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THERMAL STABILITY OF OSMIUM MIXED OXIDES.IV. $SrOsO_3$ DECOMPOSITION PRODUCTS. A NEW METASTABLE $SrOsO_4$ PHASE

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ABSTRACT

The thermal decomposition of $SrOsO_3$ in a dynamic air flow has been studied using differential thermal analysis, thermogravimetry and X-ray powder diffraction. After decomposition above 920°C, a new phase was discovered, which has the formula $SrOsO_4$, a scheelite structure and tetragonal unit cell parameters $a_0 = 5.422$ Å, $c_0 = 11.92$ Å, $Z = 4$, space group $I4_1/a$, and a pycnometric density of 6.46 g cm^{-3}. Above 1030 ± 6°C, $SrOsO_4$ decomposes into SrO, osmium tetroxide and osmium metal.

INTRODUCTION

The investigation of the thermal stability of the alkaline earth metal osmates(IV) show interesting properties which are different from other platinum metal mixed oxide decompositions. This difference is shown by the composition of the intermediates and the decomposition conditions of the primary phases. The main reasons for the observed differences are related to the components of the atmosphere and the heating rate of the sample. We have already reported the formation of new intermediates, i.e. the formation of a $Ca_2Os_2O_7$ phase with an orthorhombic structure and $Ca_2Os_2O_{7-x}$ phases with a cubic pyrochlore structure [1,2]. In part III [3], we reported on a new defect pyrochlore $Sr_2Os_2O_{6.4\pm0.2}$ and characterised some properties of the new phase.

In this paper, we present some experimental results on the decomposition process of $SrOsO_3$. In the decomposition products, we found a new phase with the formula $SrOsO_4$ which has not been identified before.

EXPERIMENTAL

The conditions of synthesis and the methods of investigation of $SrOsO_3$ samples have been published in previous papers [1—3]. In this investigation, we studied the decomposition of $SrOsO_3$ in dynamic air at a dry air flow velocity over the sample of approximately 8 ml sec^{-1} and with heating rates of 1.8, 5 and 10° min^{-1}.

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RESULTS

It has been found during this investigation that, for the three heating rates studied, the mechanism for the thermal decomposition of $SrOsO_3$ in dynamic air does not depend on the heating rate, although the thermal decomposition of $SrOsO_3$ in a flowing current of air differs markedly from the decomposition observed in static air.

The first peculiarity of $SrOsO_3$ decomposition in flowing air is the slow mass gain from 800 to 820°C; the second is the lack of a transition of orthorhombic $SrOsO_3$, into the cubic phase. On the DTA curves, there is a diffuse endothermic peak with a maximum at ~880°C at a heating rate of 1.8 deg min^{-1} or at 910°C at a heating rate of 10 deg min^{-1} (Fig. 1). The ends of the peaks coincide with the end of the mass gain process. X-Ray powder analysis of the samples which were quenched from 920 and 960°C shows a special set of diffraction lines. This set cannot be identified as a cubic phase (neither cubic $SrOsO_3$ nor the possible pyrochlore $Sr_2Os_2O_{6.4\pm n}$). Wet chemical analysis of the solid residue gives a constant strontium : osmium molar ration of 1 : 1. The mass gain is 5.2% in the temperature interval 810—900°C. The result coincides with the probable oxidation process

$$SrOsO_3 + \tfrac{1}{2}\,O_2 \rightarrow SrOsO_4 \qquad (1)$$

Chemical analysis of oxygen gives the values 19.20, 18.80 and 18.55%

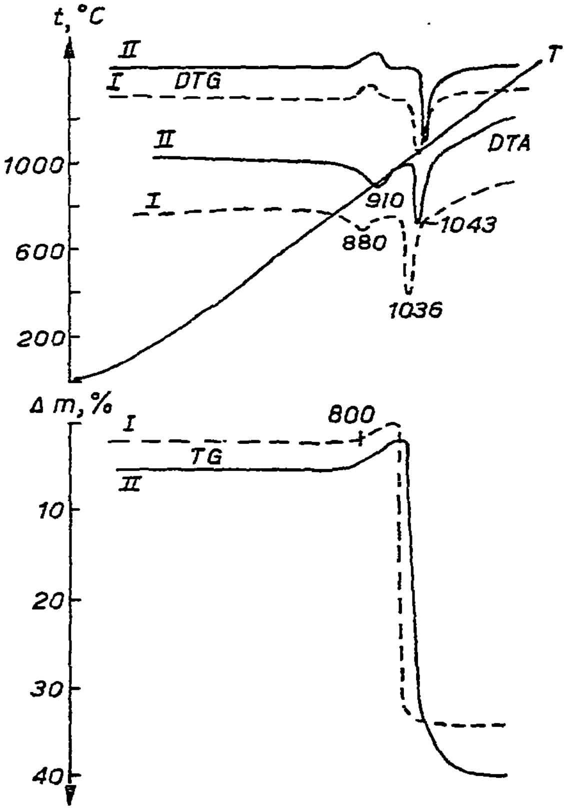

Fig. 1. The thermal decomposition of $SrOsO_3$ in dynamic air. I, Heating rate 1.8°C min^{-1}; II, heating rate 10°C min^{-1}.

(average value 18.85%) which agrees well with the theoretical oxygen content for $SrOsO_4$ of 18.72%.

The new $SrOsO_4$ phase is metastable. At a medium cooling rate (ca. 40—45 deg min^{-1}), it transforms into the initial orthorhombic modification of $SrOsO_3$ almost quantitatively. The pure $SrOsO_4$ is formed by sintering in a container in flowing air followed by very rapid quenching (1—2 sec) from 980—1000°C in liquid nitrogen. After quenching, the compound is a brownish-black powder which is stable in dry air but which absorbs moisture from the air and transforms into a greyish-black product with an indefinite composition under room conditions.

The X-ray powdergram for $SrOsO_4$ is indexed as the tetragonal system with the unit cell parameters $a_0 = 5.422$ Å and $c_0 = 11.92$ Å. The compound has the identical powdergram and close unit cell parameters as the already known $SrMoO_4$ (Fig. 2), which crystallises in the scheelite structure with the unit cell parameters $a_0 = 5.36$ Å, $c_0 = 11.94$ Å (Sillen and Nylander [4]) or $a_0 = 5.4168$ Å, $c_0 = 11.951$ Å (ASTM data [5]). From the intensity ratio and the similarity of the powdergrams and the unit cell parameters, it may be supposed that the $SrOsO_4$ phase also has the scheelite structure (space group $I4_1/a$—C^6_{4h}). The pycnometric density of $SrOsO_4$ (in dry toluene) is 6.46 g cm^{-3}. The X-ray density should be 6.476 g cm^{-3} for the formula $SrOsO_4$ with four molecules per unit cell. The X-ray powder diffraction data for $SrOsO_4$ is given in the Table 1.

$SrOsO_4$ is stable up to 1030 ± 6°C after which it begins to decompose with rapid mass loss. On the DTA curves, the process is associated with the significant endothermic peak with a maximum at 1043 ± 6°C (Fig. 1). The solid residue of the decomposition process consists of strontium oxide and osmium metal in a molar ratio of about 2 : 1.

DISCUSSION

The experimental data from this investigation together with the results of Part III [3] show an interesting and rare fact, viz. that substances are formed

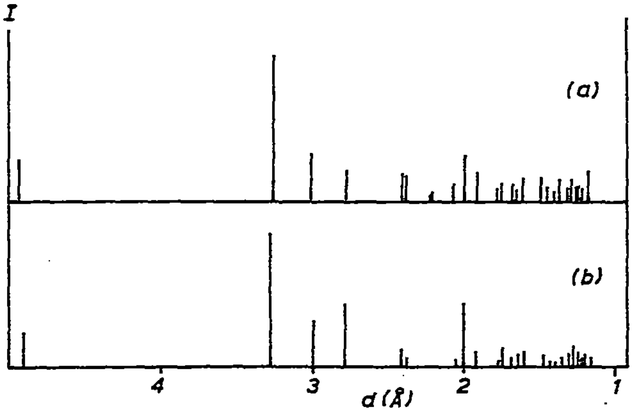

Fig. 2. The powdergrams of (a) $SrMoO_4$ and (b) $SrOsO_4$.

TABLE 1

X-Ray powder diffraction data for $SrOsO_4$

h	k	l	d_{calc} (Å)	d_{obs} (Å)	I
1	0	1	4.93	4.86	26
1	1	2	3.227	3.232	100
0	0	4	2.981	2.980	19
2	0	0	2.712	2.717	42
2	1	1	2.378	2.377	11
1	1	4	2.353	2.350	4
1	0	5	2.182		
2	1	3	2.070	2.076	2
2	0	4	2.006	2.002	46
2	2	0	1.9166	1.9182	19
3	0	1	1.7875	1.7868	4
1	1	6	1.7639	1.7648	26
2	1	5	1.7002	1.6962	5
3	1	2	1.6482	1.6510	14
2	2	4	1.6125	1.6120	18
3	2	1	1.4924	1.4932	5
0	0	8	1.4897	1.4888	6
3	0	5	1.4403	1.4388	2
3	2	3	1.4067		
2	1	7	1.3935	1.3917	3
4	0	0	1.3553	1.3559	6
2	0	8	1.3056	1.3080	11
3	1	6	1.2982	1.2988	18
3	3	2	1.2500	1.2525	10
4	0	4	1.2340	1.2340	8
4	2	0	1.2127	1.2133	10
2	2	8	1.1765	1.1768	6

with different composition and structure from the thermal decomposition of the same compound in the same gas medium (i.e. in air). From the results of the thermal decomposition of $SrOsO_3$, the conclusion may be drawn that the composition of the gas medium above the heated sample has an effect on the formation of new products and intermediates. Hence the process by which new phases are formed on heating $SrOsO_3$, namely cubic $SrOsO_3$, pyrochlore $Sr_2Os_2O_{6.4\pm0.2}$ or tetragonal $SrOsO_4$, are diffusion based only and a structural reorganisation (for example, orthorhombic $SrOsO_3$ to cubic $SrOsO_3$) or $SrOsO_3$ oxidation is significantly related to oxygen diffusion. Since we are dealing with three different processes in the case considered, it should be noted that there are three possible kinds of diffusion which may be taken into account, (a) oxygen diffusion into a solid from air, (b) oxygen diffusion within a solid accompanied by structural reorganisation and (c) oxygen diffusion from a solid into a gaseous phase. It is necessary to consider the formation of OsO_4 vapour on a solid surface and near layers of air. For a description of the exact mechanism by which the gas composition influences transitions in solids and the composition of solid products, it is necessary to do some experiments with the ^{18}O isotope.

X-Ray data on $SrOsO_4$ indicates that it has the scheelite structure. This is based on the identity of $SrOsO_4$ and $SrMoO_4$ powdergrams, the close unit cell parameters and systematic extinction of reflections corresponding to the space group $I4_1/a—C_{4h}^6$. On the basis of these results, it may be supposed that osmium has the oxidation state VI in $SrOsO_4$. The data also indicate that $SrOsO_4$ is not the mixed phase $SrOs(IV)_{0.5}Os(VIII)_{0.5}O_4$ (A) which can be formed under different initial oxidation conditions. It would not be possible to explain Os(IV) stabilisation in the oxidising phase when one half of Os(IV) is oxidised to Os(VIII) at the same time if one supposes that $SrOsO_4$ can have the formula (A).

The thermal decomposition of $SrOsO_4$ can be ascertained from the wet chemical analysis and the thermogravimetric data. The total mass loss for the decomposition of $SrOsO_4$ is 38.24 ± 0.18% and this value leads to the equation,

$$2\ SrOsO_4 \rightarrow 2\ SrO + OsO_4 + Os + O_2 \qquad (2)$$

The theoretical value for the mass loss according to this equation is 38.96%. This result is convincing evidence that the above equation for the thermal decomposition of $SrOsO_4$ is true. The total equation for the thermal decomposition of $SrOsO_4$ in dynamic air as the result of combining reactions (1) and (2) is

$$2\ SrOsO_3 \rightarrow 2\ SrO + OsO_4 + Os \qquad (3)$$

It should be emphasised that the total equation for the thermal decomposition of $SrOsO_3$ in static air has the same form as reaction (3). This is the most interesting experimental fact that arises in this investigation of mixed oxide decomposition.

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