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Studies on Pentavalent Tantalum Oxide Fluorides and the Thermal Decomposition of TaO_2F

LENA JAHNBERG

Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden

and

STEN ANDERSSON

Research Institute of National Defence, Dept. 4, Stockholm 80, Sweden

Several compounds of intermediate compositions have been found to exist in the TaO_2F-Ta_2O_5 system in the temperature range 800–1300°C. One of the compounds, Ta_3O_7F, could be prepared in two different crystalline forms, one of the $LiNb_6O_{15}F$ structure type and one of the U_3O_8 structure type. Several other compounds found in the system are all closely related to the low temperature form of Ta_2O_5.

The weight losses observed when Ta_3O_7F is formed during the thermal decomposition of TaO_2F in argon atmosphere correspond to the gas molecule TaF_5.

The substitution of F^- and OH^- for O^{2-} in pentavalent niobium oxides has been shown to occur in a number of new compounds.[1] In order to find out if F^- could substitute for O^{2-} in Ta_2O_5, phase analysis studies were made on the system Ta_2O_5-TaO_2F and the results in the temperature region 800°–1300°C will now be reported.

EXPERIMENTAL

Ta_2O_5 (99.9 %) was dissolved in concentrated hydrofluoric acid in a platinum crucible. After filtration the clear solution was evaporated to dryness. The white powder was heated for a few hours at 300°C and its X-ray Guinier powder pattern showed it to be pure TaO_2F.[2]

Mixtures of Ta_2O_5 and TaO_2F were heated in sealed platinum tubes at temperatures varying between 800–1300°C. 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.

RESULTS OF THE PHASE ANALYSIS

X-Ray powder pattern analysis of the heat-treated samples showed a single phase at the mole ratio 1:1 of TaO_2F and Ta_2O_5. The crystals formed were colourless, rod-shaped and up to 2 mm in length. Single crystal data gave approximately the same unit cell dimensions and also the same space-group alternatives as were observed for $LiNb_6O_{15}F$.[3,4] The composition was

Table 1. Guinier powder pattern of Ta_3O_7F of the $LiNb_6O_{15}F$ type.

hkl	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	I_{obs}	I_{calc}
001	0.00748	0.00747	w	2
200	0.00856	0.00852	m	8
101	0.00963	0.00960	m	5
301	0.02665	0.02663	w	2
002	0.02989	0.02986	m	6
102	0.03201	0.03199	w	6
010	0.03840	0.03832	vst	272
202		0.03838		20
401	0.04159	0.04154	st	70
210	0.04691	0.04684	w	4
111	0.04798	0.04792	vw	2
302	0.04903	0.04903	vst	160
501	0.06073	0.06071	vst	84
402	0.06394	0.06394	vw	2
311	0.06495	0.06496	vw	1
012	0.06823	0.06818	w	3
103	0.06934	0.06932	st	46
112	0.07033	0.07031	w	3
203	0.07570	0.07571	st	32
600	0.07670	0.07668	st	15
212		0.07670		9
411	0.07989	0.07987	st	33
502	0.08314	0.08311	m	8
601	0.08411	0.08414	m	6
312	0.08734	0.08735	vst	87
511	0.09901	0.09904	st	52
403	0.10127	0.10127	w	2
602	0.10646	0.10654	vw	2
113	0.10762	0.10764	st	31
701	0.11173	0.11184	vw	2
213	0.11407	0.11403	st	22
610	0.11503	0.11500	m	10
004	0.11942	0.11944	w	6
503	0.12039	0.12044	vw	2
512	0.12137	0.12143	m	7
611	0.12235	0.12246	w	4
702	0.13420	0.13422	w	5
800	0.13638	0.13631	w	6
304	0.13858	0.13861	w	4
413	0.13962	0.13959	vw	2
801	0.14372	0.14378	m	11
612	0.14482	0.14486	vw	2
711	0.15019	0.15016	vw	2
020	0.15334	0.15329	st	55

concluded to be Ta_3O_7F and the indexed Guinier powder pattern (Table 1) gave the following unit cell dimensions:

$$a = 16.690 \text{ Å}; \; b = 3.935 \text{ Å}; \; c = 8.915 \text{ Å}.$$

Samples of mole ratios from 1.5:1 up to 15:1 of Ta_2O_5 and TaO_2F gave powder patterns which were very similar to each other and to the low temperature form of Ta_2O_5. Small differences in the positions of the weak lines were generally observable in the powder patterns for every composition that was made. As no two-phase powder patterns were obtained, they could all easily have been interpreted as representing a continuous series of solid solutions. However, from the crystallographic data obtained by means of single crystal studies on samples of different compositions, it could be concluded that a series of discrete compounds exist within this composition region. The general trend showing how the powder patterns change when the composition changes is given in Fig. 1.

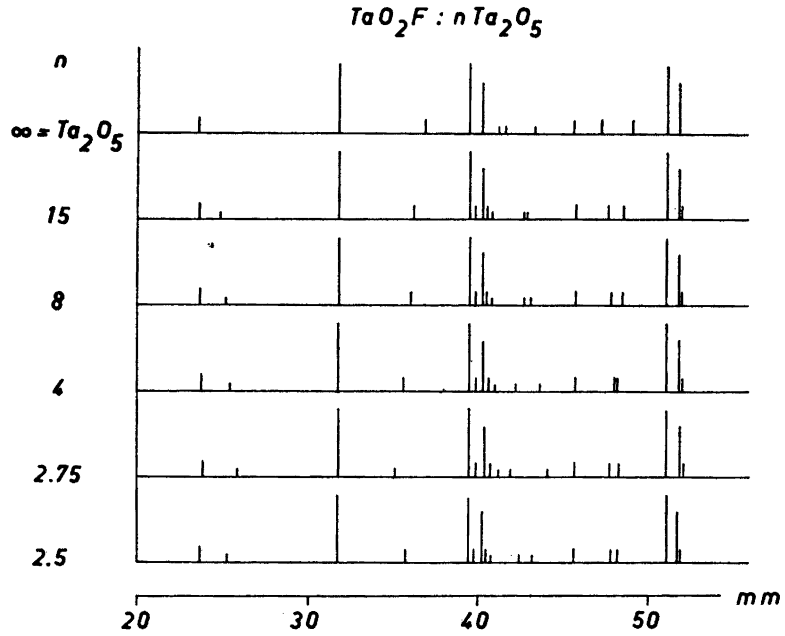

Fig. 1. Powder patterns of some preparations in the system TaO_2F-Ta_2O_5.

THE THERMAL DECOMPOSITION OF TaO_2F

TaO_2F was heated in a platinum boat in a horizontal furnace. Dried argon was passed over the sample, which was taken out after equal intervals of constant temperature (20 min) and weighed. The result of the thermogravimetric analysis is shown in Fig. 2, where every observation is marked with a

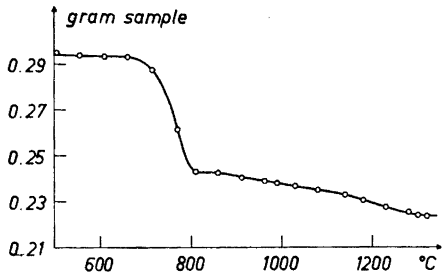

Fig. 2. The thermal decomposition of TaO_2F.

circle. A sample was taken from the plateau formed at 850°C and its X-ray powder pattern could be indexed on the basis of a unit cell of the U_3O_8 structure type [5,6] (Table 2) with the following unit cell dimensions:

$$a = 6.478 \text{ Å}; \; b = 10.496 \text{ Å}; \; c = 3.907 \text{ Å}$$

When this sample was heated in a sealed platinum capsule at 1150°C, it transformed completely into the Ta_3O_7F phase of the $LiNb_6O_{15}F$ type. The reverse reaction did not occur when the latter sample was heated for several days at 830°C.

The observed weight loss of 17.2 % agrees well with the calculated one of 17.0 % for the reaction:

$$7 \; TaO_2F = 2 \; Ta_3O_7F + TaF_5 \uparrow$$

The rate of decomposition of Ta_3O_7F to Ta_2O_5 was found to be rather low as can be seen from the slope of the curve in Fig. 2. A general observation is that both TaO_2F and Ta_3O_7F decompose with a lower rate than NbO_2F and Nb_3O_7F.[7]

Table 2. Guinier powder pattern of Ta_3O_7F of the U_3O_8 type.

hkl	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	I_{obs}
110	0.01958	0.01953	vw
020	0.02159	0.02154	w
001	0.03900	0.03888	vst
200	0.05664	0.05656	st
130	0.06278	0.06261	vst
040	0.08621	0.08617	vw
201	0.09545	0.09543	st
131	0.10142	0.10149	st
240	0.14271	0.14273	m
150	0.14877	0.14878	w
002	0.15551	0.15550	st
330	0.17570	0.17572	st
241	0.18155	0.18160	w
151	0.18777	0.18766	vw
060	0.19386	0.19388	m
202	0.21204	0.21206	m
331	0.21460	0.21460	st
132	0.21811	0.21812	st
400	0.22622	0.22623	m
061	0.23270	0.23276	w

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