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THERMAL STABILITY OF OSMIUM MIXED OXIDES. III. $SrOsO_3$ DECOMPOSITION PRODUCTS: A NEW DEFECT PYROCHLORE $Sr_2Os_2O_{6.4\pm0.2}$

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ABSTRACT

The thermal decomposition of $SrOsO_3$ has been studied by DTA, thermogravimetry and X-ray powder diffraction. The decomposition of orthorhombic $Sr_2Os_2O_7$ depends strongly on the partial pressure of air above the samples investigated. In this paper the $Sr_2Os_2O_{6.4\pm0.2}$ pyrochlore formation and some properties of the phase are described. The stability conditions of $SrOsO_3$ are also discussed.

INTRODUCTION

The strontium—osmium double oxide $SrOsO_3$ was prepared for the first time in 1972 by the present authors by means of a conventional solid-state reaction of carbonate $SrCO_3$ with osmium dioxide [1] in a study of a series of analogous compounds $MOsO_3$, where M is Ca, Sr and Ba. The compound $SrOsO_3$ has the perovskite structure with orthorhombic distortion ($GdFeO_3$ structure type) and its unit cell parameters are $a_0 = 5.32$ Å, $b_0 = 5.58$ Å, $c_0 = 7.90$ Å. After Sarkozy and Chamberland [2] the compound has two modifications: cubic and orthorhombic, both of which were synthesized by the thermal decomposition of the complex hydroxide $SrOs(OH)_6$.

In this paper we present the results of a study of the thermal decomposition of $SrOsO_3$ in air and describe the formation of a defect pyrochlore $Sr_2Os_2O_{6.4\pm0.2}$.

EXPERIMENTAL

The starting material, powdered $SrOsO_3$, was synthesized from a mixture of $SrCO_3$ and OsO_2 by a patented method given in detail in ref. 1. Thermal decomposition was carried out on Derivatograph OD-102 and OD-103 models (Hungary) in a platinum crucible (7 mm diameter) using calcined alumina as the reference material. In each case 50 and 100 mg of powdered sample with a particle size less than 36 microns were taken. The thermal decomposition was carried out in static air at heating rates of 1.8, 10 and 20 deg min^{-1}. Quenching and identification of the samples were carried out according to the methods described in ref. 3.

RESULTS

We found that in static air the decomposition mechanism of $SrOsO_3$ definitely depended on the heating rate as illustrated by Fig. 1. As can be seen from Fig. 1, decreasing the heating rate changes both the temperature interval of the decomposition and the form of DTA and TG curves.

In Fig. 1 we give the derivatogram of $SrOsO_3$ for the thermal decomposition in static air at the heating rate of 1.8 deg min^{-1}. On the DTA curve there is a small endothermic peak with a maximum at 760 ± 5°C and the peak does not concern mass loss. On powdergrams of the pattern which were heated above 770°C we have discovered a new phase. The phase is the cubic form of $SrOsO_3$ which is stable on cooling down to room temperature and has unit cell parameter a = 9.225 Å.

Above 960°C one may observe a small mass gain on the TG curve which stops at 1020 ± 6°C. Simultaneously we have not observed a peak on the DTA curve. On a powdergram of a sample quenched from 1030°C all the reflexes are new and are neither orthorhombic nor cubic $SrOsO_3$. The powdergram of the new phase was indexed in cubic symmetry and all the Miller indexes coincided with a common pyrochlor index set (space group *Fd3m*). Wet chemical analyses of the new phase gives the formula $Sr_2Os_2O_{6.4\pm0.2}$. The unit cell parameter of the phase is 10.340 Å, pycnometric density (in toluene) 7.78 g cm^{-3}, X-ray density 7.822 g cm^{-3} for the formula $Sr_2Os_2O_{6.4}$ and it contains eight molecules per unit cell. The X-ray powder pattern for $Sr_2Os_2O_{6.4\pm0.2}$ is given in Table 1.

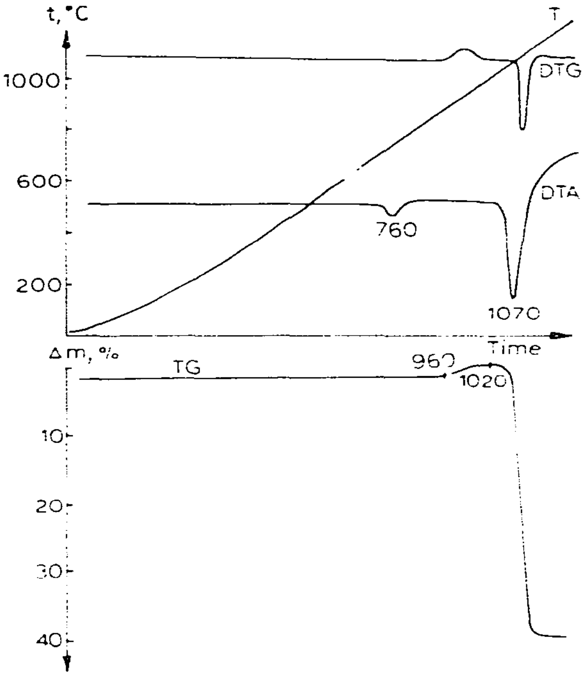
The defect pyrochlore $Sr_2Os_2O_{6.4\pm0.2}$ is stable up to 1065 ± 5°C; and after this temperature a fast mass loss occurs and on the DTA curve a large endothermic peak with maximum at 1070 ± 6°C is observed. This mass loss results from the thermal decomposition of $Sr_2Os_2O_{6.4\pm0.2}$ into several substances, two of which are in a gaseous state, namely oxygen and osmium tetraoxide. The solid residue consists of strontium monoxide and osmium metal in a molar ratio near 2 : 1 (from 2.12 to 1.85 for different samples).

The cubic phase $Sr_2Os_2O_{6.4\pm0.2}$ also occurs at fast heating rate of $SrOsO_3$ in static air (see Fig. 2). This process is carried out somewhat faster than the former and is completely finished at 1012 ± 6°C. There is no intermediate endothermic peak at 760°C on the DTA curve. The final product of the thermal decomposition of $SrOsO_3$ is also pure $Sr_2Os_2O_{6.4\pm0.2}$. The pyrochlore has the same decomposition temperature, 1065 ± 5°C.

The pyrochlore $Sr_2Os_2O_{6.4\pm0.2}$ is chemically a very stable compound and insoluble in water, mineral acids, alkalis and aqueous ammonia. It decomposes in boiling aqua regia or in molten alkalis above 250°C.

Electrical resistivity vs. temperature readings for three different samples of $Sr_2Os_2O_{6.4\pm0.2}$ were measured in the temperature interval 80—417 K. $Sr_2Os_2O_{6.4-0.2}$ exhibits metallic conductivity with an average room temperature resistivity 2.0×10^{-2} ohm cm.

We emphasize especially that there is no pyrochlore phase on heating $SrOsO_3$ in dynamic air (flow rate about 8 ml min^{-1}) for the three different heating rates (see Experimental). In this case a new phase formation occurs above 910—920°C but it has no cubic symmetry. On the basis of wet



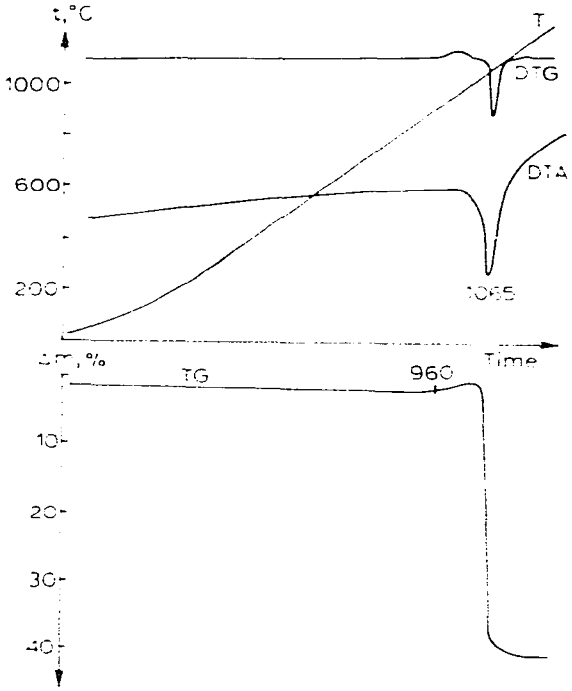


Fig. 1. The thermal decomposition of $SrOsO_3$ in static air. Heating rate 1.9°C min^{-1}.

Fig. 2. The thermal decomposition of $SrOsO_3$ in static air. Heating rate 10°C min^{-1}.

TABLE 1

X-ray powder diffraction data for $Sr_2Os_2O_{6.4}$

h k l	d_{calc} (Å)	d_{obs} (Å)	*I*
1 1 1	6.00	—	—
2 0 0	5.17	5.11	12
2 2 0	3.660	3.642	17
3 1 1	3.119	3.123	10
2 2 2	2.987	2.992	100
4 0 0	2.585	2.580	62
4 2 0	2.313	—	—
4 2 2	2.111	2.110	8
5 1 1	1.990	1.982	3
4 4 0	1.8286	1.8280	54
5 3 1	1.7483	—	—
5 3 3	1.5773	1.5777	2
6 2 2	1.5591	1.5601	59
4 4 4	1.4925	1.4922	21
7 1 1	1.4483	1.4470	3
6 4 0	1.4342	—	—
6 4 2	1.3820	1.3826	3
7 3 1	1.3464	—	—
8 0 0	1.2927	1.2926	14
6 6 2	1.1863	1.1860	18

chemical analyses the phases contains strontium and osmium in the same molar ratio 1 : 1, however from X-ray diffraction and thermogravimetric data the phase is not a pyrochlore $Sr_2Os_2O_{6.4\pm n}$ even if we assume that the n value is equal to 0.6 or more. This case is to be investigated in detail sometime in the future.

DISCUSSION

The various forms of the DTA curves in Figs. 1 and 2 are the result of a phase transition of orthorhombic $SrOsO_3$ into cubic modification. Probably the transition has a diffuse nature and occurs in some temperature interval, i.e. it is the second order transition. This is the most probable reason for the absence of a endothermic effect on the DTA curve in Fig. 2. Both at the slow heating rate and at the fast one the starting orthorhombic form of $SrOsO_3$ transforms into the cubic one. However, because of a faster heating rate of a sample in the latter case we do not observe the complete transition. That is why we have a double phase mixture of orthorhombic and cubic modifications of $SrOsO_3$ up to 1000—1020°C in the latter case. At 1000 -1020°C the fastest oxidation of the starting osmate occurs and then the pyrochlore $Sr_2Os_2O_{6.4\pm0.2}$ forms.

We believe that the main feature of pyrochlore phase formation is the appearence of the cubic form $SrOsO_3$. The most probable mechanism of pyrochlore $Sr_2Os_2O_{6.4\pm0.2}$ formation is nucleation and the existence of two simultaneous phases — cubic $SrOsO_3$ and pyrochlore $Sr_2Os_2O_{6.4\pm0.2}$ — as intermediates in the temperature interval 990—1010°C may confirm this hypothesis. The other experimental observation for this consideration is the absence of a pyrochlore phase in the thermal decomposition of $SrOsO_3$ in dynamic air, i.e. under conditions in which oxidation rate is faster and the phase transition of the orthorhombic form of $SrOsO_3$ into the cubic form does not occur. The observed phenomenon is submitted to Dankov's principle of orientational and dimensional conformity of crystalline structures [4]. According to the basic rule of the principle a reorganization of atoms from the cubic structure of $SrOsO_3$ into the cubic pyrochlore structure in our case must require small deviations of atomic positions in crystalline lattice, while the deviations would be too great for a realization of the direct structural transitions from orthorhombic $SrOsO_3$ into the cubic pyrochlore structure.

Since the pyrochlore $Sr_2Os_2O_{6.4\pm0.2}$ formation is a result of an addition of oxygen to cubic $SrOsO_3$ we have here an oxidation reaction. It is natural to believe that the oxidation process causes an alteration of the osmium oxidation state. In $SrOsO_3$ osmium has the formal oxidation state +4. If osmium transforms into the oxidation state +5 the pyrochlore should have the formula $Sr_2Os_2O_7$. However, there are published data about the stability of osmium(V) in solid oxides [2,5] and the certain stability of osmium(VI) in mixed oxides. In addition the disproportionation reaction $5\ Os^{4+} \rightarrow 4\ Os^{5+} + Os^0$ would cause an accumulation of great quantities of osmium metal and the discovery of the osmium in reaction products formed during the decomposition. This process is not observed in our case. Finally, the metallic conductivity of powder samples of $Sr_2Os_2O_{6.4\pm0.2}$ over a wide temperature interval (irrespective of the quantity of the structural oxygen in a sample) indicates that the true formula of the pyrochlore phase is probably $Sr_2Os^{IV}_{2-n}Os^{VI}_nO_{6.0+n}$ where $0.2 \leqslant n \leqslant 0.6$. We cannot yet explain this variation of n values, however, we have a series of experimental probes under different quenching conditions (i.e. quenching into liquid nitrogen from 1040°C with a cooling rate from 500 to 800°C sec^{-1}). All our experimental results give partial oxidation of osmium only and the crystalline lattice stabilization for the pyrochlore structure may be fulfulled for a very limited ratio of Os(IV) : Os(VI).

Based on the analysis of the experimental results and the above discussion we obtain equations for the $SrOsO_3$ thermal transformation process in static air. These equations are

$$SrOsO_3(\text{orthorhombic}) \rightarrow SrOsO_3(\text{cubic}) \text{ (at } 760 \pm 15^\circ\text{C)} \qquad (1)$$

$$2\ SrOsO_3(\text{cubic}) + \frac{1}{x}\,O_2 \rightarrow Sr_2Os^{IV}_{2-x}Os^{VI}_xO_{6+x} \text{ (for } 0.2 \leqslant x \leqslant 0.6\text{; temperature interval } 970\text{—}1020^\circ\text{C)} \qquad (2)$$

$$Sr_2Os^{IV}_{2-x}Os^{VI}_xO_{6+x} \rightarrow 2\ SrO + Os + OsO_4 + x\ O_2 \text{ (} 0.2 \leqslant x \leqslant 0.6 \text{ at } 1065 \pm 6^\circ\text{C)} \qquad (3)$$

Equations (1—3) describe the $SrOsO_3$ thermal decomposition for a slow heating rate (below 2° min^{-1}). For a faster heating rate, namely above 9–10° min^{-1}, eqn. (1) is realized over a wider temperature interval and apparently consists of two kinetically unequal parts. The total equation of $SrOsO_3$ thermal decomposition has the same form

$$2\ SrOsO_3 \rightarrow 2\ SrO + Os + OsO_4 \qquad (4)$$

The theoretical value of mass loss according to eqn. (4) is 38.96%. The thermogravimetric value is 39.14 ± 0.12% and the result coincides with the theoretical value very successfully. Hence, eqn. (4) for the $SrOsO_3$ thermal decomposition and our representation of the process are true.

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