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THERMAL STABILITY OF OSMIUM MIXED OXIDES
I. $CaOsO_3$ DECOMPOSITION PRODUCTS: A NEW ORTHORHOMBIC PHASE $Ca_2Os_2O_7$

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ABSTRACT

The thermal decomposition of $CaOsO_3$ by differential thermal analyses, thermogravimetry and X-ray powder diffraction has been studied. In nitrogen $CaOsO_3$ decomposes at 880 ± 10°C into CaO, osmium metal and oxygen due to the reaction $CaOsO_3 \rightarrow CaO + Os + O_2$. In static air the decomposition occurs in three stages: $2CaOsO_3 + 1/2\ O_2 \rightarrow Ca_2Os_2O_7$ (in region 775–808°C), $Ca_2Os_2O_7 \rightarrow Ca_2Os_2O_{6.5} + 1/4\ O_2$ (at a temperature interval of 850–1000°C) and in the third stage $Ca_2Os_2O_{6.5} \rightarrow 2CaO + OsO_4 + 1/4\ O_2$ (at 1005 ± 5°C). The first intermediate $Ca_2Os_2O_7$ is isostructural with orthorhombic $Ca_2Nb_2O_7$ and its cell parameters are: $a_0 = 3.745$ Å, $b_0 = 25.1$ Å, $c_0 = 5.492$ Å, $Z = 4$, space group Cmcm or $Cmc2_1$. $Ca_2Os_2O_7$ exhibits metallic conductivity and its electrical resistivity is 4.6×10^{-2} ohm-cm at 296K.

INTRODUCTION

Osmium-alkaline earth metal oxides with the general formula $MOsO_3$ (M = Ca, Sr, Ba) have been prepared by the authors for the first time in 1972 by means of conventional solid-state reactions of corresponding carbonates MCO_3 with osmium dioxide[1, 2]. A year later these compounds were prepared by the thermal decomposition of $MOs(OH)_6$ hexahydroxides to yield the corresponding $MOsO_3$ ternary oxide[3]. The orthorhombic perovskite $CaOsO_3$ decomposes at 775°C into osmium metal, calcium oxide and the pyrochlore modification $Ca_2Os_2O_7$ which has a cubic unit cell with $a = 10.21$ Å.

In the present study the thermal decomposition of $CaOsO_3$ with a new intermediate is described.

EXPERIMENTAL

The starting powdered $CaOsO_3$ was synthesized from a mixture of $CaCO_3$ and OsO_2 by a patented method given in detail in ref. 1. Differential thermal analyses

(DTA) and thermogravimetric analyses (TG) were carried out simultaneously on a Derivatograph OD-103 (Hungary) in a platinum crucible (7 mm diam.) using calcined alumina as the reference material. In each case 50 and 100 mg of powder sample with a particle size less than 40 μm were taken. The thermal decomposition was carried out in nitrogen or in either static or dynamic air atmosphere (passing over a sample at a rate of 100 ml min^{-1}), the heating rates were 1 and 10 deg min^{-1}.

For an intermediate identification powder samples annealed in a muffel kiln in air and quenched into liquid nitrogen were used. Decomposition products were analysed by the wet chemical method (after reducing a probe in hydrogen flow at 600°C) and the X-ray powder method. X-ray diffraction data were obtained at room temperature with a "DRON-1.5" diffractometer with Fe unfiltered radiation and with a 114 mm Debye-Sherrer camera with CoKα radiation.

RESULTS AND DISCUSSIONS

The thermal decomposition mechanism of $CaOsO_3$ depends strongly on a gaseous environment above a powder sample and this fact is confirmed by a different number of intermediates and decomposition stages at the investigation of the decomposition reaction in nitrogen, static and dynamic air atmosphere. In nitrogen the thermal decomposition of $CaOsO_3$ occurs in one stage at 880 ± 10°C according to the reaction

$$CaOsO_3 \rightarrow CaO + Os + O_2.$$

A derivatogramm of this process is given in Fig. 1.

In static air the mechanism of $CaOsO_3$ thermal decomposition is more complicated (Fig. 2). In this case the decomposition reaction occurs in three stages which may be represented by the equations:

$$2CaOsO_3 + 1/2\,O_2 \rightarrow Ca_2Os_2O_7 \text{ (in region 775–808°C)} \quad (1)$$

$$Ca_2Os_2O_7 \rightarrow Ca_2Os_2O_{6.5} + 1/4\,O_2 \text{ (in an interval 850–1000°C)} \quad (2)$$

$$Ca_2Os_2O_{6.5} \rightarrow 2CaO + Os + OsO_4 + 1/4\,O_2 \text{ (at 1005 ± 5°C)} \quad (3)$$

Summarizing the equations we have an equation for the thermal decomposition:

$$2CaOsO_3 \rightarrow 2CaO + Os + OsO_4 \quad (4)$$

At the first stage of reaction (1) a new phase $Ca_2Os_2O_7$ is formed. Sarkozy and and Chamberland have isolated a cubic modification of $Ca_2Os_2O_7$ with the pyrochlore structure[3]. In this investigation any intermediate phase with formula $Ca_2Os_2O_7$ had no cubic symmetry. We could not prepare a single crystal of an intermediate $Ca_2Os_2O_7$, but its powdergram was readily indexed in the orthorhombic system with unit cell parameters $a_0 = 3.745$ Å, $b_0 = 25.1$ Å, $c_0 = 5.492$ Å, $Z = 4$, the space group Cmcm or $Cmc2_1$ (from systematic extinction of reflections with $h + k = 2n + 1$ for hkl and $l = 2n + 1$ for $h0l$). From intensivety ratio and coincidence of the unit cell parameters

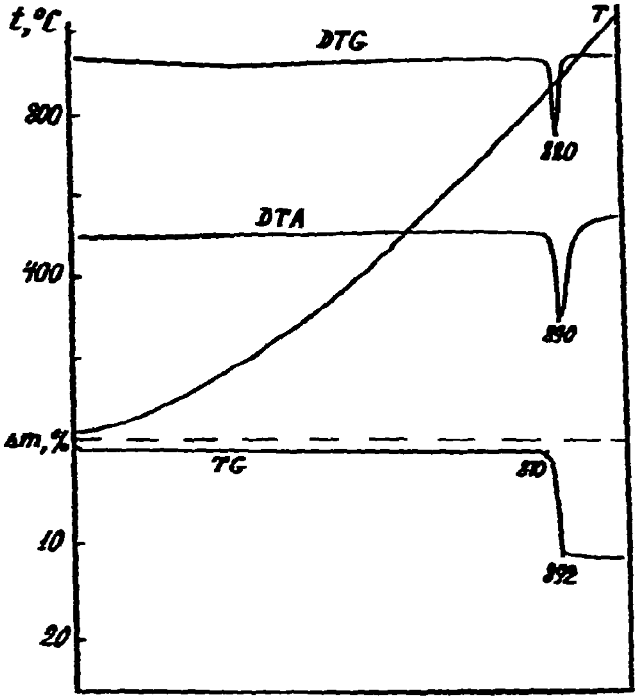

Fig. 1. The thermal decomposition of $CaOsO_3$ in nitrogen. Heating rate 10°C min^{-1}.

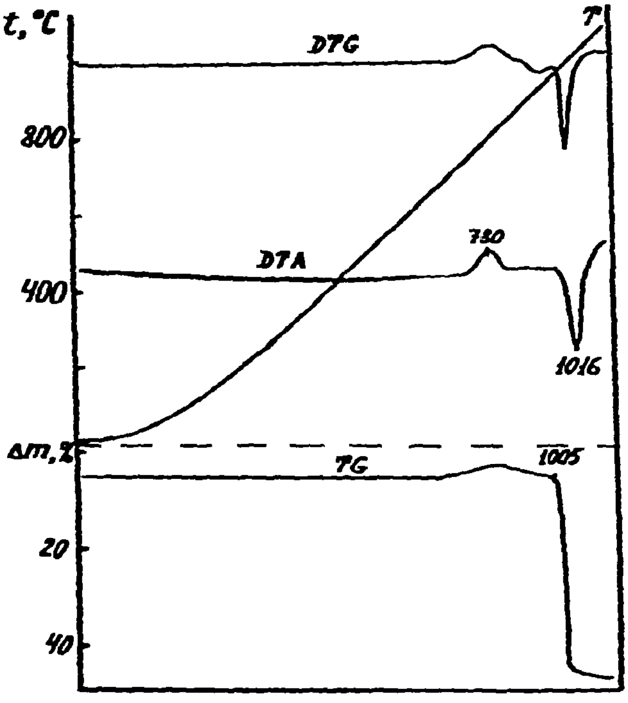

Fig. 2. The thermal decomposition of $CaOsO_3$ in static air. Heating rate 10°C min^{-1}.

and the space group, it may be supposed that the phase is isostructural with $Ca_2Nb_2O_7$[4]. The X-ray powder pattern for $Ca_2Os_2O_7$ is given in Table 1.

Pure $Ca_2Os_2O_7$ is a dark brown powder insoluble in water and mineral acids and stable at room temperature.

The new compound exhibits paramagnetic properties, its magnetic susceptibility depends very slightly on temperature. There is a small deflection from the linear function $1/\kappa = f(T)$ below 90K and it may be explained with antiferromagnetic interactions. A deflection point on the resistivity curve $\rho = f(T)$ (Fig. 3) at ~88K may confirm the hypothesis. For orthorhombic $Ca_2Os_2O_7$ metallic conductivity with an electrical resisitivity 4.6×10^{-2} ohm-cm at 296K is observed (measurements on sintered bars by four-probe techniques). The magnitude of the effective magnetic moment (1.20 M_B) of $Ca_2Os_2O_7$ is not consistent with the d^3 configuration for Os(Y), but the value is close to usual observations for Os(IY) compounds a more reasonable conclusion sums to be the orthorhombic phase is a mixture of the derivatives Os(IY) and Os(YI) than a pentavalent osmium compound.

TABLE 1

X-RAY POWDER PATTERN FOR $Ca_2Os_2O_7$

I_{obs}	d_{obs} (Å)	d_{calc} (Å)	h	k	l
8	6.32	6.30	0	4	0
11	5.07	5.05	0	2	1
6	4.18	4.18	0	6	0
19	4.12	4.13	0	4	1
28	3.71	3.702	1	1	0
5	3.432	3.410	1	3	0
22	3.312	3.328	0	6	1
100	3.137	3.133	0	8	0
39	3.066	3.071	1	1	1
31	2.908	2.900	1	3	1
41	2.743	2.747	0	0	2
24	2.724	2.724	0	8	1
68	2.628	2.632	1	5	1
34	2.510	2.506	0	10	0
11	2.279	2.282	0	10	1
4	2.235	2.235	1	9	0
19	2.066	2.066	0	8	2
9	1.885	1.882	1	7	2
16	1.874	1.872	2	0	0
26	1.850	1.856	0	10	2
22	1.733	1.733	1	9	2
28	1.703	1.707	2	4	1
		1.702	0	14	1
10	1.636	1.639	1	13	1
5	1.613	1.612	1	3	3
4	1.564	1.560	1	5	3
4	1.473	1.470	2	0	2

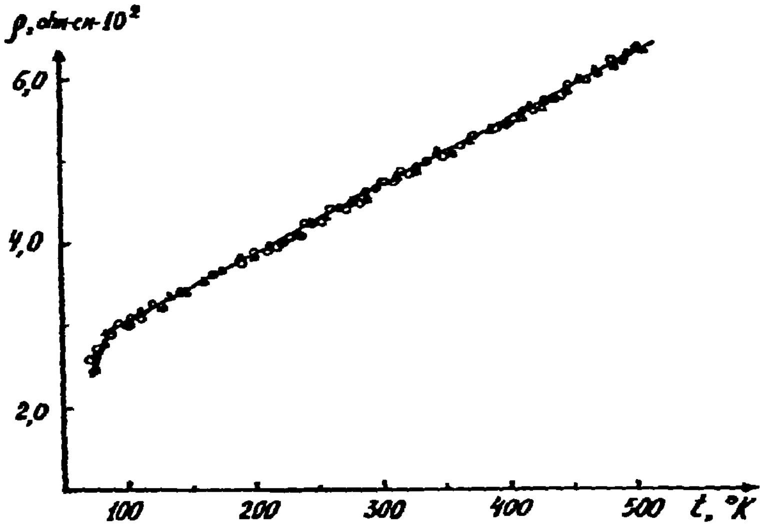

Fig. 3. Electrical resistivity of $Ca_2Os_2O_7$ vs. temperature. △, heating; ○, cooling.

During the thermal decomposition of $CaOsO_3$ in dynamic air atmosphere pure $Ca_2Os_2O_7$ is not formed and it contains calcium oxide and osmium metal as admixtures. Under these conditions the thermal decomposition may be represented as follows:

$$4CaOsO_3 + 1/2\,O_2 \rightarrow Ca_2Os_2O_7 + 2\,CaO + Os + OsO_4$$

The new orthorhombic phase $Ca_2Os_2O_7$ is thermally stable up to 850 ± 10°C and above this temperature it loses oxygen gradually with a defect pyrochlore $Ca_2Os_2O_{6.5\pm x}$ formation in which x depends on the gas composition above the sample investigated. Condition formation of defect phases with the general formula $Ca_2Os_2O_{7-x}$ will be discussed in detail in our next paper elsewhere.

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