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The Selenide Systems of Niobium and Tantalum

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The selenide systems of niobium and tantalum were investigated under high pressures in the composition limits of MX_2 to MX_3. Two distinct phases, $NbSe_2$ and $NbSe_3$, were obtained in the niobium system. In the tantalum system, there were three phases, $TaSe_2$, "$TaSe_3$," which has been thought of as a triselenide, and stoichiometric $TaSe_3$. The ratio of Se/Ta in "$TaSe_3$" was 2.8. Conversions of the triselenides under high pressure to $NbSe_2$ or $TaSe_2$ were observed at the starting composition of Se/M = 2.0 and to "$TaSe_3$" at Se/Ta = 2.8.

Introduction

Several kinds of phases having various compositions in the binary systems of niobium or tantalum with selenium have been reported (*1*, *2*). The crystal structures can be viewed as metal clusters consisting of metal–metal bonds in the metal-rich compounds such as Nb_2Se and Nb_5Se_4 (*3*). On the other hand, low-dimensional linkage of MSe$_6$ units can be observed in the chalcogen-rich region. There exist two families of low-dimensional compounds, the MX_2 layered dichalcogenides and the pseudo-one-dimensional MX_3 trichalcogenides (*4*). There are strong ionocovalent or metallic bonds inside the layers or chains. These structural units are linked together with weak interlayer or interchain bonding of the order of van der Waals force. The structural anisotropy results in a very high anisotropy in the electronic, vibrational, and mechanical properties. The most interesting physical aspects of these materials are the observation of phenomena such as Peierls transitions, Kohn anomalies, and charge density waves which are characteristic of low-dimensional compounds (*5*). From a chemical point of view, intercalations into di- and trichalcogenides have received considerable attention in recent years (*6*). The compounds can reversibly take various chemical species in and out of their van der Waals gaps. The lithium intercalation has been applied in making the cathode of a secondary battery.

Thorough understanding of these properties necessitates some knowledge of the phase relationships in these systems. Revolinsky *et al.* and Selte *et al.* have already investigated the phase relations between the composition limits M_5Se_4 and MSe$_3$ (*1*, *2*). However, the information was not sufficient in the vicinity of MSe$_3$. Selte *et al.* announced three forms of a niobium selenide with an approximate composition $NbSe_4$ (namely α, β, γ) (*2*). Meerschaut and co-workers proved that three different materials were concerned, the chemical compositions of which were $NbSe_3$, Nb_2Se_9,

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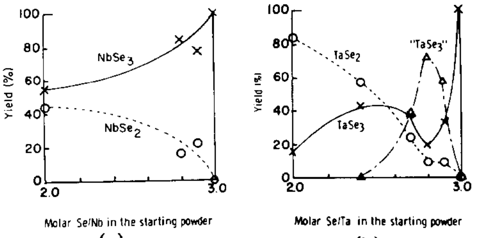
and $I_{0.33}NbSe_4$ (*7–10*). In the accompanying manuscript, Kikkawa *et al.* found a modification of $TaSe_3$ having a crystal structure similar to that of $NbSe_3$ under high pressure (*11*). These recent works stimulate some questions on the chemical composition of $TaSe_3$, for which characterizations have already been done (*12–14*).

The present study is concerned with determining the phase relations in selenides of niobium and tantalum under high pressures. The study was thus limited to the composition range from MSe_2 to MSe_3. The molar ratio of Se/Ta was about 2.8 in "$TaSe_3$," which was prepared in evacuated quartz ampoules above 700°C.

Experimental

The selenides of niobium and tantalum were prepared under high-pressure and temperature conditions using a cubic anvil-type device as described in the accompanying article (*11*). The preparations were made by changing the starting composition of Se/M from 2.0 to 3.2, reaction pressure from 1 to 5 GPa, reaction temperature from 500 to 700°C, and duration from 30 to 240 min. The phases obtained were identified using X-ray powder diffraction. The yield of each phase was calculated using characteristic diffraction lines of the basal reflection for MSe_2 at $CuK\alpha 2\theta = 14.2°$, reflections indexed as 100 for MSe_3 at $CuK\alpha 2\theta = 9.3°$, and as 001 for "$TaSe_3$" at $CuK\alpha 2\theta = 11.4°$. Relative intensities of the diffraction lines were measured. The yield of $NbSe_3$, for example, was computed as (intensity of 100 for $NbSe_3$)/{(intensity for 100 for $NbSe_3$) + (intensity of the basal reflection for $NbSe_2$)}. Thermogravimetry was applied to determine the chemical compositions of both triselenides prepared in quartz ampoules and ones under high pressures.



(a) (b)

FIG. 1. Relative yields of niobium (a) and tantalum (b) selenides in the starting composition range from Se/M = 2.0 to 3.0.

Results

Niobium Selenide System

The niobium selenide system was prepared by changing the starting composition of Se/M from 2.0 to 3.0 at 700°C and 2 GPa for 60 min. Only $NbSe_3$ was observed at the limit of Se/Nb = 3.0, as shown in Fig. 1a. $NbSe_2$ appeared and the amount of $NbSe_2$ increased with the decrease of selenium in the starting material. However, a mixture of $NbSe_2$ and $NbSe_3$ was obtained even at Se/Nb = 2.0 with coexistence of unreacted niobium. The reaction system was probably not in equilibrium under the above-mentioned reaction conditions. Thus, the duration was prolonged to 180 min under the same reaction temperature–pressure conditions at Se/Nb = 2.0. The yields of $NbSe_2$ and $NbSe_3$, respectively, increased and decreased with the duration, as represented in Fig. 2a. Three hours of duration was not enough to obtain $NbSe_2$ as a single phase. Niobium selenides were also prepared by changing the pressure over the range 2–5 GPa at Se/Nb = 3.0 at 700°C for 30 min. The products always consisted of a single phase of $NbSe_3$ in the above pressure range.

Tantalum Selenide System

The tantalum selenide system was also prepared by changing the starting composition of Se/Ta from 2.0 to 3.2 as in the case of the niobium selenide. $TaSe_3$ having a

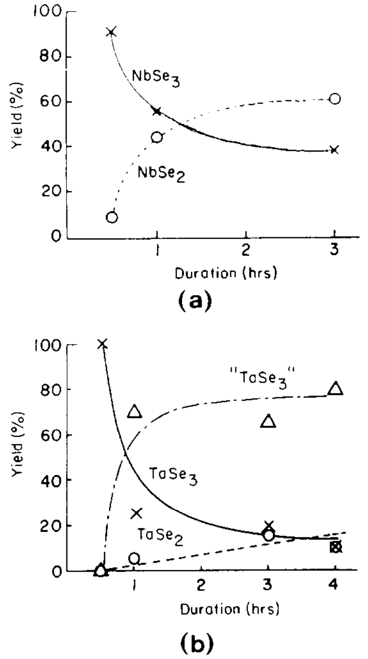


FIG. 2. Duration dependence of relative yields in the systems Se/Nb = 2.0 (a) and Se/Ta = 2.8 (b).

crystal structure similar to $NbSe_3$ was obtained without coexistence of another phase at Se/Ta = 3.0, as depicted in Fig. 1b. Coexisting selenium was observed with $TaSe_3$ at Se/Ta = 3.2. $TaSe_2$ and "$TaSe_3$," which have been obtained in evacuated quartz ampoules, appeared in the starting compositional range of less selenium than Se/Ta = 3.0. The phase "$TaSe_3$" could be observed at Se/Ta = 2.7, 2.8, and 2.9. The largest amount of "$TaSe_3$" was obtained at Se/Ta = 2.8. The relative amount of $TaSe_2$ rapidly increased with further decrease of selenium in the starting powder. However, $TaSe_2$ coexisted with $TaSe_3$ even at Se/Ta = 2.0. The yields were investigated by changing duration at Se/Ta = 2.8 and at Se/Ta = 2.0, respectively, under the reaction conditions of 2 GPa and 700°C. Only $TaSe_3$ was observed at a duration of 30 min at Se/Ta = 2.8, as shown in Fig. 2b, with slight coexistence of Ta. The amount of $TaSe_3$ quickly decreased with rapid increase of "$TaSe_3$" within 1 hr. $TaSe_2$ also appeared. The quantities of "$TaSe_3$" and $TaSe_2$ gradually increased and the amount of $TaSe_3$ decreased with longer duration. Although there were coexisting $TaSe_3$, "$TaSe_3$," and $TaSe_2$ in the reaction for 4 hr at 700°C, only $TaSe_3$ was observed at 500°C at the same duration. The rate of decomposition to "$TaSe_3$" and $TaSe_2$ is probably slow at this temperature. At Se/Ta = 2.0, 60% of $TaSe_3$ and 40% of $TaSe_2$ were observed at a duration of 30 min. The amount of $TaSe_3$ decreased to 10% and the quantity of $TaSe_2$ increased to 90% within 1 hr. The relative amounts were almost the same even at a duration of 3 hr. This situation was quite similar to the case of the niobium selenide. The phases which appeared were compared under two different pressures, 2 and 5 GPa, at 700°C for a duration of 30 min. Only $TaSe_3$ was detected at the composition of Se/Ta = 3.0 under both pressures.

Discussion

In the compositional range from MX_2 to MX_3, the niobium selenide system had two distinct phases, $NbSe_2$ and $NbSe_3$. The tantalum selenide system, on the other hand, gave an additional phase, "$TaSe_3$". The largest amount of this compound was obtained at the composition Se/Ta = 2.8 in the starting material, as shown in Fig. 1b. This fact suggests that the phase "$TaSe_3$" has less selenium composition than stoichiometric $TaSe_3$ which was first prepared under high pressures (*11*). In order to determine the chemical compositions, TG–DTA was measured on about 20 mg of "$TaSe_3$" and $NbSe_3$ prepared in evacuated quartz tubes. The corresponding diselenides were not observed in the samples by X-ray measurement. The triselenides were rapidly oxidized at around 300°C in air. Large exotherms and quick weight losses were observed. The weight of samples became constant in the temperature range 600–700°C. X-Ray diffraction showed that the samples taken out from 700°C consisted of Ta_2O_5 and Nb_2O_5. The amounts of Ta or Nb in the triselenides were estimated by weighing as Ta_2O_5 or Nb_2O_5. The results are summarized in Table I along with values for the samples prepared under high pressures. From these results, it was decided that "$TaSe_3$" had the chemical composition $TaSe_{2.8}$, and that, on the contrary, $NbSe_3$ had stoichiometric composition. The triselenides, $TaSe_3$ and $NbSe_3$, prepared under high pressures were stoichiometric, of course.

The stoichiometric $TaSe_3$ partially decomposed to "$TaSe_3$" and Se due to heating at 250°C for 1 day in an evacuated quartz tube. This fact also shows that "$TaSe_3$" has less selenium than stoichiometric $TaSe_3$. Moreover, $TaSe_3$ completely decomposed to $TaSe_2$ and Se when it was heated at 500°C for 20 hr. The rate of decomposition was depressed with the addition of selenium in the ampoule. It is quite clear that "$TaSe_3$" is a less-selenium phase and the compound obtained under high pressures is stoichiometric $TaSe_3$, considering the results of the preparations under high pressures, the chemical analysis, and the thermal decompositions.

TABLE I

CHEMICAL COMPOSITIONS OF NIOBIUM TRISELENIDE AND TANTALUM TRISELENIDE

Material	Sample wt (mg)	Metal (wt%)	Se (wt%)	Molar ratio Se/*M*	Average
"$TaSe_3$"*	14.3	$45._8$	$54._2$	2.6_8	2.8
	15.3	$44._4$	$55._6$	2.8_3	
$TaSe_3$	12.0	$43._7$	$56._3$	2.9_2	2.9
	17.9	$43._5$	$56._5$	2.9_4	
$NbSe_3$*	13.0	$27._5$	$72._5$	3.0_7	3.1
$NbSe_3$	13.4	$28._4$	$71._6$	2.9_7	3.1
	14.3	$27._0$	$73._0$	3.1_8	

Note. Materials marked with asterisks were prepared in evacuated tubes.

There are two possibilities for the phase "$TaSe_3$" of $TaSe_{3-\delta}$ and $Ta_{1+\epsilon}Se_3$. Density measurement may give the answer. However, it is very difficult to obtain enough "$TaSe_3$" without contamination of $TaSe_2$ for the measurement. Bjerkelund and Kjekshus reported the observed and calculated densities as 7.913 and 8.080 g cm^{-3}, respectively (*12*). Simple calculation using these values leads to the composition $TaSe_{3-0.1}$, which is not so reliable due to the possible contamination. Unit cell variation was also checked according to composition. The lattice parameters *a*, *b*, and *c* were calculated using 200, 020, and 006 diffractions for $TaSe_3$ on the samples prepared from the starting compositions of Se/Ta = 3.0, 2.9, and 2.8 at 700°C and 2 GPa for 60 min. The variation of these lattice parameters was less than 0.02 Å. This suggests that excess tantalum is not intercalated as the lithium intercalated into $NbSe_3$ (*15*). The parameters *a* and *c* expanded 1.4 Å and *b* did not change in the lithium intercalation. Thus, $TaSe_3$ and "$TaSe_3$" seem to have exact compositions without solid solution range. This is probably the reason why $TaSe_3$, "$TaSe_3$," and $TaSe_2$ coexisted in the preparation under pressure. The residual resistance ratio for "$TaSe_3$" was reported to be about 70 (*16*). The value is too low to consider the phase as nonstoichiometric. The crystal structure of $TaSe_3$ is not directly related to that for "$TaSe_3$" at the moment even if it is considered to be the same as that for $NbSe_3$. Structure analysis is required.

Among the three tantalum selenides, $TaSe_3$ is probably equilibrated with the highest selenium vapor pressure on decomposition. Therefore, high-pressure technique was quite effective in the preparation of $TaSe_3$. Phase relations can be schematically represented as shown in Fig. 3. $TaSe_3$ has the highest vapor pressure at every temperature. When the vapor pressure is kept at P_1 and there is a temperature gradi-

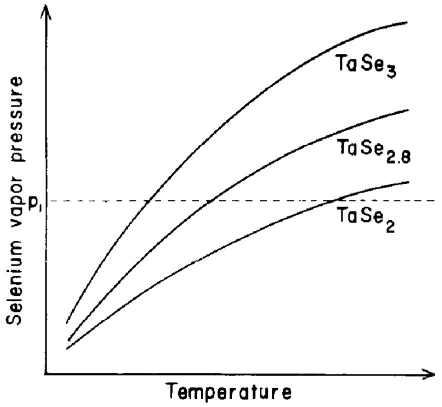


FIG. 3. Schematic pressure and temperature phase diagram of the tantalum selenide system.

ent in the reaction vessel, $TaSe_3$ crystallizes in the lowest temperature region, $TaSe_{2.8}$ in the middle, and $TaSe_2$ at the highest. This figure leads to the idea that $TaSe_3$ might be obtained even in a quartz tube if its decomposition to "$TaSe_3$" or $TaSe_2$ is well depressed. The reaction vessel was kept just above the boiling point of selenium. A very small crystal of $TaSe_3$, in fact, was prepared in an evacuated quartz tube at 450°C for 1 month. Its crystal structure analysis will be reported elsewhere.

$NbSe_3$ was obtained at the beginning and then reacted with Nb changing to $NbSe_2$ in the preparation under high pressure at the starting composition of $Se/Nb = 2.0$, as depicted in Fig. 2a. In contrast, $NbSe_3$ was directly prepared at $Se/Nb = 3.0$. $TaSe_2$ was also obtained through $TaSe_3$. MoS_2 can be prepared by the thermal decomposition of amorphous MoS_3 but the situation is different from the present case (*17*). The present reaction is not only a decomposition of triselenide to diselenide but also a recombination of the metal with the decomposed selenium. "$TaSe_3$" was also obtained through $TaSe_3$ at the starting composition of $Se/Ta = 2.8$, as shown in Fig. 2b.

In conclusion, it was shown that the tantalum selenide which has been reported as $TaSe_3$ has the actual composition of $TaSe_{2.8}$. The trisulfides of Ta and Nb also have less sulfur composition than stoichiometry. The trichalcogenides prepared under high pressure and in evacuated ampoules were not pressure modifications. They have different chemical compositions. The kinetics under high pressures were observed in the preparation of diselenides through triselenides in both systems of niobium–selenide and tantalum–selenide. $TaSe_{2.8}$ was also obtained through the recombination of $TaSe_3$ with the coexisting $TaSe_2$ and Ta.

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