ACTA CHEMICA SCANDINAVICA 18 (1964) 2233–2236

Phase Analysis Studies on Niobium Oxide Fluorides

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Two phases of intermediate compositions, Nb_3O_7F and $Nb_5O_{12}F$, have been synthesized in the Nb_2O_5-NbO_2F system in the temperature range 500—800°C. The two oxide fluorides have been studied by means of X-ray diffraction technique.

The presence of fluorine in "Specpure" niobium pentoxide is discussed.

When "Specpure" niobium pentoxide, bought from Johnnson Matthey & Co. Ltd. during the year 1961, was heated stepwise up to 1200°C in a platinum crucible, it lost ~2 % of its weight in the temperature region 400—1000°C, as shown in Fig. 1. For every observation, marked with a circle in the diagram, the sample was kept at the temperature for 30 min and then weighed at room temperature. A final heating of the sample for two days at 1100°C did not cause any further change of weight. The Guinier powder pattern of the sample thus heated was in perfect agreement with previous observations for the high temperature form of niobium pentoxide, α-Nb_2O_5.[1]

The Guinier powder pattern of the original sample was on the other hand rather complex. No lines belonging to the high temperature form of Nb_2O_5 were present. Instead it consisted of two sets of lines originating from two different phases present in roughly the same proportions. One of them could be identified from the powder pattern as being similar to what is usually called γ-Nb_2O_5, while the other phase was unknown. Small rectangular plates of crystals could be found in the original sample, and were shown by means of single-crystal studies to be the second, unknown phase. The crystal structure was determined and is described in a separate paper.[2] It was proved by the crystal structure determination that the general composition was Nb_3X_8, and from a direct synthesis the composition was derived to be Nb_3O_7F.[2]

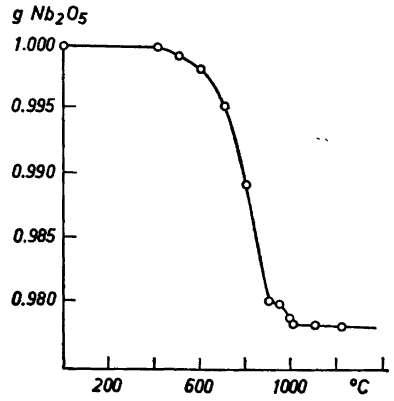

Fig. 1. Weight loss observed when heating "Specpure" Nb_2O_5 up to 1200°C.

Phase analysis studies were then taken up on the system Nb_2O_5-NbO_2F and the results in the temperature region 500—800°C will now be reported.

EXPERIMENTAL

"Specpure" niobium pentoxide was heated for several days at 1100°C in order to get the high-temperature form of niobium pentoxide, α-Nb_2O_5. NbO_2F was synthesized by reacting "Specpure" niobium metal and concentrated hydrofluoric acid in a platinum crucible until all the metal had dissolved. After filtration the clear solution was evaporated to dryness.[3] The white powder was heated for two days at 300°C and its Guinier powder pattern showed it to be pure NbO_2F. The NbO_2F structure is of the ReO_3-structure type,[3] and the indexed powder pattern is given in Table 1.

Mixtures of α-Nb_2O_5 and NbO_2F were heated in sealed platinum or gold tubes according to a technique developed by Roth.[4] The samples were examined by means of X-ray powder photographs obtained in Guinier focusing cameras of 80 mm diameter using monochromatized Cu$K\alpha$ radiation. Single-crystal photographs were taken in a Nonius Weissenberg camera using Cu$K\alpha$ radiation.

RESULTS OF THE PHASE ANALYSIS

Samples of the composition $n$$Nb_2O_5$·$NbO_2F$, where n was 5, 4, 3, 2.5, 2, 1.5, and 1, were heated for a week at 800C. For $n = 5$, the Guinier powder patterns showed, beside the strong α-Nb_2O_5 lines, a few weak lines. With decreasing n these new lines increased in intensity, and for the composition

Table 1. NbO_2F. Dimension of the cubic unit cell: $a = 3.898$ Å.

I	$\sin^2\Theta_{obs}$	h k l	$\sin^2\Theta_{calc}$
vst	0.03912	1 0 0	0.03906
st	0.07817	1 1 0	0.07812
m	0.11716	1 1 1	0.11718
st	0.15624	2 0 0	0.15624
vst	0.19535	2 1 0	0.19530
st	0.23439	2 1 1	0.23436
st	0.31232	2 2 0	0.31248
st	0.35142	2 2 1	0.35154

$2Nb_2O_5 \cdot NbO_2F$ ($Nb_5O_{12}F$) the lines belonging to the α-Nb_2O_5 phase had disappeared. With $n = 1.5$, a new set of lines was observed beside those originating from the $Nb_5O_{12}F$ phase. At the composition $Nb_2O_5 \cdot NbO_2F$ (Nb_3O_7F) the lines from the $Nb_5O_{12}F$ phase had disappeared and a single phase seemed to be present. At the composition $Nb_2O_5 \cdot 1.5\ NbO_2F$, weak lines belonging to the NbO_2F phase had started to show up and at the composition $Nb_2O_5 \cdot 2NbO_2F$ they were even stronger. The phase analysis around Nb_3O_7F and up to NbO_2F was performed at 500°C, 600°C, and 800°.

A small homogeneity range was observed only for the NbO_2F phase. The cubic unit-cell parameter derived from the two-phase pattern of a sample with the composition $Nb_2O_5 \cdot 2NbO_2F$ was found to be 3.904 Å, while for the NbO_2F phase it was found to be 3.898 Å.

Crystals of the Nb_3O_7F phase up to 0.5 mm in size, in the shape of beautiful colourless rectangular plates, could easily be grown at 800°C. In one experiment when a two-phase mixture of Nb_3O_7F and NbO_2F was heated at 800°C, colourless cubes of the NbO_2F phase, 0.5 mm in size, were also obtained. The indexed powder pattern of Nb_3O_7F is given in Table 2 and the crystallographic constants are summarized below.

Space group: *Cmmm*

$$d_{obs} = 4.27 \quad d_{calc} = 4.37$$

$$a = 20.67 \text{ Å} \qquad b = 3.833 \text{ Å} \qquad c = 3.927 \text{ Å}$$

In an attempt to grow crystals of $Nb_5O_{12}F$, a sample of the stoichiometric composition was heated in a sealed Pt-tube at a temperature of 1050°C. The material obtained was in form of irregular colourless rods, and its powder pattern was identical with the one obtained at lower temperatures. Several attempts to find a good single crystal were unsuccessful. However, some data were obtained from the rods. A subcell with strong similarities to the hexagonal α-UO_3-structure [5] could easily be recognized. The Weissenberg data also suggested an orthorhombic cell with the following dimensions: $a = 6.15$ Å, $b = 18.29$ Å, $c = 3.92$ Å.

Table 2. Nb_3O_7F. Dimensions of the orthorhombic unit cell: $a = 20.67$ Å, $b = 3.833$ Å, $c = 3.927$ Å.

I	$\sin^2\Theta_{obs}$	$h\ k\ l$	$\sin^2\Theta_{calc}$
w	0.00552	2 0 0	0.00555
w	0.02220	4 0 0	0.02221
st	0.03847	0 0 1	0.03847
vst	0.04176	1 1 0	0.04177
vw	0.04399	2 0 1	0.04402
st	0.04984	6 0 0	0.04998
w	0.05283	3 1 0	0.05287
vw	0.06061	4 0 1	0.06067
m	0.07504	5 1 0	0.07509
m	0.08020	1 1 1	0.08024
m	0.08837	6 0 1	0.08831
m	0.11347	5 1 1	0.11356
m	0.13884	10 0 0	0.13884
m	0.15384	0 0 2	0.15388
m	0.16150	0 2 0	0.16150

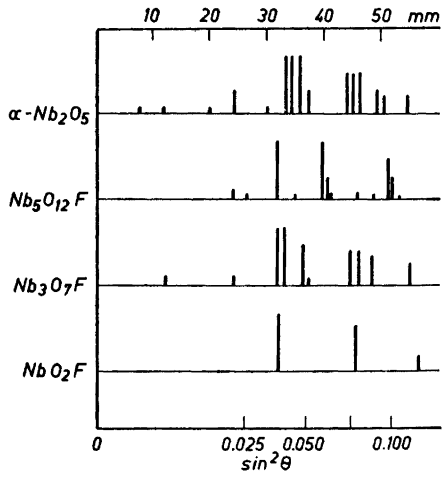

Fig. 2. Guinier powder patterns of α-Nb_2O_5, $Nb_5O_{12}F$, Nb_3O_7F and NbO_2F.

The a-axis is here the diagonal $a_{UO_2} + b_{UO_2}$ and the b-axis corresponds to five times a_{UO_2}. It was only possible to index the strong and medium lines in the powder pattern of $Nb_5O_{12}F$, the real cell probably being of still lower symmetry.

The density calculated for two formula units of $Nb_5O_{12}F$ using the unit cell given about is 5.09. The experimentally obtained one is 5.0_9.

Powder patterns of the different phases occurring in the Nb_2O_5-NbO_2F system at temperatures between 500°C and 800°C are given in Fig. 2. The figure reveals some similarities between the α-Nb_2O_5, Nb_3O_7F and NbO_2F powder patterns, while the $Nb_5O_{12}F$ powder pattern is quite different.

The powder pattern of the $Nb_5O_{12}F$ phase is extremely similar to that of the so-called γ-Nb_2O_5 phase. It is at present impossible to decide whether γ-Nb_2O_5 can be stabilized by F or OH, or also simply exist as niobium pentoxide. It is well known that it is easy to transform γ-Nb_2O_5 to α-Nb_2O_5. The reversal reaction has never been observed.[6,7] However, here has been shown how a phase very similar to γ-Nb_2O_5 can be synthesized from α-Nb_2O_5 and NbO_2F in a ratio corresponding to the composition $Nb_5O_{12}F$.

Acknowledgements. We thank Professor Arne Magnéli for valuable comments on the manuscript. The participation in this work by one of us, A. Å., has taken place within a research program supported by the *Swedish Natural Science Research Council.*

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Received July 22, 1964.