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Crystal structure of α- and β-$Na_2U_2O_7$: From Rietveld refinement using powder neutron diffraction data

D.J.W. IJdo *, S. Akerboom, A. Bontenbal [1]

Leiden Institute of Chemistry, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands

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ABSTRACT

The crystal structures of α- and β-$Na_2U_2O_7$ have been determined from neutron powder diffraction. At 293 K, the compound α-$Na_2U_2O_7$ has a monoclinic unit cell, space group $P2_1/a$, with $a=12.7617(14)$ Å, $b=7.8384(10)$ Å, $c=6.8962(9)$ Å, $\beta=111.285(9)^\circ$, and $Z=4$. At 773 K, β-$Na_2U_2O_7$ is also monoclinic, space group $C2/m$, with $a=12.933(1)$ Å, $b=7.887(1)$ Å, $c=6.9086(8)$ Å, $\beta=110.816(10)^\circ$, and $Z=4$. The structures can be described by layers $U_2O_7^{2-}$ built from corner linked deformed UO_6 octahedra with pentagonal UO_7 bipyramids in between linked with common edges to each other and to the octahedra. The Na atoms occupy the interlayer space. The $Na_2U_2O_7$ layers are similar as in $K_2U_2O_7$, but with a different stacking sequence of the layers. The layers in β-$Na_2U_2O_7$ are more symmetric. The relationship with the compounds $A_2U_2O_7$ (A=K, Rb, and Cs) is discussed.

1. Introduction

The phase relations in the pseudo-ternary system Na–U–O are of interest because sodium is used as a coolant in fast-breeder nuclear reactors. The existence of the ternary compounds $NaUO_3$ [1], $Na_2U_2O_7$ [2], Na_2UO_4 (α and β) [3] Na_3UO_4 [4] and Na_4UO_5 [5] are well known, and their structures have been determined except for $Na_2U_2O_7$ and Na_3UO_4. Cordfunke et al. [6] have studied the thermodynamic properties of $Na_2U_2O_7$. They also reported the reversible structural phase transitions in $Na_2U_2O_7$ at 638 K and 1348 K, respectively [7].

A review of the structural information on $Na_2U_2O_7$ covering the works up to 1974 is given by Keller [8]. From X-ray powder diffraction data Kovba et al. [2] determined the lattice parameters of $Na_2U_2O_7$ at room temperature. From systematic absences the space group $C2/m$ was proposed and a suggestion of the crystal structure given. However, the U–O distances in this model are unreliable. Gasperin [9] determined, from single crystal diffraction data, the crystal structure of a probable high-temperature modification, with delocalized U and O atoms. The aim of this paper is a crystal structure determination of $Na_2U_2O_7$ from neutron powder diffraction data at room temperature and at 773 K, and the relation of the structures with other $M_2U_2O_7$ (M=K, Rb and Cs).

2. Experimental

$Na_2U_2O_7$ was prepared by carefully mixing stoichiometric amounts of sodium carbonate or oxalate and U_3O_8 and heating the mixture gradually in oxygen up to 1073 K in a gold crucible for a week with intermediate grindings until the reaction was complete. X-ray powder diffraction analysis was used to follow the progress of the reaction. The compound was annealed in dry air at 573 K, which is just below the α–β transition temperature. Because Cordfunke and Loopstra [6] reported that $Na_2U_2O_7$ has reversible structure transitions, no single crystals were grown since micro twinning may hamper the structure determination from a single crystal. Neutron powder diffraction measurements at 293 K and 773 K were taken on the powder diffractometer at the HFR at NRG in Petten for structure determination. The experimental conditions were reported earlier [3]. Absorption correction was applied according to Weber [10]. The calculations were performed using the Rietica computer program [11]. The variables consist of a scale factor, twelve background parameters, three half-width parameters defining the Gaussian-like peak shape, an asymmetry parameter, the zero point correction, atomic position parameters, preferred orientation and thermal parameters.

3. Results

The X-ray diffraction powder pattern of α-$Na_2U_2O_7$ could be indexed on a monoclinic unit cell according to Kovba et al. [2] but refinement with the proposed model with space group $C2/m$ fails.

* Corresponding author. Tel.: +31 71 527 4535.
E-mail address: d.ijdo@chem.leidenuniv.nl (D.J.W. IJdo).
[1] NRG, Westerduinweg, 1755ZG Petten, PO Box 25, The Netherlands.

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From the lattice parameters of related compounds $A_2U_2O_7$ (A=Na, K, Rb, and Cs) (Table 1) some similarity to the structure of $K_2U_2O_7$ [12] is obvious; however the a-axis is doubled. A related model with a double c-axis and space group $C2/m$ was constructed. The refinement of the X-ray data gave reasonable results, but this model does not explain some small diffraction lines at room temperature in both the X-ray pattern, and more clearly in the neutron powder pattern. However, the structure of β-$Na_2U_2O_7$ at 773 K can be refined with this model in the space group $C2/m$. Details of the refinement are given in Table 2, the atomic parameters are listed in Table 3; selected bond distances are listed in Table 4.

Table 1
Lattice parameters of $A_2U_2O_7$ from the literature.

	a (Å)	b (Å)	c (Å)	ß (°)	Space group	Reference
$Na_2U_2O_7$	12.796(10)	7.822(2)	6.896(4)	111.42(6)	$C2/m$	[2]
$K_2U_2O_7$	6.984(3)	7.960(3)	6.931(3)	109.69(5)	$P2_1$	[12][a], [17]
$Rb_2U_2O_7$	7.323(2)	8.004(3)	6.950(2)	108.81(1)	$P2_1/c$	[13,18]
$Cs_2U_2O_7$	14.5293(6)	4.3233(3)	7.4899(5)	113.852(1)	$C2/m$	[14]

[a] a and c axes interchanged.

Table 2
Data collection and refinement details for α- and β-$Na_2U_2O_7$.

	α-$Na_2U_2O_7$	β-$Na_2U_2O_7$
Temperature (K)	293	773
Space group	$P2_1/a$	$C2/m$
Neutron wavelength (Å)	2.5723(2)	2.5723(2)
Cell parameters		
a (Å)	12.7617(14)	12.933(1)
b (Å)	7.8384(10)	7.887(1)
c (Å)	6.8962(9)	6.9086(8)
β (°)	111.285(9)	110.816(10)
V (Å^3)	642.78(10)	658.80(13)
Z	4	4
D_{calc} (Mg m^{-3})	6.553	6.389
2θ range (°)	5–155	5–129
Step size (°)	0.1	0.1
μR	0.09	0.09
R_{wp}	4.31	5.17
R_p	3.31	4.09
χ^2	3.50	6.28

The neutron diffraction pattern at room temperature is slightly different from the 773 K one and could be interpreted with a related model in the subgroup $P2_1/a$. In the refinement of this structure, a slight preferred orientation of 0.988(3) was found. The agreement between the observed and calculated profile of α- and β-$Na_2U_2O_7$ is shown in Fig. 1. An impression of the structure of β-$Na_2U_2O_7$ is given in Fig. 2; the U_2O_7 planes of both structures are depicted in Fig. 3.

4. Discussion

The α- and β-$Na_2U_2O_7$ have closely related crystal structures. The layer structure of β-$Na_2U_2O_7$ consist of corner-linked U1–O_6 octahedra in the [0 1 0] direction tilted about 23° around an axis parallel to a*. Between these rows are rows of U_2–O_7 pentagonal

Table 4
Selected atomic distances (Å) in α-$Na_2U_2O_7$ at 293 K and β-$Na_2U_2O_7$ at 773 K.

α-$Na_2U_2O_7$			β-$Na_2U_2O_7$		
Na1–O1	2.77(2)	(2 ×)	Na1–O1	2.829(17)	(2 ×)
Na1–O3	2.57(1)	(2 ×)	Na1–O3	2.713(8)	(4 ×)
Na1–O4	2.43(1)	(2 ×)			
			Na1–O4	2.359(10)	(2 ×)
Na2–O3	2.40(1)	(2 ×)	Na2–O3	2.396(7)	(4 ×)
Na2–O33	2.30(1)	(2 ×)			
Na2–O4	2.72(1)	(2 ×)	Na2–O5	2.876(11)	(2 ×)
Na3–O22	2.41(3)		Na3–O2	2.919(11)	(2 ×)
Na3–O3	2.73(3)		Na3–O3	2.625(8)	(2 ×)
Na3–O33	2.54(2)				
Na3–O4	2.65(2)		Na3–O4	2.700(14)	(2 ×)
Na3–O4	2.65(2)				
Na3–O5	2.69(2)		Na3–O5	2.434(15)	(2 ×)
Na3–O5	2.13(2)				
U1–O1	2.51(1)		U1–O1	2.165(4)	(2 ×)
U1–O1	1.88(1)				
U1–O2	2.20(2)		U1–O2	2.129(8)	(2 ×)
U1–O22	2.24(1)				
U1–O3	1.81(2)		U1–O3	1.857(9)	(2 ×)
U1–O33	1.90(2)				
U2–O1	2.38(1)		U2–O1	2.334(11)	
U2–O2	2.04(2)		U2–O2	2.256(8)	(2 ×)
U2–O2	2.91(1)		U2–O2	2.635(7)	(2 ×)
U2–O22	2.25(1)				
U2–O22	2.30(1)				
U2–O4	1.79(1)		U2–O4	1.844(13)	
U2–O5	1.95(2)		U2–O5	1.838(16)	

Table 3
Fractional atomic coordinates and thermal parameters (Å^2) of α-$Na_2U_2O_7$ (293 K) and β-$Na_2U_2O_7$ (773 K).

S.G.	α-$Na_2U_2O_7$ $P2_1/a$			β-$Na_2U_2O_7$ $C2/m$		
	x	y	z	x	y	z
Na1	0	0	0	0	0	0
Na2	0.5	0	0	0.5	0	0
Na3	–0.026(1)	0.258(2)	0.492(4)	0	0.026(2)	0.5
	B=0.35(24) Å^2			B=3.25(20) Å^2		
U1	0.246(1)	0.262(1)	0.008(2)	0.25	0.25	0
U2	0.2415(7)	0.017(1)	0.470(1)	0.2438(6)	0	0.4593(9)
	B=0.60(11) Å^2			B=0.60(10) Å^2		
O1	0.231(2)	–0.038(2)	0.123(2)	0.2328(4)	0	0.1146(16)
O2	0.260(2)	0.681(1)	0.302(3)	0.2625(13)	0.3012(6)	0.3102(13)
O22	0.273(1)	0.270(2)	0.347(2)			
	B=1.76(20) Å^2					
O3	0.406(2)	0.764(2)	0.090(3)	0.4026(7)	0.2230(9)	0.0961(12)
O33	0.402(2)	0.206(2)	0.099(3)	B=3.20(10) Å^2		
O4	0.409(1)	0.526(2)	0.625(2)	–0.0913(10)	0	0.6374(16)
O5	0.410(2)	0.019(2)	0.577(2)	0.3958(11)	0	0.5563(18)
B (Å^2)	B=1.63(11) Å^2			B=2.38(10) Å^2		