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$Sr_2UO_{4.5}$: A New Perovskite-Type Strontium Uranate

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A new strontium uranate with the formal composition $Sr_2UO_{4.5}$ has been found. Its perovskite-type crystal structure has been studied with neutron diffraction from which it is found that there is a statistical distribution of Sr and U (2:1) on one octahedral position and one U on the other, leading to the formula $Sr_2(Sr_{2/3}U_{1/3})UO_6$. Its thermal stability has been determined, and its relation with other perovskite-type structures is discussed.

INTRODUCTION

During fission of uranium in a nuclear reactor a large number of fission products are formed. The behavior of the fission products in the UO_2 lattice of the nuclear fuel is of special interest to the understanding of fuel performance. The divalent alkaline earth metals barium and strontium, for instance, may form solid solutions by substitution of uranium in the U lattice of the UO_2 structure. Valence compensation is obtained by oxidation of uranium in the lattice to give $M_yU_{1-y}O_{2+x}$ (1). A statistical model to express the relationship between x and y was described by Aronson and Clayton (2).

Thus, for strontium single-phase solid solutions were obtained up to $y = 0.3$ (at 1500–1800 K), whereas above this value "some strontium uranate having a Sr/U ratio ≥ 0.5" was obtained as a second phase (1). Kemmler-Sack and Seemann (3) described perovskite-type structures with pentavalent uranium, but detailed characterization of their phases has not been given. In addition, the existence of the compound $SrUO_3$, isostructural with the perovskite-type $BaUO_3$, has been suggested (4), although nobody has succeeded in preparing it in a pure form. $SrUO_3$ is claimed to be formed in solid solutions with $BaUO_3$ in the so-called "grey-phase" which, in addition, can contain other elements such as plutonium and zirconium. This grey phase is formed as inclusions in irradiated UO_2 fuel (5).

In the system Sr–U–O several hexavalent compounds have been identified (6). The crystal structures of β-$SrUO_4$, Sr_2UO_5, and Sr_3UO_6 have been reported (7) and the structure of $Sr_3U_{11}O_{36}$ was determined recently (8). Sr_3UO_6 adopts a monoclinic perovskite-like structure. A redetermination of its crystal structure with space group $P2_1/n$ led to more regular UO_6 octahedra than the earlier work suggested (9).

This paper reports an investigation into the strontium uranate phases with uranium valencies lower than six. A new phase with the formal composition $Sr_2UO_{4.5}$ has been found. Its structure and relationship with the perovskite-type MUO_3 structure will be discussed.

EXPERIMENTAL

Hexavalent strontium uranates were prepared in Sr/U ratios varying from 0.5 to 3.0 by heating mixtures of anhydrous $SrCO_3$ and U_3O_8 in dry air in platinum boats at temperatures of 1250 to 1300 K, as described earlier (6, 8). After completion of the reaction, which was checked by X-ray diffraction, the samples were reduced in an Ar–H_2 mixture at temperatures varying from 1100 to 1300 K in order to obtain strontium uranate phases with a uranium valency lower than six. In addition to these experiments, some mixtures of SrO and UO_2 were heated in an argon atmosphere at the same temperatures as described above; no reaction products were obtained in this case.

The X-ray diffraction results were obtained with a focusing Delft Instruments Guinier–de Wolff camera (Cu$K\alpha_1$ radiation) with a mixture of Si and W as internal standard. The neutron diffraction measurements were taken on the powder diffractometer at the HFR in Petten. Neutrons of $\lambda = 2.5717(3)$ Å were obtained using the beam reflected from the $hkl = (111)$ planes of a single crystal of copper and reducing the λ/n contamination to less than 0.1% by means of a pyrolytic graphite filter. Soller slits with a horizontal divergence of 30′ were placed between the reactor and the monochromator and in front of the four ^{3}He counters. The sample holder ($\phi = 10$ mm) consisted of a V tube closed with Cu plugs fitted with O-rings. The diffraction pattern was taken at 300 K, and analyzed by means of Rietveld's profile refinement tech-

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nique (10). The maximum absorption correction was 3%, $\mu R = 0.11$. For the coherent scattering lengths we used the values for O: 5.805, Sr: 7.02, and U: 8.42 fm (11).

The density measurements were done pycnometrically with double-distilled CCl_4. In order to increase the accuracy large samples ($\sim$ 4 g) of $Sr_2UO_{4.5}$ were used in the determinations which were carried out in a pycnometer with contents of 25 cm^3.

The chemical analyses were carried out after dissolution of the sample in HCl and separation of Sr with an ion exchanger (12). Sr was determined photometrically with EDTA; U^{4+} and total U were determined titrimetrically with dichromate (13). All handlings of the samples, including weighting, were carried out in an argon-filled, dry glove box.

The enthalpy of formation of $Sr_2UO_{4.5}$ was determined from its enthalpy of solution which was measured calorimetrically as described previously (14).

RESULTS

Phase Relationships: The $Sr_2UO_{4.5}$ Phase

Attempts to prepare strontium uranates with a uranium valency lower than six by heating mixtures of SrO and UO_2 in a purified argon atmosphere were unsuccessful; no reaction products were obtained in this way. However, when hexavalent uranate samples with Sr/U ratios between 1.0 and 3.0 are heated in Ar–H_2 gas mixtures at temperatures up to 1250 K, either rhombohedral (α-)$SrUO_{4-x}$ and a second phase, or Sr_3UO_6 accompanied with the same phase, are obtained. Above 1250 K Sr_3UO_6 is also reduced to give the same second phase and SrO. No indications for the formation of a $SrUO_3$-type compound were obtained neither in these samples, nor in samples with a Sr/U ratio below 1.0. The second phase obtained in the reduction experiments, appeared to be phase-pure at the Sr/U ratio 2.0. This is supported by the fact that this phase can also be obtained in a pure form by thermal decomposition of Sr_2UO_5 at temperatures above 1600 K. From chemical analysis and weight loss analysis by weighing the sample before and after the heating, its formula is undoubtedly $Sr_2UO_{4.5}$. A large phase-pure sample prepared for calorimetry and neutron diffraction analysis, had the following composition, Sr: 36.08 $\pm$ 0.05 (calc. 36.11); U^{4+}: 24.28 $\pm$ 0.03 (calc. 24.11); U (total): 48.94 $\pm$ 0.03 (calc. 49.05).

Structure Determination

The X-ray pattern of $Sr_2UO_{4.5}$ is similar to that of Sr_3UO_6 (9). It could be indexed with a pseudo-orthorhombic, unit cell with parameters $a = 6.013(1)$ Å, $b = 6.179(1)$ Å, $c = 8.610(1)$ Å, and $\beta \approx 90°$. Systematic absences $h0l$ with $h + l = 2n + 1$, and $0k0$ with $k = 2n + 1$ indicate that this compound does not have exactly the $GdFeO_3$ perovskite-type structure with the space group *Pbnm*, but instead the space group $P2_1/n$.

Since no single crystals were available Rietveld's method (10) was used for the refinement of the neutron powder diffraction data (Fig. 1). The monoclinic structure of Sr_3UO_6 was used as a trial model (9). This gives Sr(1), O(1), O(2), O(3) at $x\ y\ z$; U(1) at $0\frac{1}{2}0$ and a statistical mixture of Sr(2) and U(2) at $00\frac{1}{2}$. In the refining of the neutron diffraction data the program DBW3.2S version 8802 was used (15). The final refinement was made using 166 reflections. The variables include a scale factor, six background parameters, three half-width parameters defining the Gaussian-like peak shape, the counter zero error, an asymmetry parameter, the unit cell dimensions, atomic position parameters, and thermal parameters. The final R values obtained were $R_p = 1.97$; $R_{wp} = 2.55$; $R_{exp} = 1.86\%$; $S = 1.37$; $D\text{–}wD = 1.37$. The final coordinates are listed in Table 1, the atomic distances in Table 2, and the lattice constants in Table 3. The agreement between the observed and calculated profile is shown in Fig. 1.

Thermodynamic Stability

The standard enthalpy of formation of $Sr_2UO_{4.5}$ was determined by combining the enthalpy of solution of $Sr_2UO_{4.5}$ in an aqueous solution of $FeCl_3$ in HCl ($HCl \cdot 0.0470FeCl_3 \cdot 82.16\ H_2O$), $-(390.66 \pm 0.51)$ kJ $\cdot$ mol^{-1}, with the enthalpies of solution of $SrCl_2(s)$, $UCl_4(s)$, and γ-$UO_3(s)$ in the same solution (14) with the standard enthalpy of formation of $SrCl_2(s)$ (16), to give the value $\Delta_f H°(298.15\ K) = -(2487.3 \pm 2.5)$ kJ $\cdot$ $mole^{-1}$.

The thermal decomposition of Sr_2UO_5 according to the reaction,

$$Sr_2UO_5 = Sr_2UO_{4.5} + \tfrac{1}{4}O_2(g),$$

is reversible, and has been studied at various oxygen pressures using differential thermal analysis (DTA). Thus, at pO_2 (atm) of 1, 0.2, and 0.02 the dissociation temperatures found are 1693, 1675, and 1620 K, respectively. The accuracy of these temperatures is about 10 K. Brisi *et al.* (17), who studied the thermal decomposition of strontium uranate phases above 1645 K in air, described the formation of $SrUO_{4-x}$ and Sr_3UO_6 to all probability in samples with Sr/U ratios between 1 and 2. However, because of the close resemblance in structure between Sr_3UO_6 and $Sr_2UO_{4.5}$ they were not able to discriminate between these phases.

DISCUSSION

The $Sr_2UO_{4.5}$ phase as characterized here, is isostructural with the high-temperature form of $Ca_2UO_{4.5}$ (18),

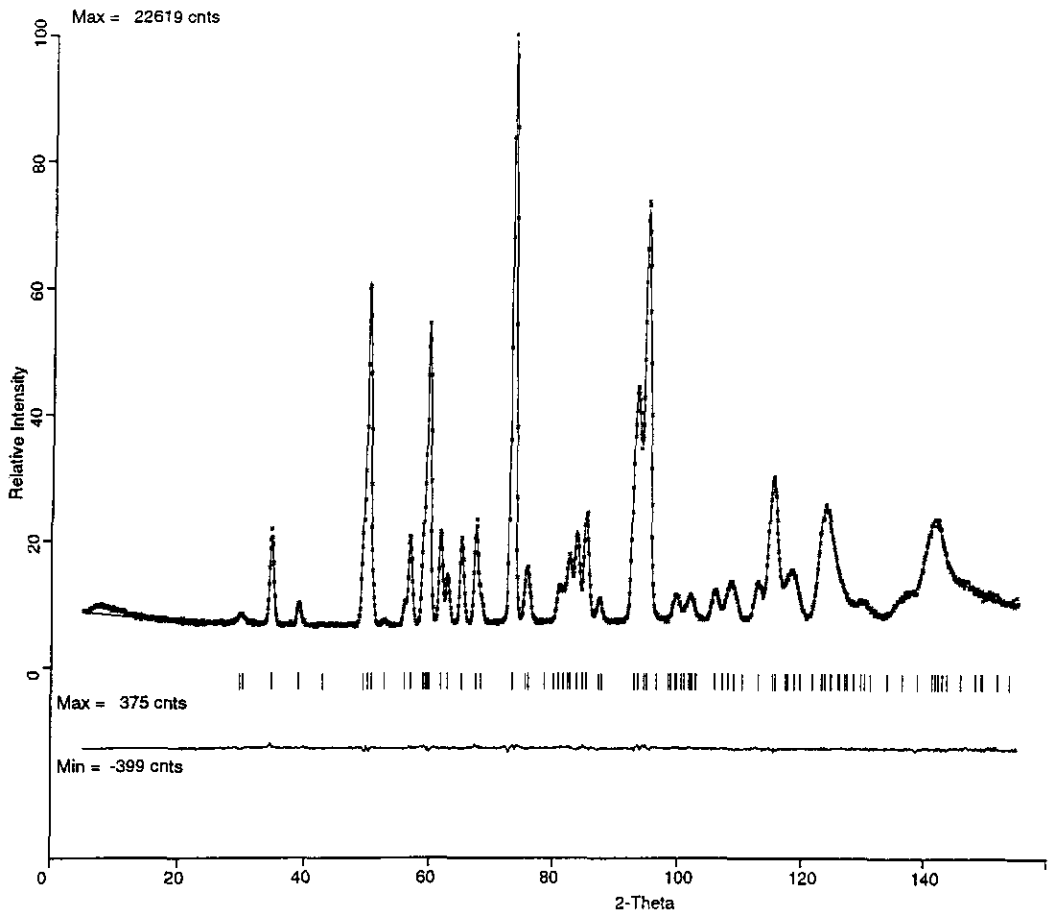

FIG. 1. Observed (dots) and calculated (full line) neutron diffraction profile of $Sr_2(Sr_{2/3}U_{1/3})UO_6$ (= $Sr_2UO_{4.5}$) at 298 K; 2θ in degrees.

and almost identical to that of the phase described by Brisi (4) which, however, was ascribed by him to the formula $SrUO_3$. As follows from the present investigation, such a composition does not exist. The diffraction pattern of the $Sr_2UO_{4.5}$ phase is also almost identical to that of the compound Sr_3UO_5 described by Charvillat *et al.* (19). However, the small differences in lattice parameters of a series of compounds A_2BUO_5 reported by Charvillat *et al.* (19) and A_2BUO_6 (20) suggest that compounds described by Charvillat do not exist, but have been oxidized to A_2BUO_6 during the synthesis. As reported already, the X-ray pattern of $Sr_2UO_{4.5}$ is similar to that of Sr_3UO_6, the U–O distances, however, being significantly larger.

The crystal structure of $Sr_2UO_{4.5}$, which is nearly equal to that of $Sr_2(Sr,U)O_6$ (= Sr_3UO_6) and Sr_2CaUO_6 (20), can be derived from $SrCeO_3$ (Table 3) which in turn is related to the cubic perovskite $SrTiO_3$. In $SrCeO_3$ with the radius of Ce^{4+} larger than the radius of Ti^{4+}, all CeO_6 octahedra

TABLE 1
Fractional Atomic Coordinates and Isotropic Thermal Parameters of $Sr_{2.67}U_{1.33}O_6$ (or $Sr_2UO_{4.5}$) at Room Temperature

	x	*y*	*z*	*B* (Å^2)
Sr1	0.5097(4)	0.5456(2)	0.2459(11)	0.93(4)
Sr/U	0.5	0	0	0.36(3)
U	0	0.5	0	0.36(3)
O1	0.1849(9)	0.2111(10)	0.9395(8)	2.06(16)
O2	0.2903(9)	0.6866(10)	0.9446(8)	1.66(17)
O3	0.3913(4)	0.9504(3)	0.2497(12)	1.96(6)

TABLE 2
Atomic Distances (Å) and Angles (°) in $Sr_2(Sr_{2/3}U_{1/3})UO_6$ at Room Temperature

$Sr1–O_8$	Bicapped prism	$(Sr/U)O_6$ octahedron		$(U)O_6$ octahedron	
Sr1–O1	2.531(9)	Sr/U–O1	2.361(6)	U–O1	2.167(6)
–O1	2.863(8)	–O2	2.360(6)	U–O2	2.148(6)
–O1	3.124(10)	–O3	2.269(10)	U–O3	2.273(10)
Sr1–O2	3.039(11)	O1–Sr/U–O2	91.3(2)	O1–U–O2	91.7(2)
–O2	2.918(9)	O1–Sr/U–O3	92.9(2)	O1–U–O3	91.8(2)
–O2	2.490(9)	O2–Sr/U–O3	94.2(2)	O2–U–O3	92.8(2)
Sr1–O3	2.600(2)				
–O3	2.487(3)				

TABLE 3
Lattice Parameters (Å) of A_2BO_6 Compounds

	a	b	c	β	V (Å)^3	Space group	Ref.
$Ca_2(Ca_{2/3}U_{1/3})O_6$	5.765(2)	5.965(3)	8.348(3)	90.21(3)	287.07	$P2_1/n$	(18)
$Sr_2CaU^{VI}O_6$	5.9377(2)	6.0734(2)	8.4563(3)	90.14(1)	304.95	$P2_1/n$	(20)
$Sr_2SrU^{VI}O_6$	6.0126(2)	6.2138(2)	8.6139(3)	90.24(1)	321.82	$P2_1/n$	(9)
$Sr_2(Sr_{2/3}U_{1/3})U^{V}O_6$	6.0245(2)	6.1753(2)	8.6102(4)	90.03(1)	320.33	$P2_1/n$	this work
$SrCeO_3$	6.0066(2)	6.1473(2)	8.5803(5)	90	316.82	$Pbnm$	(25)

are tilted to reduce the void for the Sr ion. The lattice parameters of $SrCeO_3$ are $a\sqrt{2}$, $a\sqrt{2}$, $2a$, respectively, of the original cubic perovskite. In $Sr_2(Sr,U)O_6$ the Ce is replaced by Sr and U in an ordered way so that each SrO_6 octahedron shares corners with six UO_6 octahedra and vice versa as can be seen in Fig. 2. This lowers the space group from $P2_1/b2_1/n2_1/m$ to $P2_1/n$ for $Sr_2(Sr,U)O_6$. It has to be noted that the radius of Sr^{2+} for six coordination is different to that of U^{6+}: 1.18 and 0.73 Å, respectively (21). The structure of $Sr_2UO_{4.5}$ ($=Sr_2(Sr_{2/3}U_{1/3})UO_6$) is also derived from $SrCeO_3$. The Ce is now replaced by a statistical distribution of Sr and U^{5+}(2 : 1) on one octahedral position and U^{5+} on the other, just as in $Sr_2(Sr,U)O_6$. In this case there is again difference in radius between $(2Sr + U^{5+})/3$ and U^{5+}, but smaller than in Sr_2SrUO_6 (1.04 and 0.76 Å, respectively) in agreement with the experimental data (Table 3). Probably the order between the two types of octahedra is not complete; the relatively high value of the B for the oxygen atoms in $Sr_2Sr_{0.67}U_{1.33}O_6$ may indicate this. Electron diffraction did not give any indication for deviations of the statistical distribution of U and Sr. The density calculated for $Sr_2(Sr_{2/3}U_{1/3})UO_6$ ($Z = 2$), is 6.72 g/cm^3 which compares nicely with the experimentally determined density 6.57 ± 0.02 g/cm^3.

The stability of the perovskite structures can be correlated by the Goldschmidt tolerance factor $t = (r_A + r_O)/\{2^{1/2}(r_B + r_O)\}$, in which r_A, ionic radius of the divalent ion, r_B, ionic radius of tetravalent ion, and r_O, ionic radio of oxygen. The ionic radius of B used in this study, has been taken for a coordination number of 6, and that of A for a coordination number of 12, from Shannon (21). For the reaction: $AO + BO_2 \rightarrow ABO_3$, the enthalpy of reaction $\Delta_r H°(298.15\ K)$ is a measure for the thermodynamic stability of the perovskite, and can be correlated with the tolerance factor, as has been shown for barium compounds by Morss and Mensi (22). In ideal perovskite lattices the value of r_B is close to the radius of the octahedral hole formed by the close-packed AO_3 layers, and the value of t approaches 1. With increasing values of r_B ($t < 1$), the lattice becomes less favorable, as shown in Fig. 3 for a number of strontium perovskites. The enthalpies of formation have been taken from Goudiakas *et al.* (23), and Cordfunke and Konings (24). Thus, for $SrUO_3$ with a tolerance factor of 0.89, the enthalpy of reaction from the oxides is slightly positive, and its enthalpy of formation is estimated to be $-(1675 \pm 10)$ kJ · mole^{-1}.

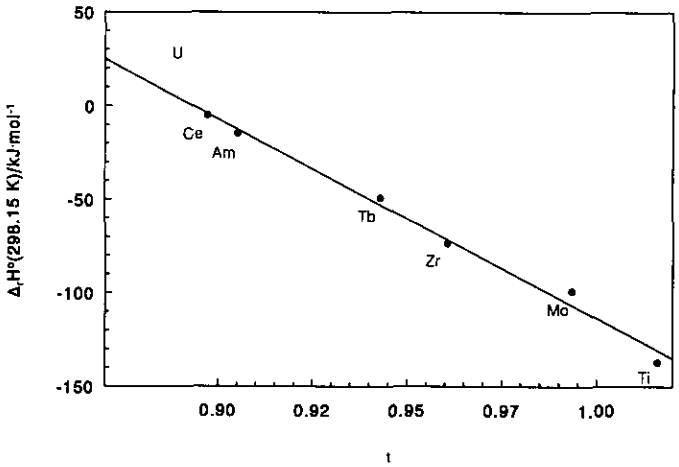

FIG. 3. The enthalpy of reaction of SrO and the oxide BO_2 to form the perovskite $SrBO_3$ as a function of the Goldschmidt tolerance factor.

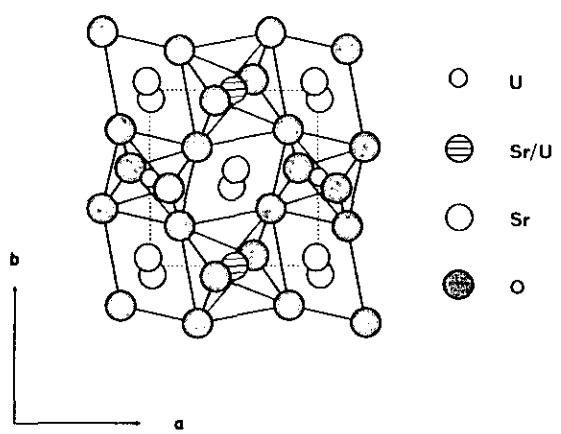

FIG. 2. Section of the structure of $Sr_2UO_{4.5}[Sr_2(Sr_{2/3}U_{1/3})UO_6]$ projected along the c axis.

With decreasing tolerance factor the O environment of the large A ion is considerably distorted but the BO_6 octahedra remain almost regular. By tilting a monoclinic distortion of the cubic perovskite structure is obtained. Groen *et al.* (26) analyzed the tilt of the octahedra for perovskite-like structures in terms of regular octahedra.

In a series of articles Kemmler-Sack and co-workers (3, 27) have shown that the perovskite structure is stabilized further either by vacancies on the A and B sites, or by occupation of B sites by A ions. The strontium uranates are an example of the latter possibility. Thus, IJdo (9) showed that Sr_3UO_6 can be described as a perovskite with almost regular SrO_6 and UO_6 octahedra, with one Sr per unit cell on a B site. The formula of Sr_3UO_6 can, therefore,

better be described as $Sr_2(Sr,U)O_6$. The compound $Sr_2UO_{4.5}$ can, thus, be considered as a member of the perovskite-series $SrUO_3$–$Sr_2UO_{4.5}$–Sr_3UO_6, in that its formula can be written as $Sr_2(Sr_{2/3}U_{1/3})UO_6$, with Sr and U statistically distributed in the ratio 2 : 1 over one of the *B* sites. According to Kemmler-Sack and Seemann (3) the composition $Sr_2(Sr_{2/3}U_{1/3})UO_6$ cannot be obtained; instead, they described compositions with less SrO and containing holes in the cation and anion lattice. The present results do not support this conclusion. Otherwise than in the barium uranate system, where a $BaUO_3$ phase can exist, the stabilization of the $SrUO_3$ phase is only possible in the presence of oxygen by the oxidation of U^{4+} to either U^{5+} (in $Sr_2UO_{4.5}$) or U^{6+} (in Sr_3UO_6) via defect chemical reactions.

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