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INVESTIGATION OF THE TRANSPLUTONIUM OXIDES BY
X-RAY AND ELECTRON DIFFRACTION*

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INVESTIGATION OF THE TRANSPLUTONIUM OXIDES BY
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INTRODUCTION

As weighable quantities of the heavy actinide elements have become available, there has been considerable interest in preparing solid compounds of these elements and in determining the lattice parameters and physical properties of such compounds. The oxides have been among the first compounds studied because of the ease of their preparation and the existence of an isostructural series for both the trivalent and tetravalent actinides.

Topics discussed in this paper include verification of the tetravalent state of Cf by the preparation of CfO_2 ; preparation of Es_2O_3 and its subsequent analysis by electron diffraction; and preparation of monoclinic Bk_2O_3 and the hexagonal forms of Cm_2O_3 , Bk_2O_3 , and Cf_2O_3 . In addition, the melting points of the oxides have been determined and a phase diagram for several of the actinide sesquioxides is presented.

EXPERIMENTAL

The isotopes used in these studies — ^{248}Cm , ^{249}Bk , ^{249}Cf , and ^{253}Es — were obtained from the Transplutonium Element Program at ORNL. The materials

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were purified by established techniques[1] and then analyzed by spark-source mass spectrometry. In all cases, they were found to contain <0.02% rare earths and <0.2 at. % total ionic impurities. Since milligram quantities of Cm, Bk, and Cf were available, it was possible to produce ultrapure solutions for preparing compounds of these elements. The oxides of Cm, Bk, and Cf were made by saturating cation exchange resin beads with the desired actinide (2-5 μg) and then calcining the beads at 1200°C[2]. Using this procedure, it was possible to obtain small spherical particles that could be further treated to prepare the different oxide phases, as well as new compounds where the element existed in another valence state.

In this work, efforts to use the microchemical, single-resin bead technique for preparing Es_2O_3 were not successful. The high specific activity of the ^{253}Es destroyed the resin matrix before a satisfactory oxide particle was made, and X-ray diffraction patterns indicated that the resulting oxide products were amorphous. Therefore, an alternative technique using electron diffraction was employed for studying Es compounds. The Es_2O_3 samples for electron diffraction were prepared by decomposing the nitrate salt of Es in a platinum dish using 4% H_2 -Ar as the calcination atmosphere. The resulting Es_2O_3 particles were then transferred to 400-mesh copper grids covered with a carbon substrate. Transmission electron diffraction patterns of the oxide were obtained using an accelerating voltage of 100 kV.

The actinide oxide samples discussed in this work were examined using standard X-ray diffraction or electron diffraction techniques which have been reported[3,4]. Line positions on the film were read by two independent observers and their results averaged. The lattice parameters were refined by the LCR-2 program[5], and intensities were calculated with the aid of the POWD program[6]. The error limits reported are given as one sigma.

RESULTS

Preparation of CfO_2

In an effort to verify the stability of the tetravalent state of Cf, a study was made of the conditions necessary to oxidize Cf_2O_3 to CfO_2 [4]. Nugent et al.[7], on the basis of electron transfer and f-d absorption band spectra of the actinides and lanthanides, predicted that the III-IV potential for Cf would be similar to that of Tb. Experimental conditions which had been successful for the preparation of TbO_2 [8] were used to prepare CfO_2 from Cf_2O_3 . It was found that high-pressure molecular oxygen at 300°C (100-atm O_2 for 100 hr) would oxidize the Cf_2O_3 to the CfO_2 . However, it was found that the oxide bead had to be "reactive" (low density) to successfully oxidize the material to CfO_2 . In many cases intermediate products, $\text{CfO}_{1.5 < x < 2.0}$, were obtained when high-density oxide spheres were used.

An alternative process using atomic oxygen was also employed to prepare CfO_2 . The Cf_2O_3 beads were heated in a platinum boat at 300°C for ~1 hr in a mixture of molecular and atomic oxygen (atomic oxygen content, ~15%) held at a pressure of 900 μ . These conditions were sufficient to oxidize the Cf_2O_3 to CfO_2 .

The black product obtained from the molecular oxygen or atomic oxygen oxidation of Cf_2O_3 (pale green) had a face-centered cubic (fcc) structure. A lattice parameter of $5.310 \pm 0.002 \text{ \AA}$ was obtained by X-ray diffraction analysis. It was noted that the CfO_2 was not stable with regard to time, and the lattice parameter gradually increased, at the rate of $0.0026 \text{ \AA}$ per day, from its initial value until it reached the value of $5.372 \text{ \AA}$. At this point the fcc X-ray diffraction powder pattern could be indexed as a rhombohedral structure with lattice parameters of $5.372 \pm 0.003 \text{ \AA}$ and $\alpha = 89.92 \pm 0.04^\circ$.

From the CfO_2 lattice parameter the ionic radius of tetravalent Cf was calculated to be $0.859 \text{ \AA}$. A plot of the cubic lattice parameters of the actinide dioxides and the corresponding ionic radii versus atomic number is shown in Fig. 1. The lattice parameter obtained for the fcc CfO_2 falls on the smooth curve which had been extrapolated to Cf.

During the course of this work it was evident that the preparation of CfO_2 was slightly more difficult than the preparation of TbO_2 and that the stability of tetravalent Cf was similar to that of tetravalent Tb, as had been predicted[7]. The relative stabilities of the dioxides of the lanthanides and the transplutonium elements can then be placed in the order: $\text{Ce} \geq \text{Bk} > \text{Am} > \text{Cm} > \text{Pr} > \text{Tb} \geq \text{Cf}$.

In the attempts to prepare CfO_2 , it was noted on several occasions that products were obtained which had not been completely oxidized to the dioxide. These products can be interpreted with the aid of the graph in Fig. 2, where a plot of the molecular volume versus apparent oxygen-to-metal

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(O/M) ratio is shown. For the plot it was assumed that the largest molecular volume obtained corresponded to $\text{CfO}_{1.5}$ and that the smallest molecular volume represented $\text{CfO}_{2.0}$. It was found that the data formed ~~these~~ ^{three} separate groups, which correspond to O/M ratios of 1.56, 1.70, and 1.80, respectively. These stability regions are quite similar to those reported for Tb and Pr oxides [9,10]. The bcc Cf_2O_3 structure was found to exist up to an O/M ratio of about 1.60. With higher O/M ratios, the bcc structure is converted first to a rhombohedral structure and finally to the fcc CfO_2 structure.

Preparation of Es_2O_3

Several attempts have been made to prepare the oxides of Es, since it is the heaviest element that will be produced in weighable quantities. However, its short half-life of 20.45 days creates two experimental problems: (1) the ^{249}Bk daughter grows into the sample at a rate of ~3% per day; and (2) its high specific activity destroys the crystal matrix. Efforts to obtain X-ray diffraction data for Es_2O_3 have been unsuccessful, although Fujita [11] was able to obtain X-ray patterns for EsCl_3 by constantly resynthesizing the crystal structure at 450°C. An attempt to anneal out the radiation damage of an Es oxide sample at temperatures up to 800°C was unsuccessful [12].

By producing Es_2O_3 particles small enough that most of the alpha energy is lost exterior to the crystals, it has been possible to prepare an Es oxide which could be analyzed. Small quantities of oxide with crystallites of this size range ($\leq 300 \text{ \AA}$) would be more suitable for analysis by electron diffraction than by X-ray diffraction. Such a technique has been used to successfully prepare and analyze samples of Es_2O_3 [13].

The Es_2O_3 samples for electron diffraction were prepared by decomposing the nitrate salt of Es in several different atmospheres and transferring the particles to electron microscope grids for analysis. Calcination of the samples at temperatures up to 1000°C in a variety of atmospheres produced only a bcc structure with lattice parameter of $10.766 \pm 0.006 \text{ \AA}$. The ionic radius of the trivalent einsteinium ion calculated from this lattice parameter was $0.928 \text{ \AA}$. This value is approximately midway between the values of $0.938 \text{ \AA}$ for Gd^{3+} and $0.920 \text{ \AA}$ for Tb^{3+} .

In order to observe the effect of radiation on the crystal structure, the calcined Es_2O_3 samples were examined as a function of time. It was found that the crystalline samples were more stable than initially anticipated, and many samples provided good quality electron diffraction patterns over a period of several days. The absence of extensive radiation damage to the Es_2O_3 particles may be explained on the basis that the range of the alpha particles in the oxide matrix was greater than the dimensions of the crystallites. Since the major portion of the energy of the alpha particles is dissipated in the last portion of its path, little damage to the oxide crystallites by the alpha particles would occur if the majority of them escaped the oxide matrix. This, of course, ignores any effect of the recoiling atoms.

Preparation of Monoclinic Bk_2O_3

The lanthanide sesquioxide system is polymorphic, and three crystal structures are known for the oxides. The low-temperature phase for the

lighter lanthanides is hexagonal but it is cubic for the other members of the series. At elevated temperatures, several of the lanthanide sesquioxides form a monoclinic structure. By increasing the temperature, the oxides of the lanthanides in the middle of the series are changed successively from a cubic to a monoclinic to a hexagonal structure[14]. In the actinide series a stable sesquioxide first occurs at plutonium. Both a low-temperature cubic form and a high-temperature hexagonal form are known for Pu_2O_3 [15]. The next element in the actinide series is americium, and its sesquioxide also exhibits a low-temperature cubic form and a high-temperature hexagonal form; in addition, there is some evidence that a monoclinic structure may form in a very narrow temperature region^{[16].} Curium sesquioxide exhibits a greater similarity to the lanthanide oxides in the middle of the series in that it has a low-temperature cubic form, a monoclinic form, and a hexagonal form that has been observed at very high temperatures. This latter form of Cm_2O_3 has also been obtained as the result of autotransformation due to alpha irradiation[17].

In the berkelium oxide system, only the cubic form of the sesquioxide has been reported[18]. Californium sesquioxide has been reported to possess both a cubic low-temperature form and a monoclinic structure at elevated temperatures[4,19,20]. Since Bk lies between Cm and Cf in the periodic table, it was thought that a monoclinic and, possibly, a hexagonal form of the sesquioxide should exist. Further, it was possible that a hexagonal form of Cf_2O_3 might also exist. The existence of these crystal forms for Bk_2O_3 and Cf_2O_3 has been experimentally verified.

Samples of cubic Bk_2O_3 were heated in a 4% H_2 -Ar atmosphere, and it was observed that an irreversible transformation from cubic to monoclinic[21] occurred at 1200°C. The monoclinic form was found to be stable up to 1700°C. The lattice parameters for the yellowish-green, monoclinic Bk_2O_3 are $a_0 = 14.197 \pm 0.007 \text{ \AA}$, $b_0 = 3.606 \pm 0.003 \text{ \AA}$, $c_0 = 8.846 \pm 0.005 \text{ \AA}$, and $\beta = 100.23 \pm 0.09^\circ$. The lattice parameters for monoclinic forms of the Bk_2O_3 are midway between the values published for the comparable Cm_2O_3 and Cf_2O_3 structures.

Preparation of Hexagonal Transplutonium Element Sesquioxides

The transformation of Cm_2O_3 from the monoclinic to the hexagonal form has been shown to be highly reversible, and attempts at quenching in the hexagonal form of Cm_2O_3 have not been successful[22]. The only means by which a room-temperature hexagonal structure of Cm oxide had been obtained was autotransformation due to alpha irradiation[17].

A very rapid, quenching technique was developed in which microgram quantities of the transplutonium element oxides could be heated to >2000°C and then quenched to essentially room temperature within 1 sec. This method involved heating the oxide bead in a tapered spiral of 0.005-mm-diam iridium or tungsten wire which was 1 mm in diameter and 3 mm long. The wire was resistance heated and, after the current had been cut off, the heat was dissipated very rapidly in the helium atmosphere since the heat capacity of the spiral was small. Using this method, the high-temperature phases of the sesquioxides have been successfully retained during the rapid cooling to room temperature.

Quenched hexagonal samples of $^{248}\text{Cm}_2\text{O}_3$ were prepared by the above method, and the lattice parameters determined by subsequent X-ray diffraction analysis were $a_0 = 3.791 \pm 0.001$ and $c_0 = 5.961 \pm 0.002$ Å. These parameters are significantly smaller than those obtained by the radiation-induced transformation, which gave lattice parameters of $a_0 = 3.799$ and $c_0 = 5.991$ Å[17]. However, this is not unexpected as the radiation-induced transformation would give an expanded cell due to the irradiation. The temperature at which the monoclinic to hexagonal transition occurs was confirmed to be $1600 \pm 25^\circ\text{C}$ [22].

The hexagonal form of Bk_2O_3 was prepared in a manner similar to that used for preparing the hexagonal form of Cm_2O_3 . The monoclinic to hexagonal transformation for Bk_2O_3 was also found to be reversible and the hexagonal structure was obtained only when the sample was rapidly quenched in a helium atmosphere. Attempts at quenching from 1800°C , in vacuum or in an argon atmosphere, gave only the monoclinic form of Bk_2O_3 . When H_2 atmospheres were used, the Bk_2O_3 reacted with the iridium wire spiral to form an alloy, similar to the alloys prepared by Erdmann and Keller with Am and Cm[23]. Once obtained, the resulting hexagonal form of Bk_2O_3 could be retained at room temperature; however, on reheating in vacuum to 500°C , it reverted to the monoclinic form. The transition temperature for converting the monoclinic form to the hexagonal structure was estimated to be about 1750°C . The lattice parameters for the hexagonal Bk_2O_3 are $a_0 = 3.754 \pm 0.002$ Å and $c_0 = 5.958 \pm 0.002$ Å.

Several experiments were made in an effort to prepare a quenched hexagonal form of Cf_2O_3 . In only one preparation was the hexagonal form observed; the other Cf_2O_3 samples were monoclinic. The X-ray diffraction pattern for the one sample was of poor quality due to incomplete crystallization. Six strong, low angle lines were observed which could be indexed as belonging to a hexagonal cell with parameters of $a_0 = 3.72 \pm 0.01 \text{ \AA}$ and $c_0 = 5.96 \pm 0.01 \text{ \AA}$. The hexagonal form of Cf_2O_3 was also observed in a Bk_2O_3 sample that had decayed for 4.75 half-lives. The ^{249}Cf content of this sample was 96%. This sample had transformed from the cubic oxide structure to the hexagonal structure as the result of self-irradiation. The lattice parameters for this Cf_2O_3 sample were essentially the same as those observed for the quenched sample.

The lattice parameters for the hexagonal plutonium to californium sesquioxides are plotted in Fig. 3. The decrease in the a_0 axis, as was initially noted between Pu_2O_3 and Am_2O_3 , continues throughout the series to Cf_2O_3 . The c_0 axis remains essentially constant at a value of $5.96 \text{ \AA}$. The values obtained with the quenched hexagonal form of $^{248}\text{Cm}_2\text{O}_3$ has simplified the diagram since these curium values fall on the line projected by the other members of the series. The slight deviation in the a_0 axis at Cm is probably due to the effect of a half-filled shell, which has been noted in other systems. The c_0/a_0 axial ratio for the hexagonal forms increases from a value of 1.55 for Pu_2O_3 to 1.60 for Cf_2O_3 .

A summary of the actinide and lanthanide sesquioxides is shown in Fig. 4, where the molecular volumes of hexagonal, monoclinic, and cubic forms of the sesquioxides are plotted. There is considerable densification in going from the cubic form (six-coordinated) to the monoclinic form (six- and seven-coordinated) and finally to the hexagonal structure (seven-coordinated). From this graph it can be seen that, when the three structures exist for a given sesquioxide, there is a considerable decrease in the molecular volume in going from the cubic to the monoclinic to the hexagonal form. It is also evident that the monoclinic structure has been observed at a larger M^{3+} radius (greater molecular volume) for the lanthanide elements as compared to the actinide series. A final observation on the two series of sesquioxides can be made by noting that in the actinide series, the hexagonal structure persists to a smaller M^{3+} radius than in the lanthanide elements. In the plots for both series, the effect of a half-filled f shell is evident.

Determination of Melting Points for Transplutonium Element Sesquioxides

The wire spiral technique enabled direct observation of the melting points of the sesquioxides through the use of a microscope of long focal length. The oxide beads were observed as the temperature of the spiral was slowly increased until melting occurred. The temperature immediately was measured with a Leeds and Northrup microoptical pyrometer. The system was calibrated with high-purity Al_2O_3 and with gold and platinum metal.

Using this method, the melting point of $^{248}Cm_2O_3$ was observed to be $2260 \pm 25^\circ C$ by heating a bead of the sesquioxide in vacuum (1×10^6 Torr)

until it melted. This value is in good agreement with Chikalla's value of 2275°C for $^{244}\text{Cm}_2\text{O}_3$ [24].

The melting point of Bk_2O_3 was similarly determined to be $1920 \pm 25^\circ\text{C}$. The average value of the melting point was obtained from eight samples which were prepared from three different purification cycles. Both iridium and tungsten spirals were used for these determinations, and there was no evidence for a reaction between the oxide and the wires.

The melting point of $^{249}\text{Cf}_2\text{O}_3$ was determined to be $1750 \pm 25^\circ\text{C}$ from a total of 15 melting point experiments. The Cf_2O_3 beads were also prepared from several different purifications, and the melting point determined in vacuum on platinum, iridium, and tungsten wire spirals. After melting, the purity of oxide was again verified to be >99.5 at. % by spark-source mass spectrometry.

Actinide Sesquioxide Phase Diagram

With the recent information on the transplutonium element sesquioxides, it is now possible to construct a partial phase diagram as shown in Fig. 5. Plutonium sesquioxide is known to exist only in the cubic (C) and the hexagonal (A) forms. The transplutonium sesquioxides show some similarity to the lanthanide sesquioxides in the middle of that series. In the actinide sesquioxide phase diagram, a straight line can be drawn through the C→B (cubic to monoclinic) transformation temperatures for the elements from Am to Cf, and it is evident that the transition temperature is higher for the heavier members. In addition, the B→A transformation is skewed toward higher atomic numbers such that only a narrow region exists near the melting point for the transformation of Cf_2O_3 to the hexagonal form. These observations

are consistent with the experimental difficulties encountered in making the hexagonal form of Cf_2O_3 . To date, Es_2O_3 has been investigated at temperatures up to 1000°C , and only the C form has been observed. This is in agreement with the extrapolated phase diagram, which would indicate that a temperature in excess of 1400°C would be necessary to bring about the C→B transition for Es_2O_3 .

The melting point curve for the actinide sesquioxides (Fig. 5) rises from Pu to Cm but then drops from Cm to Cf. The increase in the melting points in the first half of the 5f electron series is similar to that in the 4f series, as expected. However, the decrease in the melting points with the heavier transcurium elements is opposite to the trend observed in the lanthanide series. This difference is difficult to explain but may be due to a greater degree of covalent bonding after Cm. The deviation in the melting point of the transcurium sesquioxides, from the expected trend, is the first evidence of an appreciable difference in a physical property among the transplutonium elements. Significant differences in the behavior of Bk and Cf, as compared with trivalent Pu, Am, and Cm, have also been observed in many solvent extraction systems and ion exchange separations.

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FIGURE LIST

- Fig. 1. Actinide dioxide lattice parameters and tetravalent ionic radii as a function of atomic number.
- Fig. 2. Areas of stability of intermediate californium oxides.
- Fig. 3. Lattice parameters for the hexagonal Pu-Cf sesquioxides.
- Fig. 4. Molecular volumes of actinide and lanthanide sesquioxides.
- Fig. 5. Phase diagram for several of the actinide sesquioxides.