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High Temperature Behaviour of Strontium Uranates

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High temperature behaviour of strontium uranates has been studied by means of X-ray powder diffractometry, thermogravimetry, differential thermal analysis, dilatometry and high temperature X-ray diffractometry. Six compounds of strontium uranates, viz. Sr_3UO_6, Sr_2UO_5, $Sr_3U_2O_9$, $SrUO_4$, $Sr_2U_3O_{11}$ and $SrU_4O_{12\cdot60}$ have been identified in the temperature range of 1273-1673 K in air. The thermogravimetric analysis of these compounds carried out in the temperature range up to 1623 K shows that the decomposition temperature of strontium uranates decreases with decrease in strontium content. The results of DTA in the temperature range up to 1573 K show that in case of Sr_3UO_6 there is a reversible transition which is attributed to Sr_3UO_6 (monoclinic) $\rightleftharpoons Sr_3UO_5$ (orthorhombic) and in the case of $SrU_4O_{12\cdot80}$ there is decomposition of the parent compound to $Sr_2U_3O_{11}$ and U_3O_{8-y}. The results of thermal expansion studies carried out in the temperature range up to 1273 K show that the average linear and volume thermal expansion coefficients of the compounds Sr_3UO_6, Sr_2UO_5, $Sr_3U_2O_9$ and $SrUO_4$ are nearly the same ($\alpha_l \approx 10\text{-}13 \times 10^{-6}K^{-1}$ and $\alpha_v \approx 29\text{-}33 \times 10^{-6}K^{-1}$). However, the thermal expansion coefficient of $Sr_2U_3O_{11}$ shows an increase ($\alpha_l = 17{\cdot}4 \times 10^{-6}K^{-1}$ and $\alpha_v = 47{\cdot}2 \times 10^{-6}K^{-1}$) and for the compound $SrU_4O_{12\cdot80}$ it shows a sudden decrease ($\alpha_l = 3{\cdot}5 \times 10^{-6}K^{-1}$ and $\alpha_v = 13{\cdot}7 \times 10^{-6}K^{-1}$).

THE binary strontium oxide-uranium oxide system is quite complex in which no less than six compounds are formed[1,2]. The strontium uranates known in the literature are Sr_3UO_6, Sr_2UO_5, $Sr_3U_2O_9$, $SrUO_4$, $Sr_2U_3O_{11}$ and $SrU_4O_{12\cdot80}$.

While many investigators have reported the preparation and characterization of strontium uranates[1-7], very little is known about their thermal behaviour at high temperatures. Studies in the binary strontium oxide-uranium oxide system in air were, therefore, undertaken. For this purpose, different strontium uranates, were prepared and characterized by chemical and physical methods and their high temperature behaviour was studied by means of X-ray powder diffractometry, thermogravimetry, differential thermal analysis, dilatometry and high temperature X-ray diffractometry. The results of these studies are reported here.

Materials and Methods

The strontium uranates were prepared using strontium nitrate (E. Merck, GR) and nuclear pure U_3O_8.

Appropriate quantities of the carefully ground mixtures of $Sr(NO_3)_2$ and U_3O_8 to give the desired mole % of SrO and UO_3 were heated at different temperatures in the range 1273-1673 K for a period of 24 hr in air. The samples were air-quenched after the desired period of heating and ground to −200 mesh. This process was repeated if required.

Philips wide angle diffractometer with filtered CuK_α radiation (34 kV, 18 mA) was used for the identification of phases. A scanning speed of 1/2° 2θ/min was used.

For the determination of cell parameters, a slower scanning speed of 1/4° 2θ/min was used. The accurate values of cell parameters were obtained using the computer programme for least square refinement method.

The composition of the compounds was determined by chemical analysis. Strontium was determined gravimetrically[8] as $SrSO_4$ while total uranium, and oxygen to uranium ratio were determined volumetrically[9,10].

Stanton (model HT) automatic recording thermobalance of 1 mg sensitivity and range up to 1623 K was used for the thermogravimetric analysis. The TG curves were recorded with about 1 g of each sample at a constant heating rate of 10 K/minute.

Differential thermal analysis was carried out in the temperature range up to 1573 K, the maximum temperature attainable with the present DTA equipment[11]. DTA curves were recorded using about 500 mg of the sample with a recorder span of 0·5 mV. A constant linear heating rate of 10 K/min was used. Calcined alumina was used as a reference material.

Thermal expansion measurements were carried out employing dilatometric and high temperature X-ray diffractometric techniques[12] in the temperature range up to 1273 K. Type LKB 3185 dilatometer with a constant heating rate of 4 K/min was used for dilatometric studies. Samples in the form of pellets (10×12·5 mm) were used. The pellets were sintered in air for 24 hr at 1273 K. For high temperature X-ray diffractometric studies. MRC model X-86-N3 high temperature X-ray diffractometer attachment mounted on a Philips wide angle goniometer was used. The high temperature X-ray powder diffraction patterns were recorded at different temperatures in the range of 298-1273 K in air using CuK_α radiation (34 kV, 18 mA). Temperature control was maintained by the MRC X-8600-5000-2 proportional temperature controller.

Results and Discussion

The various phases identified in the system SrO-UO_3 in the temperature range of 1273-1673 K and the composition range of 25 to 80 at $\% \left(\frac{\text{uranium}}{\text{uranium+strontium}}\right)$ are schematically shown in Fig. 1.

The same six compounds of strontium uranates, viz. Sr_3UO_6, Sr_2UO_5, $Sr_3U_2O_9$, $SrUO_4$, $Sr_2U_3O_{11}$ and $SrU_4O_{12\cdot80}$ as reported earlier[1,2] were obtained in this temperature range in air. The schematic phase diagram (Fig. 1) is in good agreement with that given by Brisi *et al.*[2].

The results of the cell parameter determinations as well as the chemical analysis of the strontium uranates are summarized in Table 1.

In TGA no weight loss is observed for the compounds Sr_3UO_6, Sr_2UO_5 and $Sr_3U_2O_9$ in the entire temperature range studied, i.e. 298-1623 K in air. However, for the compounds $SrUO_4$, $Sr_2U_3O_{11}$ and $Sr_4O_{12\cdot80}$ the temperature for inception of weight loss due to decomposition decreased with decreasing strontia content and was about 1593 K, 1533 K and 1433 K respectively. The weight losses observed for the compounds $SrUO_4$, $Sr_2U_3O_{11}$ and $SrU_4O_{12\cdot80}$ are attributed to the loss of oxygen accompanied by decomposition of these compounds to $SrUO_{4-x}$, $Sr_2U_3O_{11-x}$ and $Sr_2U_3O_{11-x}+U_3O_{x-y}$ respectively as confirmed from X-ray and chemical analysis (Fig. 1 and Table 1).

The results of the differential thermal analysis of strontium uranates studied up to 1573 K in air showed the absence of DTA peaks for the compounds Sr_2UO_5, $Sr_3U_2O_9$, $SrUO_4$ and $Sr_2U_3O_{11}$. However, in the case of Sr_3UO_6 and $SrU_4O_{12\cdot80}$ DTA peaks were observed (Fig. 2).

The compound Sr_3UO_6 showed an endothermic peak with a peak width from 1473 to 1503 K during

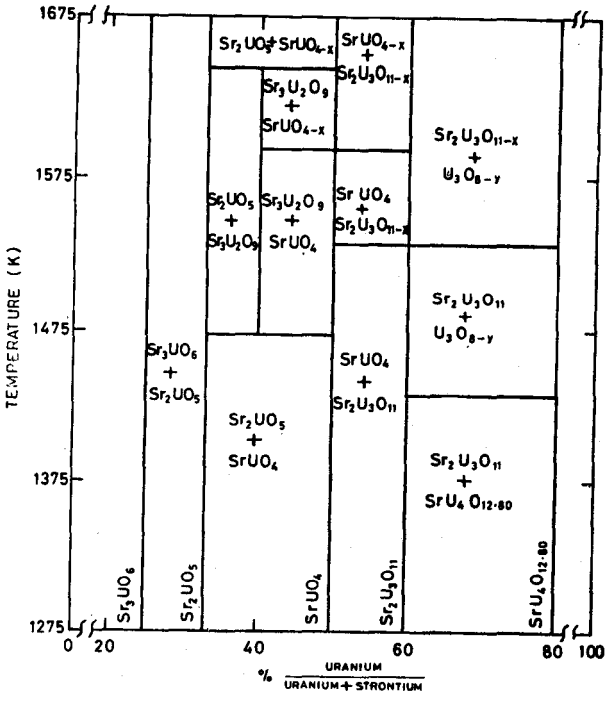

Fig. 1 — Schematic representation of the phase analysis in the system SrO-UO_3 in air

TABLE 1 — STRONTIUM TO URANIUM RATIOS, OXYGEN TO URANIUM RATIOS, DESIGNATED COMPOSITIONS AND THE CELL PARAMETERS OF STRONTIUM URANATES HEATED FOR 24 HR IN AIR IN THE TEMPERATURE RANGE OF 1273-1673 K

Heated at (K)	Sr/U (obs)	O/U (obs)	Designated composition	Crystal symmetry	Cell parameters and angles						Z
					a_0 (nm)	b_0 (nm)	c_0 (nm)	$\alpha°$	$\beta°$	$\gamma°$	
				Sr_3UO_6							
1273	3·00±0·01	3·00±0·01	3SrO: UO_3	Monoclinic	0·5964	0·6201	0·8548	—	90·32	—	2
1673	3·00±0·01	3·00±0·01	3SrO: UO_3	do	0·5964	0·6179	0·8558	—	90·19	—	2
				Sr_2UO_5							
1273	2·00±0·01	3·00±0·01	2SrO: UO_3	Monoclinic	0·8111	0·5653	1·1929	—	108·63	—	4
1673	2·00±0·01	3·00±0·01	2SrO: UO_3	do	0·8109	0·5657	1·1920	—	108·95	—	4
				$Sr_3U_2O_9$							
1473	1·50±0·01	3·00±0·01	1·50 SrO: UO_3	Orthorhombic	1·1052	0·7951	0·8003	—	—	—	6
1603	1·50±0·01	3·00±0·01	1·50 SrO: UO_3	do	1·1063	0·7943	0·7990	—	—	—	6
				$SrUO_4$							
1273	1·00±0·01	3·00±0·01	SrO: UO_3	Orthorhombic	0·5478	0·7961	0·8117	—	—	—	4
1673	1·00±0·01	2·61±0·05	SrO: $UO_{2\cdot61}$	Rhombohedral	0·6540	0·6540	0·6540	35·85	35·85	35·85	1
				$Sr_2U_3O_{11}$							
1273	0·67±0·01	2·99±0·02	·67 SrO:$UO_{2\cdot99}$	Triclinic pseudorhombohedral	0·6489	0·6530	0·6487	35·41	36·08	35·44	1
1673	0·67±0·01	2·84±0·03	·67 SrO:$UO_{2\cdot99}$	do	0·6484	0·6503	0·6482	35·64	35·89	35·65	1
				$SrU_4O_{12\cdot8}$							
1273	0·25±0·01	2·95±0·02	·25 SrO:$UO_{2\cdot95}$	Monoclinic pseudoorthorhombic	0·6730	0·4192	0·4070	—	90·09	—	2

heating with ΔH of 519·1 Joules/mole and an exothermic peak with a peak width from 1368 to 1333 K during cooling with ΔH of 374·4 Joules/mole. The transition temperatures during heating and cooling were respectively 1493 K and 1358 K. The difference in ΔH observed during heating and cooling runs could be due to the reverse reaction being sluggish during cooling resulting in loss in the observed ΔH. Also the base line does not remain flat and hence tapers off. Hence, the peak area could be in error. These peaks are attributed to the reversible crystallographic transition of

$$Sr_3UO_6 \text{ (monoclinic)} \rightleftharpoons Sr_3UO_6 \text{ (orthorhombic)}$$

as found from the high temperature X-ray diffraction studies[13].

The compound $SrU_4O_{12\cdot80}$ showed only an endothermic peak with a peak width from 1423 to 1463 K during heating with ΔH of 548·4 Joules/mole, the decomposition temperature being 1443 K. No exotherm was obtained on cooling. The endothermic peak is attributed to the disproportionation of $Sr_4O_{12\cdot80}$ into two phases $Sr_2U_3O_{11}$ and U_3O_{8-y} (Fig. 1).

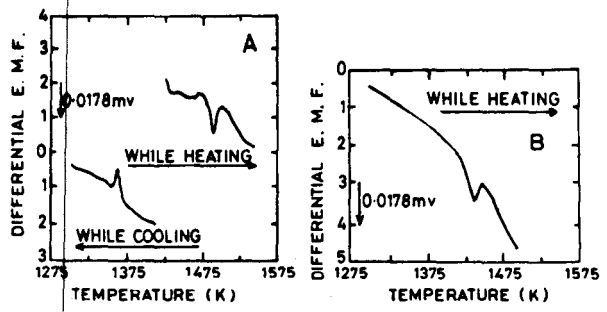

Fig. 2 — DTA curves of (A) Sr_3UO_6 while heating and cooling and (B) $SrU_4O_{12\cdot80}$ while heating only

The results of dilatometric studies showed that the per cent linear thermal expansion of all the strontium uranates increased almost linearly with increase in temperature in range 298-1223 K (Fig. 3).

The variation of per cent linear thermal expansion with temperature in this range could be expressed by the following least square fitted equations:

(1) Sr_3UO_6:

$$\% \text{ expansion} = 11{\cdot}40\times10^{-4}(T-298)+6{\cdot}12\times10^{-7}(T-298)^2-5{\cdot}37\times10^{-10}(T-298)^3 \quad \ldots(1)$$

(2) Sr_2UO_5:

$$\% \text{ expansion} = 9{\cdot}64\times10^{-4}(T-298)+1{\cdot}97\times10^{-7}(T-298)^2-4{\cdot}21\times10^{-11}(T-298)^3 \quad \ldots(2)$$

(3) $Sr_3U_2O_9$:

$$\% \text{ expansion} = 7{\cdot}53\times10^{-4}(T-298)+6{\cdot}82\times10^{-7}(T-298)^2-3{\cdot}76\times10^{-10}(T-298)^3 \quad \ldots(3)$$

(4) $SrUO_4$:

$$\% \text{ expansion} = 7{\cdot}45\times10^{-4}(T-298)+5{\cdot}96\times10^{-7}(T-298)^2-3{\cdot}18\times10^{-10}(T-298)^3 \quad \ldots(4)$$

(5) $Sr_2U_3O_{11}$:

$$\% \text{ expansion} = 9{\cdot}92\times10^{-4}(T-298)+2{\cdot}97\times10^{-7}(T-298)^2+5{\cdot}52\times10^{-10}(T-298)^3 \quad \ldots(5)$$

(6) $SrU_4O_{12\cdot80}$:

$$\% \text{ expansion} = 1{\cdot}04\times10^{-4}(T-298)+6{\cdot}46\times10^{-7}(T-298)^2-4{\cdot}07\times10^{-10}(T-298)^3 \quad \ldots(6)$$

where T is the temperature in K.

The results obtained with the high temperature X-ray diffractometric studies for the variation of the cell parameters and unit cell volume per molecule of the strontium uranates Sr_3UO_6, Sr_2UO_5, $Sr_3U_2O_9$, $SrUO_4$, $Sr_2U_3O_{11}$ and $SrU_4O_{12\cdot80}$ as a function of temperature in the range 298-1273 K in air are shown in Figs. 4(i) to (vi) and 5(i) to (vi) respectively.

The cell parameters of all the strontium uranates except $SrU_4O_{12\cdot80}$ showed a nearly linear increase

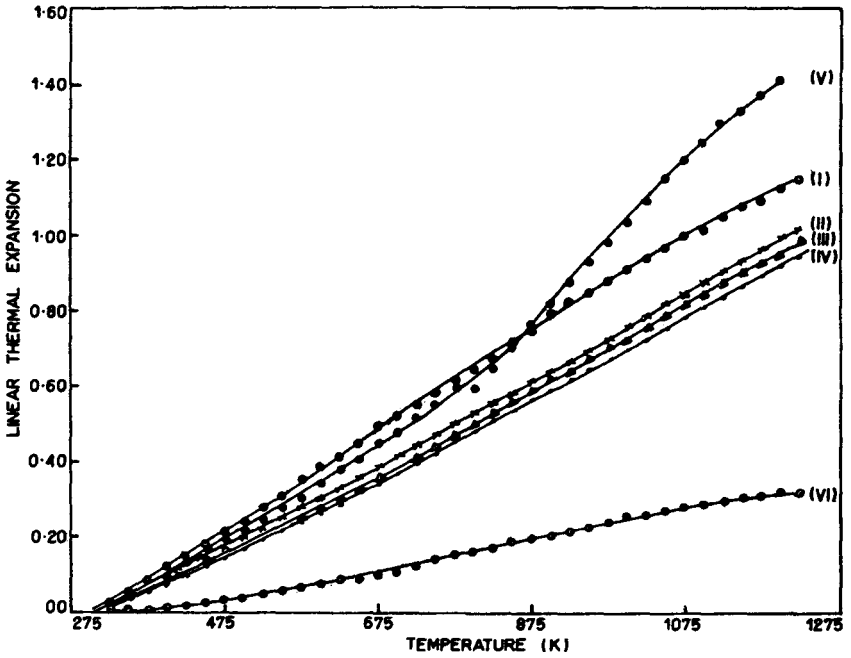

Fig. 3 — Variation of per cent linear thermal expansion of strontium uranates as a function of temperature [(I) Sr_3UO_6, (II) Sr_2UO_5, (III) $Sr_3U_2O_9$, (IV) $SrUO_4$, (V) $Sr_3U_3O_{11}$ and (VI) $SrU_4O_{12\cdot80}$]

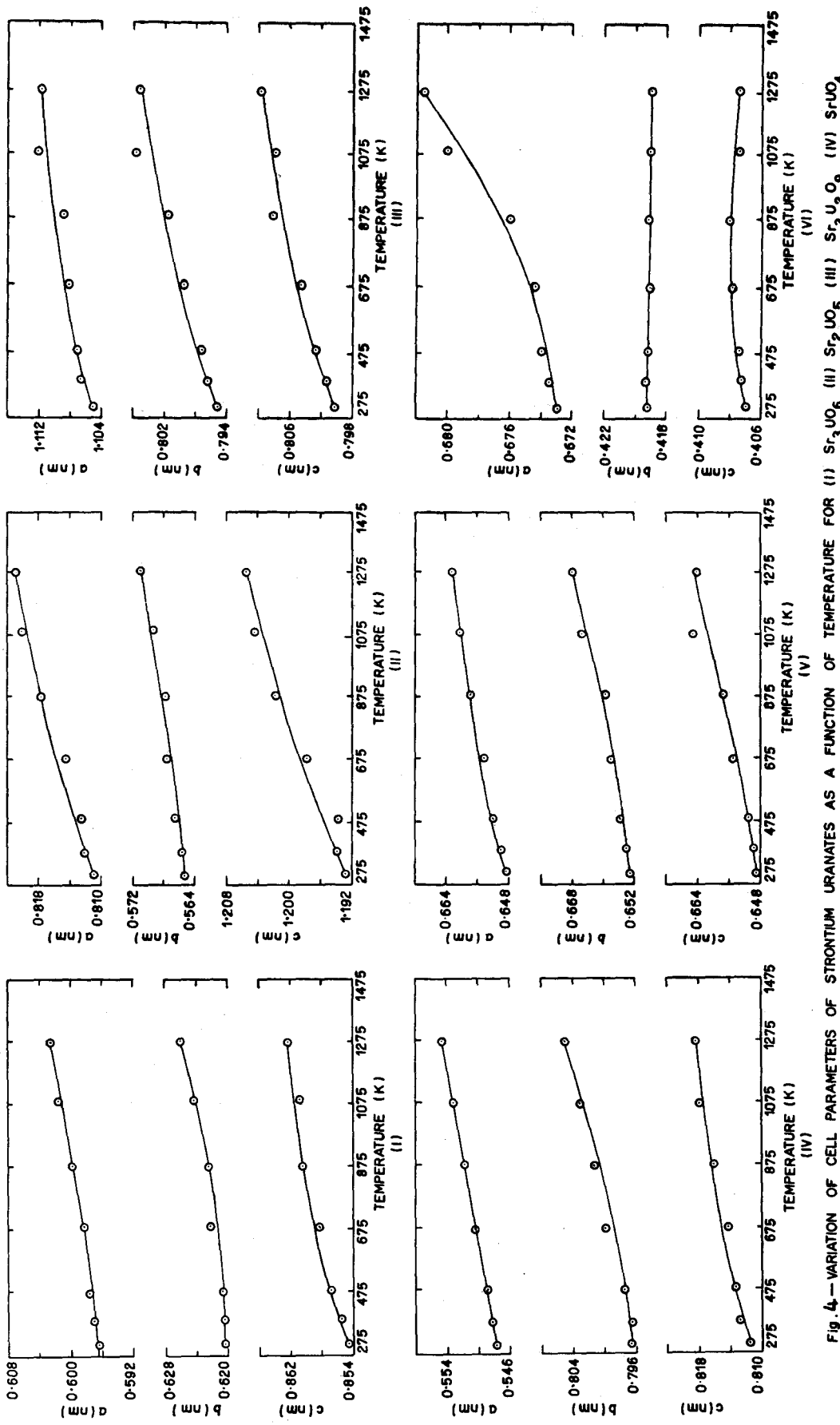

Fig. 4 — VARIATION OF CELL PARAMETERS OF STRONTIUM URANATES AS A FUNCTION OF TEMPERATURE FOR (I) Sr_3UO_6 (II) Sr_2UO_5 (III) $Sr_3U_2O_9$ (IV) $SrUO_4$ (V) $Sr_2U_3O_{11}$ AND (VI) $SrU_4O_{12\cdot80}$

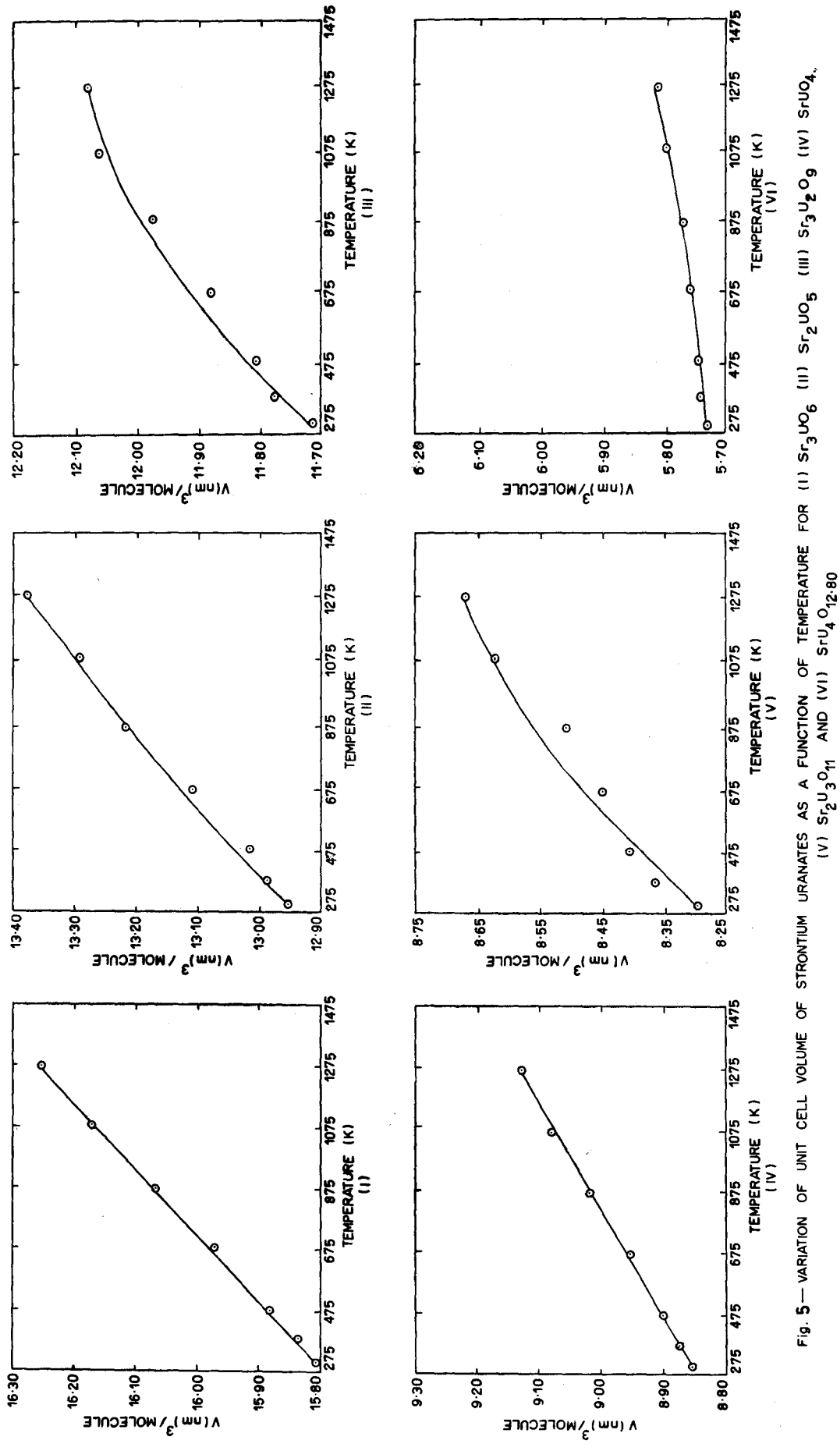

Fig. 5—VARIATION OF UNIT CELL VOLUME OF STRONTIUM URANATES AS A FUNCTION OF TEMPERATURE FOR (I) Sr_3UO_6 (II) Sr_2UO_5 (III) $Sr_3U_2O_9$ (IV) $SrUO_4$, (V) $Sr_2U_3O_{11}$ AND (VI) $SrU_4O_{12.80}$

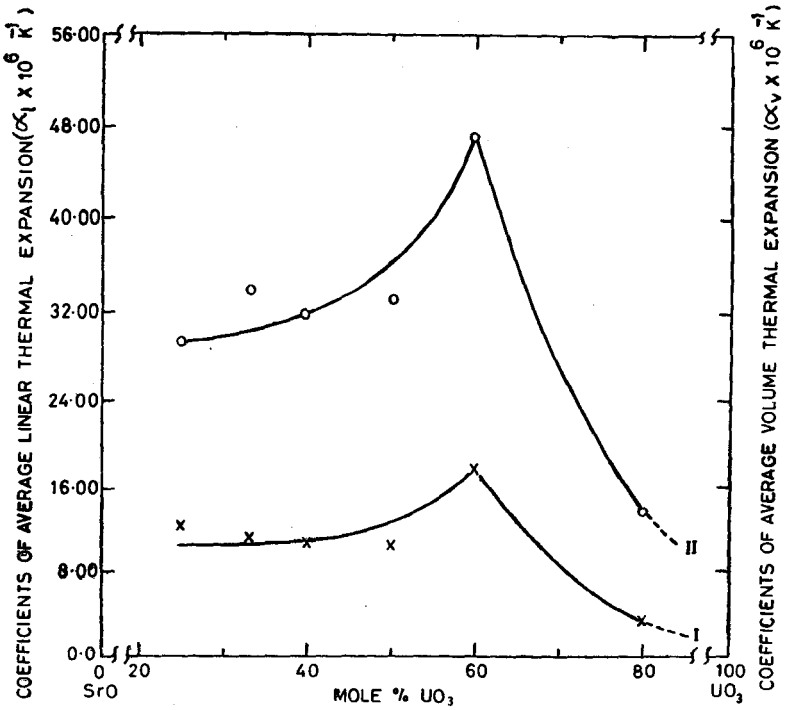

Fig. 6 — Variation of average linear (I, temp. range 298-1223K) and volume thermal (II, temp. range 298-1273K) expansion coefficient of strontium uranates versus composition

TABLE 2 — COEFFICIENTS OF AVERAGE LINEAR THERMAL EXPANSION (α_l) OBTAINED FROM DILATOMETRIC STUDIES AND THE COEFFICIENTS OF AVERAGE VOLUME THERMAL EXPANSION (α_v) OBTAINED FROM HIGH TEMPERATURE X-RAY DIFFRACTOMETRIC STUDIES FOR THE STRONTIUM URANATES

Sl No.	Compound	Crystal symmetry	α_l $\times 10^6 K^{-1}$ (298-1223 K)	α_v $\times 10^6 K^{-1}$ (298-1273 K)
1	Sr_3UO_6	Monoclinic	12·5	29·4
2	Sr_2UO_5	do	11·1	33·9
3	$Sr_3U_2O_9$	Orthorhombic	10·6	31·7
4	$SrUO_4$	do	10·3	33·0
5	$Sr_2U_3O_{11}$	Triclinic pseudo-rhombohedral	17·4	47·2
6	$SrU_4O_{12\cdot80}$	Monoclinic pseudo-orthorhombic	3·5	13·7

in '*a*', '*b*' and '*c*' axis with increase in temperature [Figs. 4(i) to (vi)]. However, for the compound $SrU_4O_{12\cdot80}$ the *a* axis increased with increase in temperature whereas the *b* axis decreased very gradually and the *c* axis increased very negligibly and then tended to decrease [Fig. 4(vi)].

The unit cell volume per molecule of all the strontium uranates except $SrU_4O_{12\cdot80}$ increased normally and almost linearly with increase in temperature (Fig. 5(i) to (v)]. For the compound $SrU_4O_{12\cdot80}$, however, the unit cell volume increased very gradually. The gradual increase in unit cell volume of $SrU_4O_{12\cdot80}$ as compared to other strontium uranates is attributed to the peculiar variation of *a*, *b* and *c* axis as shown in Fig. 4(vi).

The values of the coefficients of average linear and volume thermal expansion are given in Table 2 and plotted in Fig. 6 as a function of composition (mole % UO_3).

As can be seen from Table 2 and Fig. 6 the coefficients of average linear as well as volume thermal expansion for the strontium uranates Sr_3UO_6, Sr_2UO_5, $Sr_3U_2O_9$ and $SrUO_4$ are very nearly the same [$\alpha_l \approx 10\text{-}13 \times 10^{-6}$ K^{-1} and $\alpha_v \approx 29\text{-}33 \times 10^{-6}$ K^{-1}]. However, for the compound $Sr_2U_3O_{11}$ both these coefficients show an increase ($\alpha_l = 17{\cdot}4 \times 10^{-6}$ K^{-1} and $\alpha_v = 47{\cdot}2 \times 10^{-6}$ K^{-1}) and for the compound $SrU_4O_{12\cdot80}$ the coefficients of expansion show a sudden decrease ($\alpha_l = 3{\cdot}5 \times 10^{-6}$ K^{-1} and $\alpha_v = 13{\cdot}7 \times 10^{-6}$ K^{-1}). Thus amongst all the strontium uranates, the thermal expansion coefficient of $Sr_2U_3O_{11}$ is maximum and that of $SrU_4O_{12\cdot80}$ is minimum (Fig. 6).

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