ACTA CHEMICA SCANDINAVICA 19 (1965) 1401–1404

Two New Niobium Oxide Fluorides Formed at High Temperature

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Two new niobium oxide fluorides of the compositions $Nb_{31}O_{77}F$ and $Nb_{17}O_{42}F$ have been prepared at a temperature of 1100°C. $Nb_{31}O_{77}F$ is monoclinic with the space group alternatives $C2$, Cm, or $C2/m$ and the cell dimensions:

$$a = 37.54 \text{ Å} \quad b = 3.832 \text{ Å} \quad c = 21.18 \text{ Å} \quad \beta = 91.92°$$

$Nb_{17}O_{42}F$ is monoclinic, with the space group alternatives $P2$, Pm or $P2/m$ and the cell dimensions:

$$a = 21.09 \text{ Å} \quad b = 3.827 \text{ Å} \quad c = 23.02 \text{ Å} \quad \beta = 116.22°$$

The crystallographic data of the two compounds show them to be members of a homologous series, of the general formula $M_{3n+1}O_{8n-2}$, proposed by Gatehouse and Wadsley and also by Roth and Wadsley in their reports of the crystal structures of α-Nb_2O_5 and $TiNb_{24}O_{62}$. While these latter compounds correspond to values of n of 9 and 8, $Nb_{31}O_{77}F$ and $Nb_{17}O_{42}F$ fit into the series for $n = 10$ and 11.

Recently two new niobium oxide fluorides were reported in the Nb_2O_5—NbO_2F system, *viz.* Nb_3O_7F and $Nb_5O_{12}F$.[1] The phase analysis at that stage was performed at temperatures up to 800°C. When some samples were heated at temperatures around 1100°C, somewhat different results were obtained, which now will be reported.

The experimental technique used was the same as reported earlier.[1] Several compositions $n\ Nb_2O_5 \cdot NbO_2F$, where n was varied from 20 to 1, were prepared and heated at 1100°C. For $n = 20$ the resulting powder pattern revealed some new lines in the low angle region beside the lines originating from α-Nb_2O_5. Around the composition $15\ Nb_2O_5 \cdot NbO_2F$ there was no trace of lines belonging to the α-Nb_2O_5 pattern and a single phase was assumed to be present. For $n = 13$ some new lines were observed beside the ones belonging to the $15\ Nb_2O_5 \cdot NbO_2F$ phase. These new lines became even stronger for samples with decreasing n, and around the composition $8\ Nb_2O_5 \cdot NbO_2F$ the lines belonging to the $15\ Nb_2O_5 \cdot NbO_2F$ phase had vanished completely. The powder pattern of a sample with $n = 6$ was found to consist of lines belonging

to the 8 $Nb_2O_5 \cdot NbO_2F$ phase and of lines from the $Nb_5O_{12}F$ phase previously found.[1] When n was varied further, the results were in complete agreement with those reported earlier.[1] The exact compositions which will be used from here, $Nb_{31}O_{77}F$ and $Nb_{17}O_{42}F$, are based on crystallographic evidence shown below.

The samples obtained of both the phases $Nb_{31}O_{77}F$ and $Nb_{17}O_{42}F$ were very crystalline. Rod-like needles up to 0.3 mm in size were easily obtained after an overnight heating. The crystallographic constants were determined for both the compounds with the ordinary single crystal technique and accurate cell dimensions were obtained from the indexed Guinier powder patterns which are given in Tables 1 and 2.

Table 1. X-Ray powder data of $Nb_{31}O_{77}F$

I	$\sin^2\Theta_{obs}$	khl	$\sin^2\Theta_{calc}$
vw	0.00170	200	0.00169
w	0.00521	002	0.00529
vw	0.00680	$20\bar{2}$	0.00678
vw	0.01681	601	0.01681
vw	0.02119	$00\bar{4}$	0.02118
st	0.02247	$20\bar{4}$	0.02247
w	0.02871	801	0.02872
vw	0.04079	110	0.04085
vst	0.04214	$11\bar{1}$	0.04212
		111	0.04222
vst	0.04407	1001	0.04400
w	0.04560	$31\bar{1}$	0.04540
		311	0.04570
vst	0.04881	$20\bar{6}$	0.04875
vw	0.05091	510	0.05097
w	0.05263	$11\bar{3}$	0.05261
st	0.16173	020	0.16171

Table 2. X-Ray powder data of $Nb_{17}O_{42}F$

I	$\sin^2\Theta_{obs}$	hkl	$\sin^2\Theta_{calc}$
vw	0.00141	001	0.00139
w	0.00534	$20\bar{1}$	0.00534
vw	0.00669	200	0.00663
vvw	0.01015	$10\bar{3}$	0.01015
vw	0.01850	$10\bar{4}$	0.01855
vw	0.02132	$40\bar{2}$	0.02136
st	0.02255	$40\bar{1}$	0.02255
w	0.02963	$10\bar{5}$	0.02972
vw	0.04047	010	0.04050
vst	0.04219	011	0.04189
		110	0.04216
		$11\bar{1}$	0.04221
vst	0.04366	$10\bar{6}$	0.04368
w	0.04487	111	0.04489
		$11\bar{2}$	0.04504
vw	0.04602	012	0.04607
vst	0.04914	$60\bar{2}$	0.04915
w	0.05274	$31\bar{1}$	0.05279
vw	0.05305	013	0.05302
		$60\bar{1}$	0.05303
st	0.16201	020	0.16201

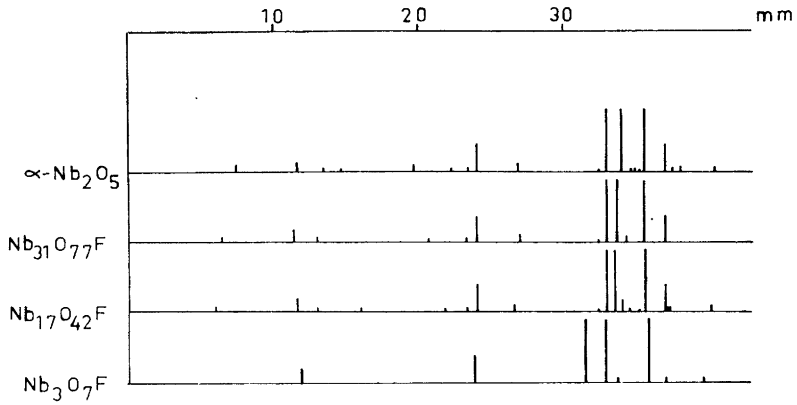

Fig. 1. Guinier powder patterns of α-Nb_2O_5, $Nb_{31}O_{77}F$ and $Nb_{17}O_{42}F$.

The powder patterns of $Nb_{31}O_{77}F$ and $Nb_{17}O_{42}F$ are very similar to each other as well as to the powder pattern of α-Nb_2O_5. This is demonstrated in Fig. 1. The single-crystal X-ray data of the two oxide fluorides were also very similar and a close structural relationship between the two phases and also the structure of α-Nb_2O_5 could thus be expected. Recently the crystal structure of α-Nb_2O_5 was derived and reported by Gatehouse and Wadsley.[2] From the structural principles of α-Nb_2O_5 they proposed a homologous series $M_{3n+1}O_{8n-2}$, α-Nb_2O_5 then being the number for $n = 9$. According to Gatehouse and Wadsley the unit-cell dimensions of $Nb_{11}O_{27}$, as given by Norin and Magnéli,[3] suggest that this compound has the structure of member $n = 7$. Later on Roth and Wadsley [4] showed by means of their structure determination of $TiNb_{24}O_{22}$ it to be member $n = 8$ of the same series. A new niobium oxide, $Nb_{25}O_{62}$, isostructural with $TiNb_{24}O_{22}$, has been found by Norin.[7] The end member of the series, $n = \infty$, has been found to be represented by the structure of Nb_3O_7F.[5]

From the sub-cell relations between any compound in the series $M_{3n+1}O_{8n-2}$ and its parent compound, Nb_3O_7F, it was possible to conclude

Table 3. Calculated unit-cell dimensions as compared with the observed ones for α-Nb_2O_5, $Nb_{31}O_{77}F$ and $Nb_{17}O_{42}F$.

Nb_2O_5				
	a	*b*	*c*	*β*
obs.	21.16 Å	3.822 Å	19.35 Å	119.83°
calc.	20.71 Å		19.27 Å	119.75°
$Nb_{31}O_{77}F$				
	a	*b*	*c*	*β*
obs.	37.54 Å	3.832 Å	21.18 Å	91.92°
calc.	37.45 Å		20.71 Å	91.23°
$Nb_{17}O_{42}F$				
	a	*b*	*c*	*β*
obs.	21.09 Å	3.827 Å	23.02 Å	116.22°
calc.	20.71 Å		23.16 Å	116.56°

that the two new niobium oxide fluorides reported in this paper are the members $n = 10$ and 11. The ideal unit-cell dimensions, calculated from the structural principles of the series $M_{3n+1}O_{8n-2}$ and assuming an octahedron edge of 2.873 Å, are compared with the observed ones as derived from single-crystal data and Guinier powder patterns in Table 3. The cell dimensions for α-Nb_2O_5, as given by Gatehouse and Wadsey [2] are included for comparison. The following row of compounds thus covers the hitherto known members of the series $M_{3n+1}O_{8n-2}$:

n	*7*	*8*	*9*	*10*	*11*	∞
	$Nb_{22}O_{54}$	$Nb_{25}O_{62}$	$Nb_{28}O_{70}$	$Nb_{31}O_{77}F$	$Nb_{34}O_{84}F_2$	Nb_3O_7F
	($Nb_{11}O_{27}$)	($TiNb_{24}O_{62}$)	(Nb_2O_5)		($Nb_{17}O_{42}F$)	

The detailed crystal structures of the two niobium oxide fluorides $Nb_{31}O_{77}F$ and $Nb_{17}O_{42}F$ are under investigation and will shortly be reported.[6]

Acknowledgement. For valuable comments in the manuscript I thank Professor A. Magneli.

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Received May 7, 1965.