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High Pressure Synthesis of Nb_3O_7F with U_3O_8-type Structure

KARL-AXEL WILHELMI and LENA JAHNBERG

Institute of Inorganic and Physical Chemistry, University of Stockholm, Box 6801, S-113 86 Stockholm, Sweden

STEN ANDERSSON

Institute of Technology, Chemical Centre, Department of Inorganic Chemistry, Box 740, S-220 07 Lund 7, Sweden

Structure determinations of niobium oxide fluorides have revealed the existence of six-coordinated metal atoms in Nb_3O_7F [1] and mixtures of six- and four-coordinated niobium atoms in the structures of $Nb_{17}O_{42}F$,[2] $Nb_{31}O_{77}F$,[2] $Nb_{65}O_{161}F_3$,[3] and $Nb_{59}O_{147}F$.[3] All these structures are related to the ReO_3 type of structure. Nb_3O_7F shows crystallographic shear in one dimension, while the others are of the Wadsley block type with shear in two dimensions.

Recently, Holmberg [4] has determined the structure of $Nb_{22}O_{55}F_5$ with the niobium atoms in six- as well as in seven-coordination, and there is no obvious relation to the ReO_3 structure.

Several compounds of intermediate compositions have also been found to exist in the system $TaO_2F-Ta_2O_5$. The compound Ta_3O_7F was reported [5] to occur in two different forms, one of the $LiNb_6O_{15}F$ structure type,[6] the other of a type related to U_3O_8.[7] Both of these have six- as well as seven-coordinated metal atoms. These structures are packed more densely than those of the corresponding niobium oxide fluoride structures that are based on the ReO_3-type building units.

The starting materials used were H-Nb_2O_5 and NbO_2F; the latter was prepared according to Ref. 8. A sample of Nb_3O_7F was obtained by heating a mixture of NbO_2F and H-Nb_2O_5 (mole ratio 1:1) at 850°C in a sealed nickel capsule.

The pressure experiments were performed in a girdle apparatus [9] at 25 kb in the temperature range 850—1100°C. Mixtures of H-Nb_2O_5 and NbO_2F in the mole ratio 1:1 as well as samples of Nb_3O_7F were exposed to the pressure for 2—14 h. Crystalline materials were always obtained and X-ray powder analysis at atmospheric pressure and room temperature indicated the presence of a new phase. A reaction time in excess of 3 h at 900°C resulted in a slight reduction of the products as evidenced by dark coloration.

Weissenberg photographs of a single crystal, selected from a white nonreduced sample prepared at 900°C and 20 kb, were taken with Cu$K\alpha$ radiation with the a axis chosen parallel to the rotation axis ($a=3.9$ Å). The Laue symmetry was *mmm*. On the Weissenberg photographs $0kl$ and $1kl$ and the powder photograph (*v. infra*) the following reflections were absent:

$$hkl \text{ for } k+l=2n+1$$

Thus probable space groups are $A222$, $A2mm$, $Amm2$, and $Ammm$.

The cell constants were derived from a powder photograph, taken with a Hägg-Guinier camera, using Cu$K\alpha_1$ radiation. All lines were indexed on the basis of an orthorhombic cell, with the following edge lengths:

$a=3.927\pm1$ Å; $b=10.514\pm1$ Å;
$c=6.475\pm1$ Å; $V=267.4$ Å^3

The indexed powder pattern is given in Table 1. The density of the sample determined from the loss of weight in benzene was 5.23 g cm^{-3}, which corresponds to two formula units of Nb_3O_7F per unit cell ($d_{calc}=5.08$ g cm^{-3}).

The composition of the starting materials as well as the observed density, suggests the formula Nb_3O_7F. The unit cell dimen-

Table 1. Guinier powder pattern of Nb_3O_7F (Cu$K\alpha_1$ radiation).

$h\,k\,l$	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	I_{obs}
0 1 1	1954	1951	w
0 2 0	2148	2146	w
1 0 0	3853	3846	v st
0 0 2	5664	5660	v st
0 3 1	6253	6245	v st
0 4 0	8589	8587	w
1 0 2	9507	9506	st
1 3 1	10096	10091	st
1 4 0	12439	12433	v w
0 4 2	14246	14247	st
0 5 1	14834	14832	w
2 0 0	15392	15386	st
0 3 3	17571	17565	st
1 4 2	18090	18093	m
1 5 1	18684	18678	w
0 6 0	19324	19320	m
2 0 2	21047	21046	m
1 3 3	21414	21412	st
2 3 1	21634	21631	st
0 0 4	22642	22640	m
1 6 0	23170	23167	m
0 6 2	24980	24980	m
0 5 3	26164	26152	v w
1 0 4	26488	26486	m
0 7 1	27711	27712	m
1 6 2	28827	28827	m
2 4 2	29631	29633	m
2 5 1	30206	30218	w
0 4 4	31223	31227	w
1 7 1	31558	31559	m
2 3 3	32943	32952	st
3 0 0	34628	34620	v w
2 6 0	34699	34707	m
1 4 4	35067	35073	w

sions, the possible space groups, and the appearance of the powder pattern indicate that the compound is of the U_3O_8 structure type.

The change in volume accompanying the phase transformation is -14 %. A structural study of the phase is in progress.

The present study suggests that application of pressure to mixtures of $NbO_2F-Nb_2O_5$ results in a series of phases having distinctly different structure types, which are related to the series of compounds observed in the system $Ta_2O_5-TaO_2F$. Further investigations are comtemplated. The high pressure chemistry of the niobium oxides has been discussed elsewhere.[10,11]

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On the Crystal Structure of V_3O_7

STEN ANDERSSON

Institute of Technology, Chemical Centre, Department of Inorganic Chemistry, Box 740, S-220 07 Lund 7, Sweden

JEAN GALY

Service de Chimie Minérale de la Faculté des Sciences de Bordeaux, 33-Talence, France

KARL-AXEL WILHELMI

University of Stockholm, Institute of Inorganic and Physical Chemistry, Box 6801, S-113 86 Stockholm, Sweden

A new vanadium oxide, V_3O_7, was reported by Tudo and Tridot [1] to be formed when mixtures of V_2O_3 and V_2O_5 were heated in sealed silica tubes at 600°C. Crystals of the same compound can be made in supercritical water [2] and from this material single crystal data were collected with CuK radiation, using ordinary film technique and an integrating Nonius Weis-