Journal of Solid State Chemistry **146,** 144–150 (1999)
Article ID jssc.1999.8320, available online at http://www.idealibrary.com on IDEAL®

The Structure of $BaSr_4U_3O_{14}$ and a Structural and Thermodynamic Characterization of $Sr_5U_3O_{14}$

E. H. P. Cordfunke,* M. E. Huntelaar,* and D. J. W. IJdo†

*Netherlands Energy Research Foundation ECN, P.O. Box 1, 1755 ZG Petten, The Netherlands; and †Gorlaeus Laboratories, Leiden Institute of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

Received November 25, 1998; in revised form March 29, 1999; accepted April 8, 1999

The structures of $Sr_5U_3O_{14}$ and $BaSr_4U_3O_{14}$ have been studied by X-ray powder diffraction and neutron powder diffraction. Both compounds could be indexed on a pseudo-tetragonal, chiolite-type structure. $Sr_5U_3O_{14}$ was shown to be orthorhombic and to have space group *Pbca* with $a = 11.2416(7)$ Å, $b = 11.2572(7)$ Å, $c = 11.0791(4)$ Å, and $Z = 4$. $BaSr_4U_3O_{14}$ was shown to be orthorhombic and to have space group *Cmca* with $a = 11.3647(7)$ Å, $b = 11.3770(7)$ Å, $c = 11.0203(5)$ Å, and $Z = 4$. The thermodynamic properties of $Sr_5U_3O_{14}$ at 298.15 K have been determined, and its thermal stability with respect to the neighboring strontium uranate phases are discussed. © 1999 Academic Press

1. 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 fuel is of interest to understand its performance. For instance, the divalent alkaline earth metals barium and strontium may form solid solutions by substitution in the uranium sublattice of the UO_2 structure. Valence compensation is obtained by oxidation of uranium (1). In addition, strontium uranates may be formed as separates phases, depending on the temperature and the oxygen pressure. A large number of phases have been found in the Sr–U–O system. The perovskite-related compound $Sr_2U^{V}O_{4.5}$ (2), in which uranium is in the pentavalent state, has been investigated by us previously, whereas the structures of the compounds with hexavalent uranium Sr_3UO_6 (3, 4), Sr_2UO_5 (3, 5), and both modifications of $SrUO_4$ (6) and $Sr_3U_{11}O_{36}$ (7) had been published before.

Recently, Sterns *et al.*, (8) reported on the existence of a new strontium uranate phase with the composition $Sr_5U_3O_{14}$ with a chiolite-like structure, but the structural details could not be determined. In this paper the structure and thermodynamic properties of $Sr_5U_3O_{14}$ are reported. In addition, the related structure of $BaSr_4U_3O_{14}$ has been determined. Both structure determinations are based on neutron powder diffraction.

2. EXPERIMENTAL

$Sr_5U_3O_{14}$ was prepared by heating a stoichiometric mixture of $SrCO_3$ and U_3O_8 with intermediate grindings in a platinum crucible in air up to 1520 K. Heating periods of 35 days were required, but Sr_2UO_5 or orthorhombic $SrUO_4$ as secondary phases were always present in the final product. $BaSr_4U_3O_{14}$ was prepared from $BaCO_3$, $SrCO_3$, and U_3O_8 in an alumina crucible in air at 1473 K with intermediate grindings for 3 days; according to the X-ray powder diffraction pattern, this sample was without any detectable impurities. Because the single-crystal structure determination of Sterns *et al.* (8) was unsuccessful through microtwinning, neutron powder diffraction measurements were taken on the powder diffractometer at the HFR at ECN, in Petten for structure determination. The experimental conditions were reported earlier (9). An absorption correction was applied according to Weber (10). For the coherent scattering lengths we used the values for O 5.805, Ba 5.07, Sr 7.02, and U 8.417 fm (11). For the refinements of the neutron diffraction data, the program DBW 9006, version 8.491, was used (12). The variables include a scale factor, five background parameters, and three half-width parameters defining the Gaussian-like peak shape, the counter zero, atomic position parameters, and an overall thermal parameter.

The chemical analysis of $Sr_5U_3O_{14}$ was carried out after dissolution of the sample in HCl and separation of Sr with an ion exchanger. Sr was determined photometrically with EDTA; U^{4+} and total U were determined titrimetrically with dichromate (13). All handlings of the samples, including weighing, were carried out in an argon-filled, dry glove box.

The enthalpy of formation of $Sr_5U_3O_{14}$ was determined from its enthalpy of solution which was measured calorimetrically as described before (14). The low-temperature heat capacities were measured at Utrecht University, The Netherlands, in an adiabatic calorimeter (laboratory designation Cal V) over the temperature range 4–420 K in 10 runs. The calorimeter and its calibration have been

0022-4596/99 $30.00

TABLE 1
Data Collection and Refinement Details for $Sr_5U_3O_{14}$ and $BaSr_4U_3O_{14}$

	Compound	
	$Sr_5U_3O_{14}$	$BaSr_4U_3O_{14}$
Space group	*Pbca*	*Cmca*
Neutron wavelength	2.5724(9)	2.5724(9)
Cell parameters		
a (Å)	11.2416(7)	11.3646(7)
b (Å)	11.2572(7)	11.3770(7)
c (Å)	11.0791(4)	11.0203(5)
V (Å)^3	1402.0(1)	1424.87(14)
Z	4	4
D_x (Mg m^{-3})	6.519(2)	6.647(2)
$D_{exp}{}^a$	6.40(5)	
2Θ range (°)	5–155	5–155
Step size (°)	0.1	0.1
μR	0.05	0.05
R_p	2.59	2.93
R_{wp}	3.37	3.90
S	1.47	1.48
D–w*D*	1.49	1.14

[a] Reference (8).

described previously (15). The temperature of the sample was measured with a 100 Ω platinum thermometer. For the measurements 4.2484 g of $Sr_5U_3O_{14}$ was loaded into the calorimeter. After evacuation, helium was added at a pressure of 2 kPa (T = 300 K) to enhance thermal contact between the sample and the calorimeter.

3. RESULTS

The X-ray diffraction powder pattern of $Sr_5U_3O_{14}$ was indexed on a pseudo-tetragonal unit cell with $a = b = a_c\sqrt{2}$ and $c = c_c$; a_c and c_c are the chiolite-like lattice constants. The X-ray data are consistent with space group *Cmca*. Octahedral rotations are largely responsible for transforming the ideal chiolite structure to a lower symmetry. A trial model based on space group *Cmca* could be constructed by tilting the octahedron at 000 of the ideal chiolite model about the two-fold axis along [110] of the parent structure: Sr1 in 4*b* $00\frac{1}{2}$; Sr2 in 8*c* $\frac{1}{4}y\frac{1}{4}$, $y = 0.02$; Sr3 in 8*f* $\frac{1}{2}yz$, $y = z = 0.25$; U1 in 4*a* 000; U2 in 8*c* $\frac{1}{4}\frac{1}{4}0$; O1 in 8*f* $0yz$, $y = -0.07$ and $z = 0.16$; O2, O3, and O4 in 16*g*. With this model the neutron data refine to R_p = 3.25, R_{wp} = 4.18, $S = 1.82$, D–w$D = 0.99$, and an overall $B = 0.85$ Å^2. With the subgroup *Pbca* a successful model could be derived where the octahedron at 000 has a small additional tilt around the *c* axis. The subgroup *Pbca* is in agreement with the electron diffraction results of Sterns *et al.* (8). Details of the refinements are given in Table 1.

The structure of $BaSr_4U_3O_{14}$ could be refined with the space group *Cmca*. Atomic parameters are listed in Table 2; selected bond distances are listed in Table 3. The agreement between the observed and calculated profile is shown in Fig. 1. The structure of $BaSr_4U_3O_{14}$ is shown in Fig. 2.

Thermodynamic Characterization of $Sr_5U_3O_{14}$

A careful chemical analysis of samples of $Sr_5U_3O_{14}$ shows that this compound does not contain U^{4+} and, as a consequence, is one of the many strontium uranate phases in which uranium is hexavalent. To determine the relative

TABLE 2
Fractional Atomic Coordinates and Thermal Parameters (Å)^3 of $Sr_5U_3O_{14}$ and $BaSr_4U_3O_{14}$

	$Sr_5U_3O_{14}$ *Pbca*			$BaSr_4U_3O_{14}$ *Cmca*		
Space group	*x*	*y*	*z*	*x*	*y*	*z*
Sr1 (Ba)	0	0	0.5	0	0	0.5
Sr2	0.2582(7)	0.0189(5)	0.2546(12)	0.25	0.0176(5)	0.25
Sr3	0.5010(14)	0.2503(5)	0.2774(3)	0.5	0.2527(5)	0.2766(5)
U1	0	0	0	0	0	0
U2	0.2518(9)	0.2475(8)	0.0016(11)	0.25	0.25	0
O1	− 0.0210(7)	− 0.0685(4)	0.1569(5)	0	− 0.0671(4)	0.1614(5)
O2	0.1320(11)	0.1156(11)	0.0856(7)	0.1263(4)	0.1179(4)	0.0732(3)
O22	0.6211(11)	0.6247(11)	0.0694(7)			
O3	0.1683(9)	0.3647(11)	0.1119(12)	0.1693(3)	0.3625(3)	0.1166(3)
O33	0.6601(8)	0.8692(12)	0.1141(12)			
O4	0.1484(8)	0.3164(9)	− 0.1247(9)	0.1415(3)	0.3257(4)	− 0.1232(3)
O44	0.6349(9)	0.8273(9)	− 0.1233(9)			
B (Å^2)	0.55(7)			0.50(6)		

TABLE 3
Selected Atomic Distances (Å) in $Sr_5U_3O_{14}$ and $BaSr_4U_3O_{14}$ at 295 K

$Sr_5U_3O_{14}$		$BaSr_4U_3O_{14}$	
Sr1–2O3	2.727(11)	Ba–4O3	2.793(3)
–2O33	2.647(11)		
–2O4	2.994(10)	Ba–4O4	2.892(4)
–2O44	2.819(10)		
Sr2–O1	2.844(11)	Sr2–2O1	3.155(3)
–O2	2.589(15)	–2O2	2.660(4)
–O22	2.657(15)		
–O3	2.489(16)	–2O3	2.473(5)
–O33	2.484(16)		
–O4	2.598(13)	–2O4	2.579(6)
–O44	2.561(14)		
Sr3–O1	2.448(7)	Sr3–O1	2.411(7)
–O2	2.602(15)	–2O2	2.674(5)
–O22	2.601(14)		
–O3	2.588(17)	–2O3	2.578(5)
–O33	2.553(16)		
–O4	2.484(15)	–2O4	2.498(5)
–O44	2.452(14)		
U1–2O1	1.916(5)	U1–2O1	1.936(5)
–2O2	2.190(12)	–4O2	2.124(4)
–2O22	2.101(12)		
U2–O2	2.210(15)	U2–2O2	2.210(4)
–O22	2.175(16)		
–O3	2.029(16)	–2O3	2.032(4)
–O33	2.086(16)		
–O4	1.978(15)	–2O4	2.026(4)
–O44	2.037(15)		

stability of $Sr_5U_3O_{14}$ with respect to the neighboring phases $SrUO_4$ or Sr_2UO_5, we have determined its enthalpy of formation and entropy at 298.15 K. Since the samples prepared always contained either $SrUO_4$ or Sr_2UO_5, we used a sample contaminated with β-$SrUO_4$ of which the thermodynamic properties are known well enough. The chemical analysis of this sample (31.301 ± 0.055 mass% Sr; 52.215 ± 0.005 mass% U) indicated that the sample contained 4.62 mass% of β-$SrUO_4$. The enthalpy of solution of this sample in 5.08 mol dm^{-3} HCl(aq) was measured calorimetrically. After a correction for the enthalpy of solution of β-$SrUO_4$ (16), the resulting enthalpy of solution was combined with auxiliary values for the enthalpies of formation of $SrCl_2$(aq), $SrCl_2$(s), and γ-UO_3 in the same solution to give the standard enthalpy of formation of $Sr_5U_3O_{14}$: $\Delta_f H^\circ(298.15\ \mathrm{K}) = -(7265.8 \pm 7.5)\ \mathrm{kJ\ mol^{-1}}$.

The same sample used for the solution calorimetry was used to measure the low-temperature heat capacity adiabatically from 4 to 420 K. The experimental values below 18 K were fit with a $c_p = \alpha T^3$ function, to obtain the value for $S^\circ(10\ \mathrm{K})$ which was used as the starting value for the integration from 10 to 298.15 K. The resulting value for the entropy of the mixture, $S^\circ(298.15\ \mathrm{K}) = 499.56\ \mathrm{J\ mol^{-1}\ K^{-1}}$, was corrected for the presence of 4.62 mass% β-$SrUO_4$ of which the entropy, $S^\circ(298.15) = 153.15\ \mathrm{J\ mol^{-1}\ K^{-1}}$, has been measured by Westrum *et al.* (17).[1] We thus obtain for the entropy of pure $Sr_5U_3O_{14}$ the value $S^\circ(298.15\ \mathrm{K}) = 558.8\ \mathrm{J\ mol^{-1}\ K^{-1}}$. The Gibbs energy of $Sr_5U_3O_{14}$ can now be calculated from the relationship (18)

$$\Delta_f G^\circ(T) = \Delta_f H^\circ(298.15\ \mathrm{K}) - T\Delta_f S^\circ(298.15\ \mathrm{K}), \qquad [1]$$

assuming no phase changes occur in the temperature range given. Thus, for the equilibrium

$$Sr_5U_3O_{14}(s) = 3\beta\text{-}SrUO_4 + 2Sr(g) + O_2(g),$$

we obtain

$$\begin{aligned}\Delta_r G^\circ(T) &= -RT \ln K_p \\ &= -RT \ln (p_{Sr}/p^\circ_{Sr})^2 (p_{O_2}/p^\circ_{O_2}) \qquad [2]\end{aligned}$$

as the basis for Fig. 4. The same can be done for the other strontium uranate phases, and their relative stabilities can then be calculated. The enthalpies of formation of all strontium uranates have recently been measured and evaluated (16). The situation with respect to the entropies is, as usual, poor. Only the entropies of β-$SrUO_4$ and $Sr_5U_3O_{14}$ have been measured, and the values of the other strontium uranates have to be estimated. This has been done by taking the contributions of SrO and UO_3 in the hexavalent uranates as additives, and assuming $\Delta_r S^\circ = 0$ at 298.15 K. The entropies thus obtained have been adjusted slightly to get the proper sequences in the phase diagram. The results are listed in Table 4. The relative stabilities in the Sr–U–O system at 1250 K are shown in the predominance area diagram (Fig. 4). One can see that $Sr_5U_3O_{14}$ has a narrow area of stability which explains the difficulty in preparing it in a pure form. DTA and quenching experiments show that $Sr_5U_3O_{14}$, when heated in air, disproportionates into $SrUO_4 + Sr_2UO_5$ above 1600 K, immediately followed by decomposition of Sr_2UO_5 into $SrUO_4$ and Sr_3UO_6. This follows from the X-ray powder patterns of DTA samples taken after quenching from various temperatures.

---

[1] In the publication the notation "α-$SrUO_4$" should apparently be β-$SrUO_4$ in view of the comment on the structure given by the authors on p. 147.

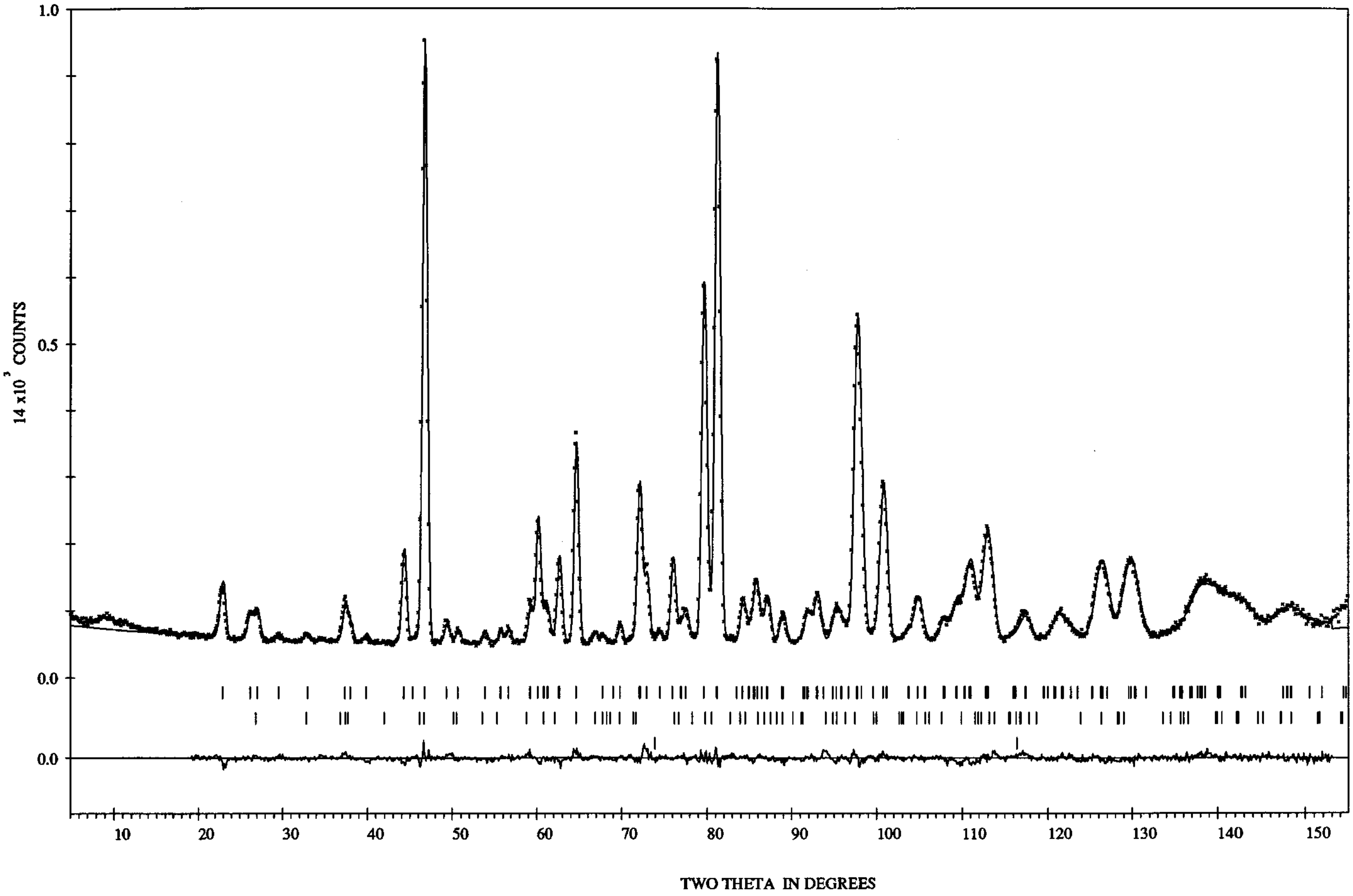

FIG. 1. Observed (dots) and calculated (full line) neutron diffraction profile of $BaSr_4U_3O_{14}$. Upper row: tick marks below the profile indicate the position of the Bragg reflections of the compound; the lower row indicates the position of the Bragg reflections of a small amount of β-$SrUO_4$. Difference (observed − calculated) curve appears at the bottom of the plot.

4. DISCUSSION

When the enthalpies of formation from the oxides of the hexavalent strontium uranates are plotted against the Sr/U mole ratio, two different series can be observed (Fig. 3). The compounds $Sr_3U_{11}O_{36}$ and $Sr_2U_3O_{11}$ belong, together with α-UO_3, to the same pseudo-hexagonal, U_3O_8-type series, having an almost linear increase in the enthalpy of formation per mole of UO_3. In the second series again a linear, though different, increase is observed in the sequence of the compounds $Sr_5U_3O_{14}$, Sr_2UO_5, and Sr_3UO_6 which have a pseudo-cubic, monoclinic structure.

Stern *et al.* (8) already observed that the X-ray powder pattern of $Sr_5U_3O_{14}$ is almost identical to the nonindexed pattern listed by Brisi (19), as given in the JCPDS file no. 30-1312 (20). The present investigation confirms this observation. The structures of all known strontium uranates have been determined now, with the exception of that of $Sr_2U_3O_{11}$ (21).

Although the structures of $Sr_5U_3O_{14}$ and $BaSr_4U_3O_{14}$ determined above resemble the chiolite structure of $Na_5Al_3F_{14}$ (22), the details of octahedral tilting are different. In the absence of octahedral tilting, the ideal chiolite (parent) structure consists of a framework where BX_6 octahedrons are linked by their corners to form layers. By every fourth octahedron a linear group BX_2 is substituted by an $A1$ atom; the remaining A atoms are between the layers. A third of the octahedra share four corners; two-thirds share two corners and are free to rotate along an axis connecting these corners for a better coordination of the $A1$ atom. The layer composition is B_3X_{14}. Alternate layers are staggered by half the base diagonal of the unit cell so that the c axis is twice the interlayer distance. The parent $A_5B_3X_{14}$ structure has tetragonal symmetry $I4/mmm$ with $a_c = 4(r_B + r_X)$ and $c = 10$–11 Å for $X = $ F or O, depending on the radius of A.

The voids for $A1$ atoms are too big to accomodate these atoms. The voids are reduced in size by tilting of the octahedra. In $Na_5Al_3F_{14}$ the rotation in one layer is 14.5°

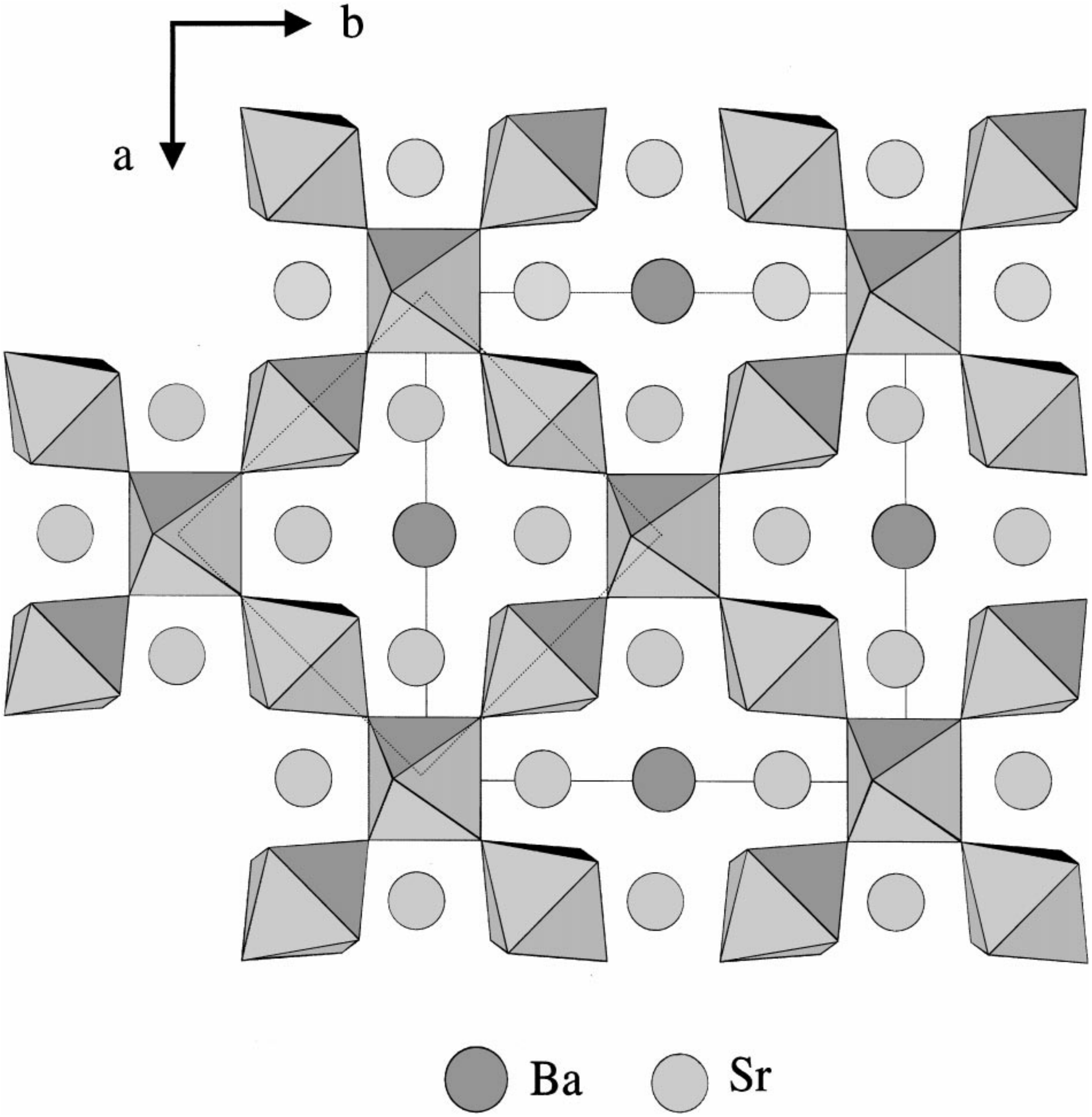

FIG. 2. The structure of $BaSr_4U_3O_{14}$ at $z \approx 0$. The dimensions of the unit cell are given by full lines, that of the chiolite subcell by a dotted line.

along an axis parallel to the c axis. In the alternate layer the rotation is opposite, resulting in space group $P4/mnc$. In the compounds above, the octahedra of the parent structure are rotated along a two-fold axis in the layer plane, destroying two symmetry planes, resulting in space group *Cmca* for opposite rotations in the alternate layer and an $a_c\sqrt{2}$, $a_c\sqrt{2}$, c_c unit cell. A second small rotation parallel to the c axis led to the subgroup *Pbca* for $Sr_5U_3O_{14}$. The Srl atoms are in eight coordination; the other Sr atoms have seven or six oxygen neighbors.

The refinement gives unusually large Sr1 oxygen distances (Table 3), 2.80 vs 2.64 Å for ionic radii (23). Since replacement of Sr1 by the larger Ba atom could fill the void better, we prepared $BaSr_4U_3O_{14}$ with indeed the higher space group *Cmca* and a more regular structure. The structural results for $Sr_5U_3O_{14}$ and $BaSr_4U_3O_{14}$ are not very different. Sr(Ba) and U atoms are in both compounds, nearly on the same position (Table 3). The UO_6 octahedra are tilted around a two-fold axis in the plane for 23.6° and 22.3°, respectively. For $Sr_5U_3O_{14}$ there is an additional tilt

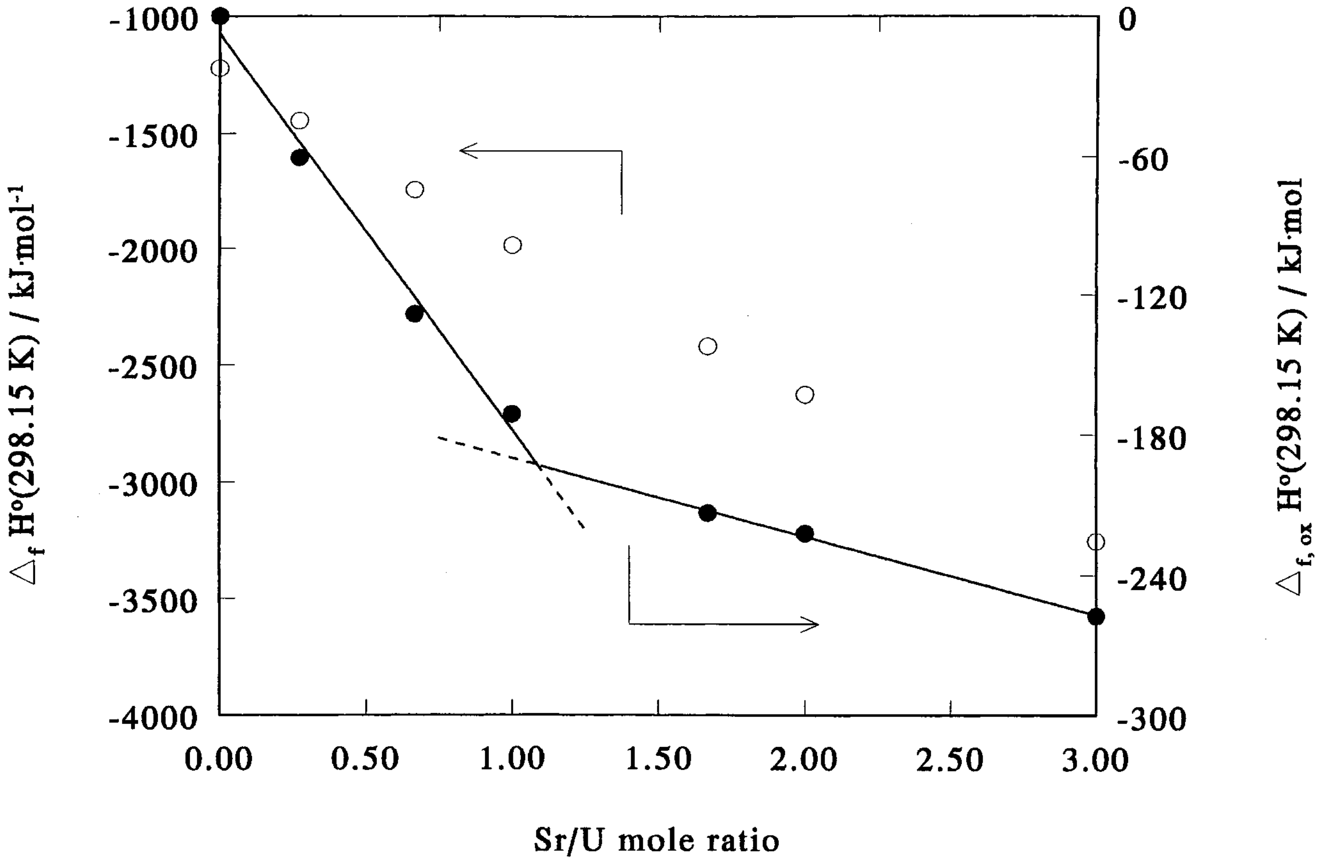

FIG. 3. The standard molar enthalpies of formation of the hexavalent strontium uranates from the elements (open symbols), and from the oxides (solid symbols), as a function of the Sr/U mole ratio.

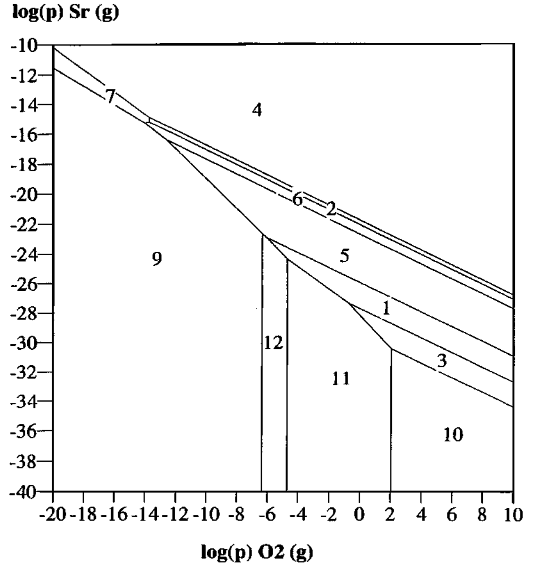

FIG. 4. The predominance area diagram of the Sr–U–O system at 1250 K. 1 = $Sr_2U_3O_{11}(s)$, 2 = $Sr_2UO_5(s)$, 3 = $Sr_3U_{11}O_{36}(s)$, 4 = $Sr_3UO_6(s)$, 5 = $SrUO_4(s)$, 6 = $Sr_5U_3O_{14}(s)$, 7 = $Sr_2UO_{4.5}(s)$, 8 = U(s), 9 = $UO_2(s)$, 10 = $UO_3(s)$, 11 = $U_3O_8(s)$, and 12 = $U_4O_9(s)$.

parallel to the *c* axis of about 2.3°. It is possible that this compound has the *Cmca* structure at high temperatures and that at a lower temperature a second-order transformation to *Pbca* occurs; twinning is then most likely, as has been reported by Sterns *et al.* (8).

A new type of deformation of the parent chiolite structure has been demonstrated. The octahedra in $BaSr_4U_3O_{14}$ are

TABLE 4
Thermochemical Properties of the Strontium Uranates at 298.15 K

Compound	Enthalpy of formation $\Delta_f H^\circ$ (kJ mol^{-1})	Entropy S° (J mol^{-1} K^{-1})[a]
$Sr_3U_{11}O_{36}$	− 15900 ± 17	[1210]
$Sr_2U_3O_{11}$	− 5236.4 ± 4.8	[415]
β-$SrUO_4$	− 1985.1 ± 1.4	153.15 ± 0.25
$Sr_5U_3O_{14}$	− 7265.8 ± 7.5	558.8 ± 1.0
Sr_2UO_5	− 2626.9 ± 2.0	[209]
Sr_3UO_6	− 3252.4 ± 2.1	[262.7]
$Sr_2UO_{4.5}$	− 2488.0 ± 2.5	[203]

[a] Estimated values in parentheses.

rotated over large angles along a two-fold axis in the layer; in $Sr_5U_3O_{14}$ a small additional rotation perpendicular to the layer is present. The octahedra in the $Na_5Al_3F_{14}$ structure are only rotated along a four-fold axis perpendicular to the layer, thus conserving the tetragonal symmetry.

ACKNOWLEDGMENTS

The authors thank A. Bontenbal for providing the neutron diffraction patterns and P. van Vlaanderen for experimental assistance.

REFERENCES

1. T. Fujino, T. Yamashita, and H. Tagawa, *J. Solid State Chem.* **73,** 544 (1988).
2. E. H. P. Cordfunke and D. J. W. IJdo, *J. Solid State Chem.* **109,** 272–276 (1994).
3. B. O. Loopstra and H. M. Rietveld, *Acta Crystallogr. B* **25,** 787 (1969).
4. D. J. W. IJdo, *Acta Crystallogr. C* **49,** 650 (1993).
5. J. O. Sawyer, *J. Inorg. Nucl. Chem.* **34,** 3268 (1972).
6. H. W. Zachariasen, *Acta Crystallogr.* **1**, 281 (1948).
7. E. H. P. Cordfunke, P. van Vlaanderen, M. Onink, and D. J. W. IJdo, *J. Solid State Chem.* **94,** 12 (1991).
8. M. Sterns, R. L. Withers, P. Midgeley, and R. Vincent, *Austr. J. Chem.* **49,** 817–826 (1996).
9. E. H. P. Cordfunke, A. S. Booij, V. M. Smit-Groen, P. van Vlaanderen, and D. J. W. IJdo, *J. Solid State Chem.* **131,** 341 (1997).
10. K. Weber, *Acta Crystallogr.* **23,** 720 (1967).
11. F. Sears, *Neutron News* **3,** 26 (1992).
12. D. B. Wiles and R. A. Young, *J. Appl. Crystallogr.* **14,** 149 (1981).
13. W. A. Lingerak, P. C. Konijn, and J. Slanina, "Proceedings of the First Annual Symposium on Safeguards and Nuclear Material Management," p. 157. Vienna, Italy, 1979.
14. E. H. P. Cordfunke and W. Ouweltjes, *J. Chem. Thermodyn.* **20,** 235 (1988).
15. J. C. van Miltenburg, G. J. K. van den Berg, and M. J. Bommel, *J. Chem. Thermodyn.* **19,** 1129 (1987).
16. E. H. P. Cordfunke, A. S. Booij, and M. E. Huntelaar, *J. Chem. Thermodyn.*, in press.
17. E. F. Westrum, Jr., H. A. Zainel, and D. Jakes, "Proceedings Symposium on Thermodynamics of Nuclear Materials 1979," Vol. II, pp. 143–154 Vienna, Italy, 1980.
18. C. B. Alcock, *Nature* **209,** 198–199 (1966).
19. C. Brisi, M. Montorsi, and G. A. Burlando, *Rev. hautes Temp. Réfract.* **8,** 37 (1971).
20. JCPDS powder diffraction file 30-1312, International Center for Powder Diffraction Data, Pennsylvania, U.S.A.
21. E. H. P. Cordfunke and B.O. Loopstra, *J. Inorg. Nucl. Chem.* **29,** 51 (1967).
22. C. Jacoboni, A. Lebel, and J. Rousseau, *J. Solid State Chem.* **36,** 297 (1981).
23. R. D. Shannon, *Acta Crystallogr. A* **32,** 751 (1975).