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HIGH TEMPERATURE PHASE TRANSFORMATIONS IN
SOME LANTHANIDE AND ACTINIDE OXIDES(a)

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ABSTRACT

The melting behavior of the actinide dioxides and sesquioxides from thorium through curium is reviewed. Melting points of two actinide oxides, heretofore unreported, have been determined: NpO_2 melts at $2560 \pm 50^\circ\text{C}$ and Am_2O_3 melts at $2205 \pm 15^\circ\text{C}$. High temperature phase transformations in Cm_2O_3 , Pm_2O_3 , and Sm_2O_3 have been studied, and all three of these oxides exhibit five solid-state polymorphic modifications. The phase transformation behavior in the actinide sesquioxides is very similar to the lanthanide oxides, and the thermal stability domains of the various polymorphs in both series correlates well with the trivalent ionic radii. The volume change on melting in Sm_2O_3 has been determined as 4.3%. Other properties of liquid Sm_2O_3 studied include surface tension and liquid expansion.

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INTRODUCTION

In recent years, there has been an increasing effort aimed at determination of high temperature physical and chemical properties of lanthanide and actinide oxides. This stems not only from a need to understand the basic high temperature behavior of these materials, but also from a practical standpoint since there are important high temperature commercial applications for these refractory oxides. For example, the actinide oxides ThO_2 , UO_2 , and PuO_2 are extensively utilized as nuclear fuels, and in practice operate with centerline temperatures approaching 2500°C . In addition, several isotopes of both lanthanide and actinide elements have specific activities which make them very attractive for radioisotope heat source applications. In order to design and evaluate efficient high temperature nuclear reactor fuels and radioisotope heat source systems, it is necessary to thoroughly understand the high temperature properties. This is particularly true of melting and phase transformation behavior since these properties can influence the system design and impose operational limitations.

Stable actinide oxides with cation oxidation states of +3, +4, and +6 have been identified as shown in Table I; in addition, several discrete compounds based on mixed oxidation states are also known to exist. The general trend with increasing atomic number is one of decreasing stability of the higher valence states and increasing

TABLE I. Actinide Oxide Compounds.

<u>Z</u>	<u>Oxygen/Metal Ratio</u>								
	<u>1.50</u>	<u>1.60</u>	<u>1.71</u>	<u>1.83</u>	<u>2.00</u>	<u>2.25</u>	<u>2.50</u>	<u>2.66</u>	<u>3.00</u>
90					ThO ₂				
91					PaO ₂		Pa ₂ O ₅		
92					UO ₂	U ₄ O ₉		U ₃ O ₈	UO ₃
93					NpO ₂			Np ₃ O ₈	
94	Pu ₂ O ₃	Pu ₅ O ₈			PuO ₂				
95	Am ₂ O ₃				AmO ₂				
96	Cm ₂ O ₃		Cm ₇ O ₁₂	Cm ₆ O ₁₁	CmO ₂				
97	Bk ₂ O ₃				BkO ₂				
98	Cf ₂ O ₃				CfO ₂				
99	Es ₂ O ₃								

stability of the trivalent oxidation state. For example, at $Z = 94$ (Pu) and above, no oxidation states greater than +4 exist, and even CfO_2 is prepared with difficulty requiring 100 atm O_2 at 300°C .⁽¹⁾ It is anticipated that at $Z = 99$ (Ls) and above, only the actinide sesquioxides will exist. In contrast, the lanthanide oxides show a high degree of stability in the trivalent state and only Ce, Pr, and Tb have been identified as existing with a +4 cation. Equilibrium oxygen decomposition pressure measurements have been carried out in all +3/+4 lanthanide-actinide oxide systems (except Cf) and suggest the following ranking, in terms of decreasing stability of the +4 cation:

Pu, Ce, Bk, Am, Pr, Cm, Tb, and Cf

Thus, in these oxide systems, it is necessary that one be concerned with stoichiometry alterations when making high temperature property measurement. In this sense, it is impossible to obtain a melting point for the dioxide unless the equilibrium oxygen dissociation pressure is maintained at the melting temperature.

The lanthanide sesquioxides have been shown to exist in several crystal modifications which have been designated A (hexagonal), B (monoclinic), and C (cubic). In addition, there has been recent evidence for two new high temperature phases termed H and X. The H form is also hexagonal, while the structure of the X phase is unknown. These phases have been previously reported for all lanthanide oxides except promethium, whose high temperature behavior has not been studied heretofore because of the radioactivity associated with Pm-147. Based on the similarity in chemical behavior and ionic radii, one might also expect these phases to exist in actinide sesquioxides; some of these phases have indeed been observed, as will be discussed below.

EXPERIMENTAL

A. Melting Point

Melting points have been determined for a number of actinide oxides using a resistance heated filament furnace. In this apparatus, a small amount of sample is placed in the apex of a V in a 0.13 mm thick tungsten or rhenium filament. After evacuation and backfilling with an inert or reducing gas, the sample is rapidly heated to about 200°C below the melting temperature after which the power input rate is reduced to allow close observation of the specimen during melting. A micro-optical pyrometer is used to measure the temperature. A thermal correction curve was constructed from several determinations on the melting temperatures of high purity platinum, alumina, iridium, and molybdenum in a procedure identical to that performed on the unknown specimens. The apparent temperatures were corrected with this calibration which provided correction for instrumental error, emissivity of the tungsten, and absorption in the furnace and glove box windows. This calibration was checked frequently during the course of the experiments.

B. Phase Transformation Temperatures

Solid-state phase transformation temperatures were determined using a differential thermal analyses (DTA) apparatus based on the design of Rupert.⁽²⁾ The system, shown schematically in Figure 1, has provision for heating in a vacuum of $< 10^{-5}$ Torr. Heat input is supplied through a 20 kW/480 kc induction generator, and a current concentrator with an 8:1 ratio is used to couple the small diameter load to a nine-turn, 10.3 cm diameter work coil. The powdered oxide sample is loaded into a 0.63 cm diameter x 0.63 cm high tungsten or rhenium cup placed into one of two identical cavities in a graphite susceptor. In operation, reverse biased photo-diodes look through a heat shield at the two cavities while an automatic optical pyrometer

looks at the lid of the container. The pyrometer output is part of a closed control loop with the induction generator so that the temperature can be increased, held constant, or decreased according to a predetermined program. The temperature difference between the sample and the graphite is obtained by subtracting the amplified output of one diode from the other. This difference is plotted on the vertical axis of a storage oscilloscope or x-y recorder, while the temperature of the graphite is plotted on the horizontal axis. Phase transformations appear as exothermic or endothermic peaks on this plot and can be observed to 2500°C. The system was calibrated at the melting points of gold, platinum, alumina, and iridium.

C. Volume Change on Melting

X-radiography of an oxide in a sealed refractory metal capsule can be used to observe the temperature dependence of the volume of both the solid and liquid phases and to deduce the volume change accompanying melting. In addition, the surface tension of the liquid can be determined from the shape of the meniscus. In this method, the sample is radiographed with a 300 kv x-ray source. An x-ray image intensifier and vidicon camera are used to monitor the sample continuously, and a film is also inserted for a permanent record. A tungsten-mesh resistance heating element surrounded by split radiation shields allows x-radiography under essentially isothermal conditions with a minimum of absorbing material in the image forming x-ray beam. The furnace can be operated with an inert or reducing gas or in vacuum.

The density of the molten oxide is calculated from the known mass of sample inserted into the capsule and its volume as a function of temperature. The volume is calculated by measuring the height of the liquid column from the radiographs and using the inside diameter of the refractory metal crucible corrected for thermal expansion. Corrections are also made for the volume of material contained within the meniscus. The volume change on melting is determined by extrapolating

the measured volume of the solid as a function of temperature to the melting point and extrapolating the volume of the liquid as a function of temperature to the melting point. The difference between these two volumes is the volume change on melting.

The surface tension can also be obtained from analysis of the shape of the meniscus. Utilizing a measurement of the coordinates of the meniscus profile and the liquid density, the surface tension is calculated based on the method of Bashforth and Adams.⁽³⁾

MELTING BEHAVIOR IN ACTINIDE OXIDES

A. Thorium Oxide

The melting point of 99.99% pure ThO_2 was measured by Lambertson et al.⁽⁴⁾ ThO_2 crucibles were suspended via tungsten wires into a tungsten heater tube. Difficulty in obtaining reproducible data was encountered due to the high temperatures involved, and it was concluded that the melting point of ThO_2 is $3300 \pm 100^\circ\text{C}$. This is the highest melting point reported for any oxide material.

B. Protactinium Oxide

The melting point of PaO_2 has not been measured.

C. Uranium Oxide

Numerous melting points have been reported for uranium dioxide with values ranging from 2400°C to 2900°C . The difficulties associated with measurement of an accurate melting point for UO_2 are due to (a) the high temperature involved, (b) stoichiometry effects, and (c) vaporization which complicates a visual measurement. The melting point for $\text{UO}_{2.00}$ obtained in this work using the filament technique

described above was $2805 \pm 15^{\circ}\text{C}$ and is in excellent agreement with that reported by Hausner⁽⁵⁾ who used a thermal arrest method employing a sealed tungsten capsule. In contrast, Latta and Fryxell⁽⁶⁾ report a melting point for $\text{UO}_{2.00}$ of $2881 \pm 4^{\circ}\text{C}$ using a thermal arrest method, while Bannister,⁽⁷⁾ with a tungsten filament apparatus, reports $2860 \pm 70^{\circ}\text{C}$.

The melting point of UO_{2+x} is strongly dependent on the O/U ratio and this is partially responsible for the wide scatter in the reported melting values. We have investigated the melting behavior of UO_{2-x} compositions which were prepared by equilibrating UO_2 and uranium metal in vacuum at temperatures between 1600°C and 2600°C . After quenching to room temperature, the samples were metallographically examined and the stoichiometry determined by oxidation to U_3O_8 . About 15 measurements of each composition were made using the tungsten filament furnace and a purified argon atmosphere and are shown plotted as a function of composition in Figure 2. These results are in reasonable agreement with the solidus of Bannister⁽⁷⁾ and with Latta and Fryxell,⁽⁶⁾ although their curve is more steeply sloped and rises to a maximum value of 2881°C at $\text{UO}_{2.00}$. The melting value reported by Christensen⁽⁸⁾ for $\text{UO}_{2.2}$ is also shown in Figure 2. Thus, the melting behavior of UO_{2+x} is characterized by a maxima occurring in the vicinity of $\text{UO}_{2.00}$. The $\text{UO}_{2-x}/\text{U}_l$ phase field boundary was constructed by assuming that equilibrium compositions were attained in the sample preparation anneals. The data which describe this boundary are shown plotted versus reciprocal temperature in Figure 3 and may be represented by the following linear relationship

$$\ln (2\text{-O/U}) = 3.82 - 13,750/T$$

whose slope yields, for the heat of solution of uranium in UO_{2-x} , a value of $\Delta H = 27.3 \text{ kcal/mole}$, in good agreement with Edwards and Martin.⁽⁹⁾

D. Neptunium Oxide

The melting point of NpO_2 was determined to be $2560 \pm 50^\circ\text{C}$ in a helium atmosphere using a tungsten filament. Since only a small amount of sample was available, a large number of determinations, which would have contributed to a smaller uncertainty, could not be carried out. The as-melted sample stoichiometry could not be determined; however, since this value agrees reasonably well with other results on a plot of actinide dioxide melting point versus atomic number (as shown later), it is felt that very little or no decomposition occurred. No other measurements have been reported for NpO_2 .

E. Plutonium Oxide

The early determinations of the melting point of PuO_2 in inert atmospheres yielded anomalously low values due to decomposition of the starting dioxide. Russell⁽¹⁰⁾ has reported the melting point of $\text{PuO}_{2.0}$ to be 2400°C and the equilibrium oxygen decomposition pressure to lie between 0.1 and 1 atmosphere. This value is in excellent agreement with Lyon and Bailly⁽¹¹⁾ who melted PuO_2 in sealed refractory metal capsules to effectively minimize oxygen losses. A melting point of $2390 \pm 20^\circ\text{C}$ was obtained utilizing a thermal arrest method. Hexagonal Pu_2O_3 melts congruently at $2085 \pm 25^\circ\text{C}$,⁽¹²⁾ and this value has been confirmed by Harwell workers.⁽¹³⁾ There is some variation in the melting point of $\text{PuO}_{1.6\text{P}}$ and the mean of the two reported values, $2280 \pm 100^\circ\text{C}$, has been suggested.⁽¹³⁾ A comprehensive analysis of the work on the plutonium - oxygen system has been reported,⁽¹⁴⁾ and the high temperature portion of the phase diagram from that review is given in Figure 4. It should be mentioned that the liquidus - solidus relationships in this system have not been determined experimentally, and the diagram shown in Figure 4 including the congruent melting minima is hypothetical.

F. Americium Oxide

The melting point of a composition near AmO_2 was reported⁽¹⁵⁾ to be 2120°C ; however, this must surely refer to a grossly substoichiometric oxide since the oxygen dissociation pressure over $\text{AmO}_{2.00}$

is one atmosphere at about 1000°C .⁽¹⁶⁾ The above melting point, however, is not far from that expected for AmO_2 (2175°C) based on an extrapolation of other actinide dioxide data. The implication is little dependence of melting temperatures on stoichiometry in this system. In the present experiments, AmO_2 of greater than 99.7% purity was reduced to Am_2O_3 in hydrogen at 800°C and subsequently melted in the tungsten filament furnace; Am_2O_3 was also formed by reduction of AmO_2 on the filament at 1300°C in hydrogen. In both cases, the product was rust color as is typical of the sesquioxide. The average of 20 observations on the melting point of Am_2O_3 , determined by two observers, was $2205 \pm 15^{\circ}\text{C}$.

G. Curium Oxide

CmO_2 decomposes very easily with temperature,⁽¹⁷⁾ and the sesquioxide may be formed simply through vacuum reduction. In the present work, CmO_2 of 97 and 97.5% purity (major impurity in each sample was Am-243) was reduced to Cm_2O_3 on either a tungsten or rhenium filament. Melting points obtained on both filaments agreed within experimental error suggesting no compatibility interactions in either case. Forty-five determinations carried out by two observers gave a mean melting point for Cm_2O_3 of $2275 \pm 25^{\circ}\text{C}$. This value was also confirmed by high temperature differential thermal analysis and is in excellent agreement with that found by Smith,⁽¹⁸⁾ who also used a filament technique.

H. Summary

There are no melting point data reported for oxides higher than curium. The melting points discussed above are tabulated in Table II and plotted versus atomic number in Figure 5. (A plot versus ionic radius is very similar.) A reasonably linear decrease in the melting point of the dioxides with increasing Z is observed while the opposite trend is true for the sesquioxides. The heats of formation of the actinide dioxides decrease in a similar manner which reflects the lowering of bond energies in MO_2 with increase in atomic number. The greater

TABLE II. *Structures and Melting Points of Actinide Oxides.*

<u>Oxide</u>	<u>Known Crystal Forms</u>	<u>Melting Point ($^{\circ}\text{C}$)</u>	<u>Reference</u>
ThO_2	FCC	3300 ± 100	(4)
PaO_2	FCC	unknown	
UO_2	FCC	2805 ± 15	(35)
NpO_2	FCC	2560 ± 50	this work
PuO_2	FCC	2390 ± 20	(11)
Pu_2O_3	Cubic		
	Hexagonal	2085 ± 25	(12)
AmO_2	FCC	decomposes	
Am_2O_3	Cubic		
	Monoclinic		
	Hexagonal	2205 ± 15	this work
CmO_2	FCC	decomposes	
Cm_2O_3	Cubic		
	Monoclinic		
	H, X	2275 ± 25	(36)
BkO_2	FCC	decomposes	
Bk_2O_3	Cubic		
Cf_2O_2	FCC	decomposes	
Cf_2O_3	Cubic		
	Monoclinic		

stability of the sesquioxides with increasing Z is evident from the trend in the melting points for the three oxides on which data exists. In the lanthanide sesquioxides, the melting point increases with Z to a maximum at Gd_2O_3 , whereafter it remains essentially constant.⁽¹⁹⁾ If the same behavior occurs in the actinides, this maximum may exist at Cm_2O_3 which, based on electronic configuration, is the actinide homologue of Gd_2O_3 . In contrast, there is a good correlation for both lanthanide and actinide sesquioxides in the temperature dependence of the phase transformations of the various allotropes and ionic radius. If size is the dominant factor in the solid $\rightarrow$ liquid transition also, then Es_2O_3 may be the highest melting actinide sesquioxide since the radius of Es^{+3} is expected to be about that of Gd^{+3} .

PHASE TRANSFORMATION BEHAVIOR

Three crystallographic modifications of the lanthanide sesquioxides were first reported by Goldschmidt,⁽²⁰⁾ while two additional high temperature forms have recently been observed.⁽²¹⁾ The coordination in the A (hexagonal), B (monoclinic), and C (cubic) phases has been reviewed by Eyring and Holmberg.⁽²²⁾ The stability regions of these polymorphs depends upon the size of the lanthanide ion and upon temperature. In general, the A modification is found in the lighter lanthanides, the B form exists (at high temperatures) for the intermediate members of the series, while the C type exists over a wide temperature range in the heavy lanthanide sesquioxides. The C $\rightarrow$ B transformation has been shown to be irreversible for Sm_2O_3 , Pm_2O_3 , Eu_2O_3 , and Gd_2O_3 .

In the actinides, A and C forms of Pu_2O_3 have been shown to exist, though the cubic form is thought to occur at $O/Pu = 1.515$. The A and C modifications of Am_2O_3 have also been identified⁽²³⁾ and an indication of B- Am_2O_3 , as a minor phase in an x-ray pattern, has also been reported.⁽²⁴⁾ The cubic modification of Bk_2O_3 has been prepared independently by Baybarz⁽²⁵⁾ and by Peterson and Cunningham,⁽²⁶⁾

and though a B form has not yet been reported, it's existence can almost certainly be predicted. Both cubic and monoclinic phases of Cf_2O_3 have been identified by Cunningham and co-workers. ^(27,28)

Curium oxide exists in several allotropic forms. The cubic to monoclinic transformation is second order, irreversible, and occurs in the vicinity of 1000°C . The kinetics of this transformation have been studied by Mosley ⁽²⁹⁾ using high temperature x-ray diffraction. At higher temperatures, the monoclinic form transforms reversibly to a hexagonal structure. This transformation has been determined by our DTA measurements to occur at $1615 \pm 20^\circ\text{C}$, and the existence of the hexagonal (A) structure above 1600°C has been verified by x-ray diffraction. ⁽²⁹⁾ Continued heating results in two additional reversible solid-state transformations occurring at $2000 \pm 20^\circ\text{C}$ and $2210 \pm 20^\circ\text{C}$. Figure 6 shows an oscilloscope trace of the 2000°C transformation. Though these two high temperature phases have not been unambiguously identified via x-ray diffraction, it is highly plausible that they are analogous to the H and X phases reported by Foëx and Traverse ⁽²¹⁾ and are referred to as such. The various allotropes of the actinide sesquioxides are summarized in Table II.

Promethium is a synthetic lanthanide, produced only during fission. Pm-147 is a beta emitter with a half life of 2.6 years and this radioactive decay causes in-growth of the daughter Sm-147 at the rate of 2.2% per month. Very recently cubic, monoclinic, and hexagonal modifications of Pm_2O_3 were reported. ⁽³⁰⁾ The C-B transformation is irreversible and occurs in the vicinity of 800°C . ⁽³¹⁾ Using the high temperature DTA, we have observed additional high temperature transformations in Pm_2O_3 (containing 2% Sm_2O_3) as follows:

B $\rightleftharpoons$ A	1740°C
A $\rightleftharpoons$ H	2135°C
H $\rightleftharpoons$ X	2225°C
X $\rightleftharpoons$ Melt	2320°C

The reproducibility in these runs suggests an uncertainty of about $\pm 20^{\circ}\text{C}$ in these values. The melting point of Pm_2O_3 was also confirmed using the resistance filament method where a value of $2320 \pm 25^{\circ}\text{C}$ was obtained. All of the above transformations were present both on heating and cooling, including quenching, indicating reversibility in all reactions. Consistent observation of the $A \rightarrow B$ transformation on quenching in the DTA apparatus served as a deterrent to performing detailed x-ray examinations on the quenched material, since it clearly was not the pure hexagonal allotrope. A mixture of the hexagonal and monoclinic phases was only retained in experiments in which a few milligrams of Pm_2O_3 were placed on a resistance heated rhenium strip, melted, and quenched by turning off the power. The observation of the exothermic peak accompanying the $A \rightarrow B$ transformation on cooling in DTA reflects the influence of cooling rate, which was significantly less in this apparatus than on the resistance heated strip.

The $B \rightleftharpoons A$, $A \rightleftharpoons H$, $H \rightleftharpoons \text{melt}$ transitions were also observed in Sm_2O_3 at 1930, 2160, and 2365°C , respectively, though the $H \rightleftharpoons X$ transformation was not detected in this oxide. All of these reactions were completely reversible. The Pm_2O_3 and Sm_2O_3 transformation temperatures, as well as those for $(\text{Pm}_x, \text{Sm}_{1-x})_2\text{O}_3$ solid solutions are tabulated in Table III. In several experiments, a shift in the endo- and exothermic peak accompanying the transformation was observed after a few heating and cooling cycles. On subsequent cycles, the peak temperature was constant at the value shown. There is no ready explanation for this unusual observation. Possible explanations might include vaporization of impurities, selective vaporization of one of the components, or reaction with the crucible; however, if any of these were operative, one would expect this effect to be observed consistently.

The transformation temperatures observed in this work for Cm_2O_3 , Pm_2O_3 , and Sm_2O_3 are plotted as a function of the trivalent ionic radii in Figure 7 together with the transformation temperatures given by Foex and Traverse⁽²¹⁾ for lanthanide sesquioxides. The lanthanide ion radii are taken from Templeton and Dauben,⁽³²⁾ while the actinide ion radii are from Peterson and Cunningham.⁽²⁶⁾ Both sets of radii were calculated in a consistent manner using $1.38 \text{ \AA}$ as an effective

TABLE III. Phase Transformation Temperatures for Pm_2O_3 , Sm_2O_3 , and $(\text{Pm}_x, \text{Sm}_{1-x})_2\text{O}_3$ Solid Solutions.

<u>Transformation</u>	<u>x = 0.98</u>	<u>0.59</u>	<u>0.26</u>	<u>0.09</u>	<u>0</u>
B $\rightleftharpoons$ A	1740°C	1740°C	1780°C	1880°C	1930°C
A $\rightleftharpoons$ H	2135	2115	2065	2112	2160
H $\rightleftharpoons$ X	2225	2250	2245	2252	--
Melting	2320	2360	2330	2325	2365

O^{2-} radius. The high temperature portion of Figure 7 differs slightly from that drawn originally by Foëx and Traverse since the phase transformations are plotted as a function of ionic radius instead of atomic number. This, plus the inclusion of our promethium and samarium oxide data, results in a slight plateau in the A $\rightleftharpoons$ H transformation in the vicinity of these two oxides. Also included in Figure 7 are the low temperature data of Warshaw and Roy⁽³³⁾ for the C $\rightleftharpoons$ A transformation in Nd_2O_3 and the C $\rightleftharpoons$ B transitions in Sm_2O_3 , Eu_2O_3 , and Gd_2O_3 . Though the boundary for both these transformations are drawn as a line, there is some evidence that the C $\rightleftharpoons$ A and C $\rightleftharpoons$ B transformation for these oxides may occur over a temperature range.⁽³⁴⁾

The Cm_2O_3 A $\rightleftharpoons$ B and H $\rightleftharpoons$ X transformation temperatures agree very well with the lanthanide oxide data while the A $\rightleftharpoons$ H transformation is anomalously low. As with the other actinide sesquioxides, Cm_2O_3 melts at a significantly lower temperature than the corresponding lanthanide oxide. All of our results for Sm_2O_3 are slightly above the transition temperatures reported by Foëx and Traverse but still fit the stability diagram well. Our lack of observation of the H $\rightleftharpoons$ X transformation in Sm_2O_3 is puzzling. The results for Pm_2O_3 at each transformation conform well to the stability regions expected for this oxide. Including the cubic phase, it is noted that Pm_2O_3 , Sm_2O_3 , and Cm_2O_3 are among the members of this family of sesquioxides that exhibit five different solid crystallographic modifications.

It is to be noted in Figure 7 that the radius of Pu^{+3} is such that only the cubic or hexagonal forms are stable. The steep slope of the A-B boundary is drawn to intersect the cubic phase boundary at a radius in-between Am^{+3} and Pu^{+3} . This suggests a very narrow domain for B- Am_2O_3 and is consistent with its observation as a minor phase in samples quenched from 800-900°C.⁽²⁴⁾ Monoclinic Cf_2O_3 has been prepared at 1100°C⁽²⁷⁾ while cubic Cf_2O_3 has been shown to form upon oxidation of a californium oxy-halide in the temperature interval 500-730°C.⁽²⁸⁾ Both of these results are in accord with the stability diagram of Figure 7.

The Pm_2O_3 - Sm_2O_3 System

The beta decay of promethium-147 with the resultant homogeneous in-growth of samarium presents an ideal method for study of the phase relationships in the Pm-Sm oxide system. As discussed above, Pm_2O_3 and Sm_2O_3 exhibit the same allotropic forms and the trivalent cation radii are within about 2% of each other. A continuous series of solid solutions between the end components at all temperatures is, therefore, likely. X-ray diffraction examination was performed on numerous $(\text{Pm}_x, \text{Sm}_{1-x})_2\text{O}_3$ compositions in which the samarium was introduced by beta decay; through coprecipitation of the mixed oxalates; or through direct "alloying" of Pm_2O_3 and Sm_2O_3 powders followed by heat treatment at 1500°C . Since the monoclinic form is stable at low temperature after it is once formed, it is present over the widest temperature range and was the subject of the majority of the x-ray diffraction studies. All x-ray patterns of $(\text{Pm}_x, \text{Sm}_{1-x})_2\text{O}_3$ compositions were single phase and the isomorphous replacement of promethium by samarium in the monoclinic phase produced a nearly linear lattice spacing/composition diagram. The cell parameters are shown as a function of composition in Figure 8, and it is concluded that a homogeneous solid solution exists over the entire composition range.

X-ray diagrams were not obtained for a series of cubic (Pm,Sm) oxide compositions; however, based on the considerations of isomorphism of the end members as well as ionic size differences, it is likely that complete miscibility also exists in the cubic phase. The high temperature phases could not be quenched-in due to rapid transformation to the monoclinic structure. Phase transitions were detected, however, by DTA at intermediate compositions as shown in Table III. Further, the endo- and exothermic peaks accompanying these transformations were nearly as sharp as those detected for the end members, implying that the two-phase regions exist over very small temperature intervals. These results have been compiled into a pseudo binary phase diagram as shown in Figure 9. The open circles represent melting temperatures obtained by a filament technique and agree well with the DTA measurements. The temperature range of the irreversible C $\rightleftharpoons$ B transformation is taken as linear between Pm_2O_3 and the results of Stecura⁽³⁴⁾ for Sm_2O_3 .

VOLUME CHANGE ON MELTING AND SURFACE TENSION OF Sm_2O_3

The volume change on melting and surface tension of Sm_2O_3 were determined by the method described in the Experimental Section. The surface tension is obtained by the size and shape of pendant drops, sessile drops, or capillary menisci. Bashforth and Adams⁽³⁾ derived the theoretical shape of pendant and sessile drops and calculated tables of drop contours. Their tables can be used to determine the surface tension by fitting a theoretical curve to the experimental curve; a very tedious procedure. A computer program worked out by Butler and Bloom⁽³⁷⁾ for generating a theoretical curve which would fit the experimental curve has been used with modification as the basis for the work reported here. The same theory is used to calculate surface tension from the shape of a sessile drop, a pendant drop, or a cylindrical meniscus. When two fluids are separated by an interface, the shape of the interface is governed by the fundamental equation for the definition of surface tension:

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{P}{\gamma} \quad (1)$$

where R_1 and R_2 are the principal radii of curvature at a point on the surface, P is the pressure difference across the interface at the point, and γ is the interfacial tension. When the pressure difference is due to gravitation, values for R_2 and P can be combined with Equation (1) to give the fundamental equation for the shape of a cylindrically symmetric drop,

$$\frac{b}{R_1} = 2 + \beta \frac{z}{b} - \frac{\sin \phi}{(x/b)} \quad (2)$$

where

$$\beta = \frac{gb^2}{\gamma} (\rho_1 - \rho_2), \quad (3)$$

b is the radius of curvature at the base or top of the drop, g is the gravitational constant, ρ_1 and ρ_2 are the fluid densities, X and Z are the coordinates of points along the line of interaction of the drop surface and a plane containing the radius of curvature b, and ϕ is the angle formed by a line tangent to the drop at the point (X,Z) and the X-axis (Figure 10).

The parameter β describes the shape of the drop; all drops with the same value of β are geometrically similar. The value of b determines the drop size. β is positive for oblate figures of revolution, i.e., for a sessile drop or a meniscus in a capillary and negative for prolate figures of revolution, i.e., for a pendant drop, according to the original notation of Bashforth and Adams.⁽³⁾

The differential equation describing the shape of a pendant drop is obtained by substituting the values for R_1 and $\sin \phi$ obtained from analytical geometry into (2). The result is

$$bf''(Z) = \left(2 + \frac{\beta Z}{b}\right) \left\{1 + [f'(Z)]^2\right\}^{3/2} - \frac{b}{X} \left\{1 + [f'(Z)]^2\right\} f'(Z) \quad (4)$$

where

$$f'(Z) = \frac{dZ}{dX} \quad \text{and} \quad f''(Z) = \frac{d^2X}{dZ^2}.$$

This equation is solved for values of β and b which are then used to obtain the surface tension.

The results of the property measurements on molten Sm_2O_3 are as follows:

Surface Tension

Meniscus	785 ± 125 dynes/cm	$(2350 < T(^{\circ}\text{C}) < 2445^{\circ}\text{C})$
Pendant Drop	815 ± 168 dynes/cm	(2350°C)

Volume Change on Melting

$$\Delta V = 4.3\%$$

Liquid Density

$$\rho \text{ (gm/cm}^3\text{)} = 7.10 - 1.43 \times 10^{-4} T \quad (2350 < T(^{\circ}\text{C}) < 2560)$$

Liquid Thermal Expansion

$$\alpha = 12.6 \times 10^{-6} / ^{\circ}\text{C} \quad (2350 < T(^{\circ}\text{C}) < 2560)$$

The surface tension at each temperature was based on nine determinations, and the high uncertainty associated with these values results from the inability to outline the profile accurately. This error arises from the density gradient observed in the radiographs, which results from the varying thickness of the oxide which must be penetrated along the drop or meniscus profile. The scribe marks used to define the Z parameters on the photographic enlargements, however, could be read to better than $\pm 2.5 \times 10^{-2}$ mm. While the diffuse nature of the meniscus profile had a very significant effect on the surface tension measurements, it has less influence in the results on volume change on melting, liquid density, and liquid thermal expansion.

The volume change on melting of 4.3% is lower than that measured for other oxides: Al_2O_3 , 24%; 0.5 MgO - 0.5 Al_2O_3 (spinel), 14.1%; 0.6 Al_2O_3 - 0.4 MgO , 17.4%; 0.2 Y_2O_3 - 0.8 Al_2O_3 , 13.5%; 0.375 Y_2O_3 - 0.625 Al_2O_3 (YAG), 7.8%; and 0.2 Sm_2O_3 - 0.8 Al_2O_3 , 10%. This low value for the ΔV_m of Sm_2O_3 was noted in other experiments where the addition of 20% Sm_2O_3 to Al_2O_3 results in a 58% decrease in the volume change on melting of pure Al_2O_3 . The value of 4.3% for the volume change on melting is based on the measured liquid and solid densities just above and below the melting point, the latter density being corrected for the presence of porosity in the sintered Sm_2O_3 . The results on ΔV_m , liquid density, and liquid expansion are estimated to be accurate to better than 5%.

FIGURE CAPTIONS

- FIGURE 1. Schematic Diagram of High Temperature Differential Thermal Analysis Apparatus.
- FIGURE 2. Melting Temperatures of Nonstoichiometric Uranium Oxide.
- FIGURE 3. Least Squares Fit to Composition/Temperature Relationship for the U_x/UO_{2-x} Phase Boundary.
- FIGURE 4. Liquid - Solid Relationships in the Plutonium - Oxygen System.
- FIGURE 5. Melting Points of Actinide Di- and Sesquioxides.
- FIGURE 6. Oscilloscope Trace of Hexagonal (A) $\rightarrow$ Hexagonal (II) and Hexagonal (H) $\rightarrow$ Hexagonal (A) (Upper and Lower Curves, Respectively) Transformations in Cm_2O_3 . Transformation Temperature is $2000 \pm 20^\circ C$.
- FIGURE 7. Stability Diagram of Polymorphic Forms of Lanthanide and Actinide Sesquioxides. $\bullet$ and ∇ are results of Foex and Traverse⁽²¹⁾ and Warshaw and Roy,⁽³³⁾ respectively. $\circ$, $\square$, and $\triangle$ are transformation temperatures in Cm_2O_3 , Pm_2O_3 , and Sm_2O_3 found in present work.
- FIGURE 8. Lattice Constants of Monoclinic $(Pm, Sm)_2O_3$ Solid Solutions.
- FIGURE 9. Pm_2O_3 - Sm_2O_3 Phase Diagram. Open circles are melting points obtained by a filament technique and closed circles are DTA results. The two-phase regions are extremely narrow and are represented by a single line. The C $\rightarrow$ B transformation is irreversible and occurs over a temperature range.
- FIGURE 10. Parameters for Determination of Surface Tension from the Shape of a Pendant Drop.

FIGURE 1. Schematic Diagram of High Temperature Differential Thermal Analysis Apparatus.

FIGURE 2. Melting Temperatures of Nonstoichiometric Uranium Oxide.

FIGURE 3. Least Squares Fit to Composition/Temperature Relationship for the U_x/UO_{2-x} Phase Boundary.

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FIGURE 7. Stability Diagram of Polymorphic Forms of Lanthanide and Actinide Sesquioxides. ● and ▽ are results of Foëx and Traverse⁽²¹⁾ and Warshaw and Roy,⁽³³⁾ respectively. ○, □, and Δ are transformation temperatures in Ce_2O_3 , Pm_2O_3 , and Sm_2O_3 found in present work.

FIGURE 8. Lattice Constants of Monoclinic (Pm,Sm)₂O₃ Solid Solutions.

FIGURE 9. Pm_2O_3 - Sm_2O_3 Phase Diagram. Open circles are melting points obtained by a filament technique and closed circles are DTA results. The two-phase regions are extremely narrow and are represented by a single line. The C $\rightarrow$ B transformation is irreversible and occurs over a temperature range.

FIGURE 10. Parameters for Determination of Surface Tension from the Shape of a Pendant Drop.

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