0.02
3 $USiO_4 \cdot ThSiO_4$	7.007±.005	6.275±.003	1.1167	7.04± .02
$USiO_4 \cdot ThSiO_4$	7.039±.003	6.294±.002	1.1184	6.91± .01
$USiO_4 \cdot$ 3 $ThSiO_4$	7.071±.002	6.314±.003	1.1199	6.80± .01
$ThSiO_4$	7.128±.004	6.314±.003	1.1289	6.67±0.01

* A value previously reported for $USiO_4$ (Hoekstra and Fuchs, 1956), varies slightly from the value given here, since the earlier value was based on an incomplete indexing of the powder pattern.

in Table II. We also include in this table x-ray data for the several uranothorite samples which were prepared by the hydrothermal process developed for coffinite. The only variation in technique involves the preparation of thorium and uranium tetrachloride solutions in the desired concentrations. Reference to Table II shows that the cell dimension changes are uniform throughout the composition range.

We have also attempted to determine the oxygen positions in coffinite and thorite from powder patterns. Although the oxygen scattering is very small, the assigned positions are necessary in order to obtain reasonable agreement between observed and calculated intensities.

The atomic positions are assumed to be those for zircon, D_{4h}^{19}—$I_4/a\ md$ and are as follows:

4 Th or 4 U in (a)

4 Si in (b)

16 O in (h) (International Tables)

The only variables are u and v for oxygen and these were determined by trial methods. The resulting values for the oxygen positions are given in Table III. The extent of agreement between observed and calculated intensities is shown in Table I. The observed intensities were deduced from microphotometer tracings and the calculated intensities were obtained from the formula

$$I \sim F^2 p \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}$$

TABLE III. OXYGEN POSITIONS

	u	v
$USiO_4$	.180±0.010	.347±0.010
$ThSiO_4$	.166±0.010	.347±0.010

TABLE IV. BOND LENGTHS

$USiO_4$	U—4 O	2.32 Å ± .08 Å
	U—4 O	2.52 Å ± .09 Å
	Si—4 O	1.58 Å ± .09 Å
$ThSiO_4$	Th—4 O	2.46 Å ± .08 Å
	Th—4 O	2.50 Å ± .09 Å
	Si—4 O	1.55 Å ± .09 Å
$ZrSiO_4$	Zr—4 O	2.05 Å
	Zr—4 O	2.41 Å
	Si—4 O	1.62 Å

where p is the multiplicity factor and the other quantities have their usual significance.

The bond distances which result are shown in Table IV. The bond lengths in zircon (Wyckoff and Hendricks, 1927) are given for comparative purposes.

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