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TECHNIQUES OF PREPARATION AND CRYSTAL CHEMISTRY OF TRANSURANIC CHALCOGENIDES AND Pnictides*

MASTER

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MASTER

Abstract

The crystal chemistry of a number of transuranic chalcogenides and pnictides has been investigated using ^{243}Am , ^{248}Cm , ^{249}Bk , and ^{249}Cf . These compounds were prepared from the corresponding metals by direct reaction with the chalcogen or pnictogen element at elevated temperatures. Higher chalcogenides were thermally dissociated to yield ones of lower stoichiometry, terminating with the sesquichalcogenides; only monopnictides of these transplutonium elements were found. All products were examined by X-ray powder diffraction.

In this paper the methods for preparing the actinide chalcogenides and pnictides on a gram scale are reviewed, and the microtechniques used for submilligram quantities of the transamericium elements are presented. The results obtained during this study are compared to data previously reported for the lighter actinide compounds, and the trends observed across the

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series are discussed.

La crystallochimie d'un certain nombre de chalcogénures et pnictures d'éléments transuraniens a été étudiée en utilisant les isotopes ^{243}Am , ^{248}Cm , ^{249}Bk et ^{249}Cf . Les composés ont été préparés par réaction directe du métal avec l'élément chalcogène ou pnictogène à température élevée. Les chalcogénures supérieurs ont été dissociés thermiquement pour donner des composés à stoechiométrie plus basse dont les sesquichalcogénures constituent la limite. Seuls les monopnictures de transplutoniens ont été trouvés. Tous les composés ont été étudiés par la technique de diffraction des RX a les poudres.

Dans cet article on a revu toutes les méthodes de préparation des chalcogénures et pnictures à l'échelle du gramme. On présentera les méthodes utilisées pour synthétiser les composés transamériciens à une échelle inférieure au milligramme. Les résultats obtenus au cours de cette étude seront comparés aux résultats de la littérature concernant les composés des actinides légers et on discutera des variations de propriétés le long de la série.

I. INTRODUCTION

Chalcogen and pnictogen elements belong to the VIth and Vth columns of the periodic classification, respectively: they are, namely, O, S, Se, Te and N, P, As, Sb (Table I). Among the chalcogen elements, oxygen exhibits a crystal radius which is clearly lower than the crystal radii of the heavier members of the group. As a result, oxides are quite different, both in composition and in structure, from the other chalcogenides, which often form isostructural compounds. Similarly in the pnictogen family, nitrides stay slightly apart. It is interesting to note that the couples sulfur-phosphorus, selenium-arsenic, and tellurium-antimony have very similar crystal radii. Thus, the substitution of one of these elements for the other allows

Table I

Crystal Radius Derived from Rare Earth Monocompounds [1] Å

Chalcogen element		Pnictogen element	
O	(1.40)*	N	1.549
S	1.844	P	1.920
Se	1.953	As	1.993
Te	2.135	Sb	2.171

* Pauling's radius [2].

for the modification of the bonding (chalcogen and pnictogen elements are involved in compounds essentially as 2- and 3- species, respectively) without modifying significantly the interatomic distances.

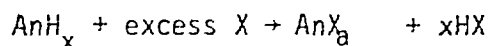
Among the compounds formed by these elements, the ones formed with the d transition and 5f metals have been, and are still, intensively investigated because of the variety of their physical properties - semiconducting, conducting, and even superconducting materials are found [3]. As examples, the molybdenum chalcogenides are known to be superconducting compounds with high transition temperatures, and recently all the lanthanum pnictides were reported to exhibit superconductivity [4]. During the last decade efforts have also been made by many laboratories to study the 5f element chalcogenides and pnictides, but the radioactivity and also the scarcity of the materials have increased considerably the problems encountered in their preparation and their physical property measurements.

In this paper, we shall review the methods used in the preparation of the various early actinide pnictides and chalcogenides (for uranium, neptunium and plutonium, the syntheses can be performed on a gram scale; for americium and, to a lesser extent, for curium-244, on a multimilligram scale). Then we shall describe the techniques which we have used for the microscale prepara-

tions of curium-248, berkelium-249 and californium-249 compounds.

II. MACROSCALE PREPARATIONS

On the several mg to the multigram scale, actinide pnictides and chalcogenides can be prepared starting from the metal hydride or the metal itself. The hydride process leads to a more homogeneous product and faster reactions. Typically, hydride and an excess of chalcogen or pnictogen element (X) are sealed in a quartz tube under high vacuum and heated at moderate temperature (450-700°C). The chemical reaction can be represented as:



The compound depends upon the particular metal and non-metal that are used.

In the 5f series, two distinct groups of compounds are found: (1) The uranium crystal-type compounds: $\text{U}(\text{S},\text{Se})_3$, UTe_5 , $\text{Np}(\text{S},\text{Se})_3$, $(\text{Np-U})\text{Se}$, USb_2 . (2) The rare-earth crystal-type compounds: $(\text{Pu},\text{Am},\text{Cm})(\text{S},\text{Se})_2$, $(\text{Np},\text{Pu},\text{Am},\text{Cm})\text{Te}_3$, $(\text{Np},\text{Pu},\text{Am})\text{Sb}_2$.

In the first group the cations are thought to carry a charge close to 4+, while in the second group the charge is approximately 3+. With neptunium, the 3+ state is stabilized when Sb is substituted for As, since the diarsenide exhibits the tetragonal, UAs_2 -type structure, while the diantimonide crystallizes the orthorhombic LaSb_2 structure type. Similarly, the assigned charge of the neptunium cation decreases from 4+ in NpS_3 and NpSe_3 to 3+ in NpTe_3 .

Chalcogenides or pnictides of lower stoichiometry can be obtained by thermal dissociation of the higher ones, either in a sealed tube where one end of which is kept outside the furnace to allow for the deposition of the non-metal element, or in a vacuum thermobalance, which yields more information about the stoichiometry of the products formed.

In figure 1, the thermograms of PuTe_3 and NpAs_2 are compared. In its stability range, from 300 to 600°C, NpAs_2 does not change its stoichiometry. On the contrary, on the thermogram of PuTe_3 , in the temperature range corresponding to the ditelluride (between points A and B), there is no constant weight, showing that the ditelluride exhibits a wide range of composition (PuTe_2 - $\text{PuTe}_{1.7}$). Further dissociation leads to the sesquitelluride, as verified by X-ray diffraction. Although actinide mononictides can be obtained by thermal dissociation of a higher pnictide, the monochalcogenides require direct preparation. The following procedure is recommended:

1) Heating at moderate temperature (700-800°C) of a stoichiometric amount of chalcogen element with the metal hydride in a quartz tube sealed under high vacuum.

2) Pelletizing of the product formed.

3) Heating of the pellets at high temperature (1200-1600°C) in tantalum or tungsten crucibles. This high-temperature heating is performed under high vacuum or in an inert atmosphere.

These macroscale synthesis techniques have been used successfully from thorium through plutonium [5] and to a lesser extent for americium and curium-244 [6,7]. For the heavier actinides, the scarcity of the elements does not permit the use of macro-amounts of material. ^{248}Cm ($T_{1/2} = 3.4 \times 10^5 \text{ y}$) is a much more suitable isotope than ^{244}Cm ($T_{1/2} = 18.1 \text{ y}$), but like ^{249}Bk ($T_{1/2} = 314 \text{ d}$) and ^{249}Cf ($T_{1/2} = 350.6 \text{ y}$), it is only available in multimilligram quantities. Thus the synthesis of compounds from these isotopes have to be performed on the submilligram scale using microchemical techniques.

III. MICROSCALE PREPARATIONS

1) Metals

The starting materials required for the preparation of curium, berkelium and californium chalcogenides and pnictides are the corresponding metals,

and thus we shall describe first their preparation. The microscale techniques of metal preparations have been first developed at Berkeley [8] and then at Oak Ridge [9]. ^{248}Cm and ^{249}Bk were obtained by reduction of their tetrafluorides with Li metal vapor. (CmF_4 and BkF_4 were obtained by heating the corresponding trifluorides in an atmosphere of ClF_3 or F_2 at $\sim 350^\circ\text{C}$). The different products were handled in a helium atmosphere gloved box (O_2 , H_2O , N_2 ; all ≤ 10 ppm). The tetrafluoride pieces were placed in a tungsten wire spiral, which was attached to the top of a tantalum crucible containing the lithium metal [10]. The tantalum crucible was put in a tantalum heating coil that was coated with a refractory material [9]. The system was evacuated to 5×10^{-6} mm Hg and then heated to initiate the reduction reaction. Lower temperatures and shorter heating times were used with Bk than Cm, to minimize the loss of Bk metal due to its higher volatility.

The reductions of the fluorides were carried out on the 100- μg to 1-mg scale. The curium metal samples were not melted in bulk and appeared as shiny pieces with shapes similar to the initial fluoride pieces.

X-ray studies showed that this well-crystallized metal exhibits the dhcp structure. The lattice constants, averaged from 6 independent preparations, are $a_0 = 3.495(4)\text{\AA}$ and $c_0 = 11.33(3)\text{\AA}$ (to be compared to the values $a_0 = 3.498\text{\AA}$ and $c_0 = 11.340\text{\AA}$ for ^{244}Cm metal [11] and $a_0 = 3.500(3)\text{\AA}$ and $c_0 = 11.34(1)\text{\AA}$ for ^{248}Cm [12]). The curium metal can be melted in an electrically heated tungsten spiral. The current is shut off as soon as melting occurs so that the metal is quenched. These metal samples exhibited either a single fcc phase or mixtures of the fcc and dhcp phases. The lattice constant of the fcc curium phase varies with the sample [12], suggesting possible vacancies in the structure. The following lattice parameters have been found: $5.060(2)\text{\AA}$, $5.084(2)\text{\AA}$, $5.076(2)\text{\AA}$, $5.068(2)\text{\AA}$. Berkelium metal has a melting point ($\sim 1000^\circ\text{C}$) lower than that of curium, so it was obtained as a melted ingot after the lithium reduction. No structural information

could be obtained from this material since it was amorphous. Californium metal has been prepared by reduction of the sesquioxide with lanthanum metal at high temperature in a tantalum apparatus [13], distilling it and then depositing it on a tantalum condenser. Reductions were performed on the mg scale. X-ray patterns of the metal samples were not very sharp but indicated that this material exhibited the fcc form with lattice parameter $a_0 = 4.94\text{\AA}$. Samples of these metals were submitted for mass analysis, and the results are reported in Table II for curium 248 (in ppm).

Table II
 ^{248}Cm Analysis

Ta	Mo	Ni	Fe	Cr	V	Cs	K	S
≤ 60	100	10	20	5	20	3	2	30
Si	Al	Na	Mg	Pb	W	Cs	Pr	
10	1	1	11	-	-	-	-	

2) Compounds

Starting from these actinide metals, pnictides and chalcogenides were prepared on a 20-30 μg scale in quartz capillaries suitable for subsequent X-ray examination. It was preferred to use the pure metals rather than their hydrides in order to retain small pieces rather than powders, which would be very difficult to handle and transfer without loss. Special care was taken to avoid contamination by metallic impurities as well as oxygen, nitrogen and water vapor. This was accomplished by pretreatment of the capillaries and reagents. The capillaries were first leached with hydrochloric acid, then washed with distilled water and alcohol. Following drying, they were heated under high vacuum and kept under vacuum with a stopcock system, which was opened only in the dry-helium atmosphere box used for the transuranic metals. The chalcogen and pnictogen elements were of high purity and had been melted or sublimed and stored under vacuum before use. Typically a capillary

was loaded with the appropriate transuranic metal and non-metal element, sealed under high vacuum (residual pressure $\leq 10^6$ mm Hg) and heated. S, Se, Te and As were reacted with Cm, Bk and Cf metals at 450-500°C, but the reaction temperature with Sb must be higher than 550°C to get a rapid reaction. Heating times of 15 hours were found to be sufficient to provide a complete reaction and to yield good crystallinity. Most of the time the compounds had a gray metallic appearance, except for the tritellurides, which were golden. During heating a small temperature gradient ($\sim 20^\circ\text{C}$) was maintained along the capillary to obtain a compound free of excess chalcogen or pnictogen element. The thinner part of the capillary, which will be in the X-ray beam for characterization and where the 5f metal is located, was placed in the warmer part of the furnace. After heating the product obtained was free of excess pnictogen or chalcogen element, which had gathered at the colder extremity of the capillary.

Dissociations of the higher chalcogenides were performed in a micro-furnace consisting of a platinum wire wound on a quartz tube. Only the part of the capillary containing the product was located inside the furnace, allowing the chalcogen or pnictogen element to deposit in the outer part of the capillary. The maximum temperatures used are limited by possible reactions of the compounds with the quartz. Such problems started to appear around 800°C, but it was still possible to use this dissociation method up to $\sim 1000^\circ\text{C}$ for very short periods of time (a few seconds).

Following the various heating steps, the samples were submitted for X-ray analysis using standard powder techniques.

IV. RESULTS AND DISCUSSION

Previously unknown tritellurides, dichalcogenides and sesquichalcogenides of berkelium and californium have been prepared and characterized by X-ray diffraction. They are presented in Table III.

Table III

(Cf,Bk)Te ₃	(Cf,Bk)Te _{2-x}	ε Bk ₂ Te ₃	
	(Cf,Bk)Se _{2-x}	η Bk ₂ Se ₃	γ Cf ₂ Se ₃
		γ Bk ₂ Se ₃	
	(Cf,Bk)S _{2-x}	α Bk ₂ S ₃	γ Cf ₂ S ₃
		γ Bk ₂ S ₃	

All the berkelium and californium chalcogenides appear to be isostructural with the corresponding rare-earth ones [14].

Tritellurides. Like the preceding transuranic elements, berkelium and californium tritellurides exhibit the orthorhombic, NdTe₃-type structure [6] which is observed for all the trivalent rare-earth tritellurides. The lattice parameters for BkTe₃ are: $a_0 = 4.318(2)\text{\AA}$, $b_0 = 4.319(2)\text{\AA}$, $c_0 = 25.467(6)\text{\AA}$. The unit cell is composed of two superposed ditelluride cells, shifted by $a_0/2$, and separated by a Te layer.

Dichalcogenides. From their X-ray powder patterns, all the berkelium and californium disulfides, diselenides and ditellurides were found to crystallize in the tetragonal, anti-Fe₂As type structure, like the corresponding plutonium, americium and curium compounds.

In the case of the ditellurides, the americium-243 compound was considered to be representative of the transuranic ditellurides, and its crystal structure has been refined from single-crystal data [15]. The anti-Fe₂As structure was confirmed, and the stoichiometry was shown to be AmTe_{1.73} (axial ratio $c_0/a_0 = 2.071$). The tellurium vacancies are randomly distributed in the basal plane of the cell. An increase of the tellurium vacancies decreases the a_0 lattice constant without modifying significantly the c_0 axis, so that the c_0/a_0 axial ratio increases. This ratio can therefore be used as an indication of the compound's stoichiometry. It varies from 2.03 to 2.07-2.08 in neptunium and plutonium compounds, corresponding to

the stoichiometries (Np or Pu)Te₂ and (Np or Pu)Te_{1.7}, respectively [6,16]. In going from curium to californium the c₀/a₀ ratio is found to remain close to 2.06-2.08, irrespective of the temperatures of the preparations, indicating that these ditellurides are always prepared as substoichiometric compounds with compositions close to (Cm, Bk, or Cf)Te_{1.7}.

For the disulfides and the diselenides, such variations along the transuranium series are much smaller. The c₀/a₀ axial ratios are 2.02-2.03 for the disulfides from Pu through Cf, and 2.04-2.05 for the corresponding diselenides. This indicates that the compositions of these compounds remain essentially constant and are practically independent of the preparation conditions.

Sesquichalcogenides. Transuranium element sesquichalcogenides crystallize in 4 different structure types: α, γ, η and ξ where

α is the orthorhombic, La₂S₃ type [17,18.] (CN 7 and 8),

γ is the body-centered cubic, anti-Th₃P₄ type [19.], (CN 8)

η is the orthorhombic, U₂S₃ type [20.] (CN 7), and

ξ is the orthorhombic Sc₂S₃ type [21.] (CN 6).

The actinide sulfides exhibit the α form through Bk and the γ form through Cf. (Although the α form has not been definitively observed with Cf, we cannot exclude the existence of this phase.) Isostructural phases are found in the rare-earth sesquisulfides from lanthanum through dysprosium for the α form and through terbium for the γ one. The η sesquiselenides have been observed for Pu, Am, and Bk in the actinides and from Gd through Dy in the lanthanides. The γ form extends from Np through Cf and from La through Dy, respectively. (The γ form represents here M₂X₃ as well as M₃X₄ or any intermediate composition.)

The η and γ sesquitellurides are formed from Np through Cm and from Np through Am, respectively. Berkelium is the first transuranic element to exhibit the Sc₂S₃-type structure.

The same $\eta \rightarrow \xi$ transition occurs in the rare-earth series at Tb, the homolog of Bk, so that in their sesquiterellurides Bk and Tb have similar crystal radii.

Monopnictides. Few compounds other than monopnictides are formed between transuranium and pnictogen elements. Using preparation techniques similar to those described earlier, ^{248}Cm , ^{249}Bk and some ^{249}Cf monopnictides have been prepared as single-phase materials. They exhibit the cubic, NaCl-type structure like the other actinide monopnictides. The lattice parameters (\AA) found are listed in Table IV .

Mononitrides. Nitrides were prepared directly by heating the corresponding metals on a tantalum filament up to 1300°C in an atmosphere of nitrogen, which had been purified by passing it over uranium nitride at 600°C. This apparatus had been previously tested with americium-243. The lattice constant of ^{243}AmN was found to be $4.9907(3)\text{\AA}$, which is in good agreement with previously reported data (5.00\AA [22] and 4.995\AA [23]). Stevenson has reported lattice constants for ^{248}CmN (5.027\AA) and BkN (5.010\AA) [12]. Our present values agree very well in the case of curium mononitride, but a noticeable difference occurs in the berkelium nitrides.

Table IV

	N	P	As	Sb	References
^{248}Cm	5.027				[12]
	5.027	5.743	5.887	6.243	This work
^{244}Cm	5.041	(5.72)	5.901	6.248	
	5.010				
^{249}Bk	4.95	5.669	5.833	6.195 6.188	This work
^{249}Cf	-	-	5.809	6.165	This work

Likely due to less radiation damage, the curium-248 nitride has a lower

The monochalcogenides were not obtained as single-phase materials. Although they constitute the major phase, γ sesquisulfide, γ sesquiselenide, and η sesquitelluride lines were present in the X-ray patterns, along with some oxychalcogenide lines.

It is of interest to compare the lattice constants of curium monosulfides and monoselenides to those of the rare earths and the other transuranium elements fig. (2). The curium compounds exhibit lattice parameters which are lower than the corresponding americium ones. On the contrary, curium mononictides, fig. (3), exhibit the highest lattice parameters in the transuranic series. This difference in behavior between americium and curium in their monochalcogenides and mononictides can be understood by assuming that americium is partially divalent in the monochalcogenides. The chalcogen elements are ligands which favor low valencies of the cations, as can be seen from examination of the rare-earth monochalcogenides. Of course americium would be far from purely divalent, since for divalent americium monosulfide, for example, a lattice constant of the order of 5.9 \AA would be expected. The possibility of divalent character for americium in monochalcogenides, proposed here from a comparison with the corresponding curium compounds, had previously been strongly suggested by Johansson on the basis of thermodynamic considerations [24]. Another possible explanation is that the 5f electron participation in the bonding is very weak in americium monochalcogenides. In this case the decrease in the lattice constant from americium to curium reflects the 5f contraction between two adjacent trivalent actinides. Pnictogen elements have been shown to enhance the actinide 5f electron participation more than the chalcogen elements. Thus, in the mononictides, the maximum in a_0 at curium would mean that the 5f electron participation in americium compounds exists enough to lower significantly their lattice constants.

In figure 4, the variations of the lattice parameters of the trans-uranium and rare-earth cubic sesquioxides are presented. For these more ionic compounds, from curium through einsteinium, the curve is parallel to the corresponding rare-earth one, and the lattice constants of the transuranium element sesquioxides are higher than the isoelectronic rare-earth sesquioxides. On the contrary, the lattice constants of berkelium and californium arsenides and antimonides stay close to those of terbium and dysprosium, suggesting that the actinide lattice constants are decreased as a result of covalency effects.

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