JOURNAL OF SOLID STATE CHEMISTRY 2, 24–26 (1970)

Studies in Tantalum Oxide Crystal Growth*

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Received September 25, 1969

Crystals of β-Ta_2O_5 and γ-Nb_2O_5 have been grown from molten KPO_3 and mixtures of KPO_3 and KVO_3. A search for additional polymorphs of β-Ta_2O_5 in this system has instead revealed five not hitherto reported tantalum compounds containing potassium or phosphorus or both and, in one case, vanadium.

1. Introduction

The unit cell of β-Ta_2O_5 has long been the subject of controversy (*1*). Recently, we obtained this information when we succeeded in growing three-dimensional single crystals of β-Ta_2O_5 and the isomorphous γ-Nb_2O_5 (*2*).[1] There appeared reason to believe, however, that other polymorphs of β-Ta_2O_5 could exist, and our crystal-growth experiments were continued in order to explore this possibility.

Five additional crystalline species were obtained. Initially, some of these appeared to be the suspected polymorphs, but ultimately all were shown to be hitherto unreported compounds of tantalum oxide with potassium or phosphorus or both and, in one case, vanadium. Table I summarizes the crystal growth experiments, and Table II lists the crystallographic data.

II. Compositions

The compositions listed in Table II were ascertained as follows. Since there was insufficient material available for wet chemical analysis, a small crystal of each compound was subjected to electron microprobe analysis.[2] Emission lines for potassium, phosphorus, vanadium, and tantalum were observed where present, and their relative intensities established a *relative* scale of concentrations for these elements. Enough material for a quantitative spectrographic analysis was then isolated for compounds β-3 and GF, and the results were compared

TABLE I

Solvent	Solute	Products
KPO_3 67 w/o	Nb_2O_5 33 w/o	γ-Nb_2O_5, small amount of PNb_9O_{25} (*3*)
	Ta_2O_5 33 w/o	β-Ta_2O_5, very small amount of β-2
	Nb_2O_5–Ta_2O_5 33 w/o	Solute ratios used 9:1, 8:2, 7:3, 6:4 Solid solution crystals with γ-Nb_2O_5 structure
KPO_3 95 w/o	Ta_2O_5 5 w/o	β-3 and some M-4
KVO_3 67 w/o	Nb_2O_5 33 w/o	α-Nb_2O_5, extremely small, acicular crystals
	Ta_2O_5 33 w/o	GF, extremely small, acicular crystals
KVO_3 60 m/o KPO_3 30 m/o	Ta_2O_5 10 m/o	GF, larger, rectangular crystals
KPO_3 85 m/o KVO_3 5 m/o	Ta_2O_5 10 m/o	M-4 and β-3, small amounts of M-5 and β-Ta_2O_5
Li_2MoO_4	Ta_2O_5	$LiTaO_3$
Li_2CO_3	Ta_2O_5	A tetragonal bronze, yellow needles
MoO_3		$a_0 = 12.573$ Å, $c_0 = 3.96$ Å
Flame fusion	Ta_2O_5	Poor quality crystals of α''-Ta_2O_5 (*4*)
Pressed and sintered powders	Nb_2O_5, 70–80% Ta_2O_5, 20–30%	Polycrystalline solid solutions with α-Nb_2O_5 structure

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* This work was supported by the United States Air Force under Air Force Contract No. FO4701-69-C-0066.

[1] R. S. Roth of the U.S. National Bureau of Standards believes, on the basis of his own studies (private communication), that our β-Ta_2O_5 and γ-Nb_2O_5 crystals contain some K^+ ions as essential parts of the structure. This possibility is being investigated.

[2] Microprobe work done by Dr. J. Ogren, Autonetics Division, North American Rockwell Corp., Anaheim, Calif.

TABLE II

LATTICE PARAMETERS OF COMPOUNDS OBTAINED

Compound	Lattice Parameters	Multiples of Octahedral Diagonals	Space Group	Composition	Morphology and Remarks
γ-Nb_2O_5	14.70 31.36 9.376	4 × 3.675 8 × 3.92 3 × 3.13	*Pn*2₁*a*	Nb_2O_5	{010} slabs, twinned (010)
β-Ta_2O_5	14.648 31.197 9.395	4 × 3.66 8 × 3.90 3 × 3.13	*Pn*2₁*a*	Ta_2O_5	$(0\bar{1}0)$, (010), (110), $(\bar{1}10)$, {201}, {101} twinned {010}, elongated *c*
β-2	7.551 18.446 3.66	2 × 3.78 6 × 3.07 1 × 3.66	$(Pb2_1m?)$ *Pb***	$Ta_2O_5 + 0.13\ K_2O$ $+ 0.03\ P_2O_5$	Clear, six-sided (010) plates, elongated *a*
β-3	6.621 11.271 5.279	$3 \times 3.12/\sqrt{2}$ 3 × 3.76 $2 \times 2.73/\sqrt{2}$	*Pbnb*	$Ta_2O_5 + 0.3\ KPO_3$	Variable morphology
M-4	(I) 8.532 5.305 8.099 93.0°	(II) 8.488 5.305 8.910 106.8°	(I) *C** (II) $P2_1/$*	$Ta_2O_5 + 0.26\ K_2O$ $+ 0.66\ P_2O_5$	2 species intergrowth, mica-like, pseudohexagonal flakes. Some thick pseudohexagonal plates (001)
M-5	12.45 5.314 10.27 97.2°		$P2_1/$*	$Ta_2O_5 + 0.5\ KPO_3$	Prismatic *b*
GF	17.712 17.712 3.918	Pseudotetr. 12.524 3.918	Pseudo *P*4*bm*	$Ta_2O_5 + 0.16\ K_2O$ $+ 0.02\ V_2O_5$	Isostructural with $PbTa_2O_6$ Compare $NaNb_3O_8$ with lat. par.: 12.372, 3 × 12.372, 3.954 (*5*)

with known standards. This furnished data to put the relative concentrations on an absolute scale. In view of the approximations involved in these procedures, the compositions listed should be regarded accurate only within about 10%.

III. Choice of Solvents

Ta_2O_5 is not soluble in common oxide solvents such as PbO and B_2O_3. V_2O_5 would form extensive solid solutions. KF and PbF_2 would form tantalum oxyfluorides readily. Attempts to use $NaPO_3$ were unsuccessful, but KPO_3 was found empirically to be suitable for Ta_2O_5 crystal growth.

However, KPO_3 polymerizes during the process and is converted either into an insoluble glass or into crystals of the *A* (high-temperature) form of KPO_3. It is then necessary to separate the products from the solidified solvent by hand under the microscope. It was thought that KVO_3, being related chemically, might also prove to be a suitable solvent but might remain soluble. These expectations were indeed met, but the products were different. It was found that the addition of as little as 5% KVO_3 to KPO_3 keeps the latter soluble, while, unfortunately, at the same time it promotes reactions with the solvent.

IV. Comments on Individual Compounds

The numbers given for γ-Nb_2O_5 and β-Ta_2O_5 in the multiples column of Table II represent multiples of the body diagonals of metal–oxygen octahedra and are equal, respectively to b_0, c_0, and $a_0/2$ of the subcell given by Lehovec (*1*). Corresponding entries for β-2 and β-3 represent attempts to interpret these compounds as different superstructures of the same subcell. β-Ta_2O_5 has 48 formula units per unit cell, and if the unit cell volumes of β-2 and β-3 are compared with it, β-3 gives an integral Z of 18, but β-2 a nonintegral value of $5\frac{3}{4}$. Both were proven to be something other than Ta_2O_5 by the chemical analyses, as foreshadowed by the mismatch of the multiples.

It is remarkable that Nb_2O_5 can be crystallized as the α form from KVO_3 and as the γ form from KPO_3. However, while the γ crystals were large, the α

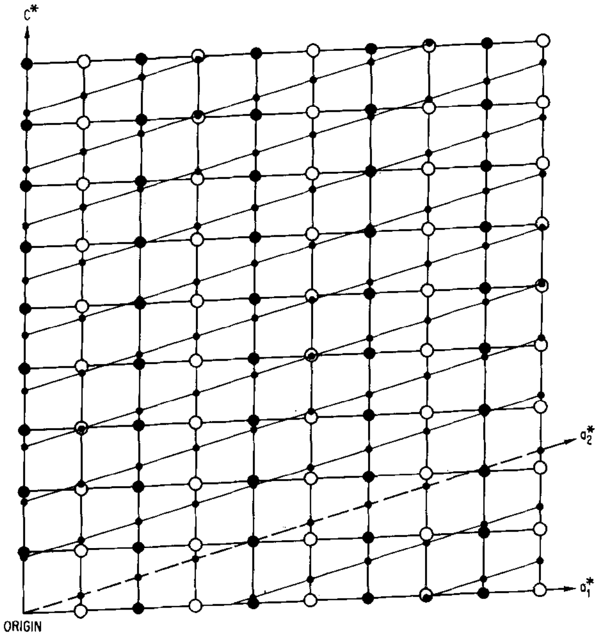

FIG. 1. Reciprocal net $h0l$ of M-4 intergrowth

crystals were too small for single-crystal work and could be identified only through their powder pattern.

In the case of Ta_2O_5 ,the product–solvent relationship is not so simple. KPO_3 gives the β-form, in addition to several compounds, but KVO_3 gives only a compound, designated here GF (green ferroelectric). Pure KVO_3 again yielded crystals too small for single-crystal work. The powder pattern resembled that of orthorhombic, not that of tetragonal, $PbNb_2O_6$. The larger crystals obtained from a mixed solvent (see Table I) gave precession photographs of perfect tetragonal symmetry, and a precision diffractometer measurement showed *a* and *b* to be equal within one part in 20,000. However, optically, the crystals were biaxial without any question, and they were visibly twinned by a 90-deg rotation about *c*. Hence, they can only be orthorhombic. These facts are best explained by assuming that crystallization occurred close to the Curie temperature, and that attainment of equality between *a* and *b* does not fully coincide with the attainment of full structural tetragonality.

The crystals designated M-4 have the same appearance as, but different lattice parameters from, KNb_3O_8, described by Nassau and Shiever (*6*). In addition to numerous large flakes of poor crystallographic quality, several thick plates were found that were suitable for X-ray analysis. The crystals were an intergrowth of two monoclinic species with a common *b* axis. The reciprocal c^* axes were parallel and had repeat distances in the ratio 10:11. a^* (I) coincides with $[40\bar{1}]^*$ (II). Figure I is a drawing of the $h0l$ reciprocal net. The two components are set apart by the use of large and small circles. Open circles represent space-group extinctions for one component.

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