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X-Ray-Diffraction and Absorption-Spectrophotometric Studies of AmI_3 and AmOI*

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SUMMARY

The anhydrous tri-iodides and the oxyiodide of americium were investigated by X-ray diffraction and absorption spectrophotometry. From the X-ray analysis of the tri-iodide, an orthorhombic form ($PuBr_3$-type structure) has been identified, which is isostructural with the lighter actinide (U-Pu) tri-iodides. A hexagonal form (BiI_3-type structure) of the tri-iodide was also found. The transition temperature for converting the orthorhombic form to the hexagonal form was established to be 400 ± 30°C. Room temperature lattice parameters for the tri-iodide are: (1) a_o = 0.428(4), b_o = 1.394(1) and c_o = 0.9974(7) nm for the orthorhombic form; and (2) a_o = 0.7637(4) and c_o = 2.091(2) nm for the hexagonal form. Tetragonal parameters for the oxyiodide are a_o = 0.4010(3) and c_o = 0.9038(6) nm. From differences in the absorption spectra of the solids at 25°C, it is possible to differentiate between these three materials by absorption spectrophotometry.

MASTER

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INTRODUCTION

A systematic study of the first five transplutonium halides and oxyhalides has been undertaken in our laboratory, using X-ray powder diffraction and absorption spectrophotometry, in order to compare the chemical and physical properties of these 5f compounds to the corresponding 4f materials. During the investigation of americium tri-iodide it became apparent: (1) that our lattice parameters for the hexagonal crystal form were not in accord with those previously reported [1]; and (2) that a second crystal form existed for this compound.

Described here are the results of examining americium oxyiodide and both crystalline forms of anhydrous americium tri-iodide by X-ray powder diffraction and absorption spectrophotometry. A comparison of these results with data for selected lanthanide tri-iodides and oxyiodides is also presented.

EXPERIMENTAL

Material. The americium tri-iodides were prepared using the ^{243}Am isotope (t1/2 = 7950 yr), by both direct combination of the elements and by treatment of americium dioxide with gaseous hydrogen halides at elevated temperatures. Americium oxyiodide was prepared by treating the tri-iodide with most hydrogen iodide vapor at temperatures above 550°C.

High purity americium metal (<250 ppm cationic impurities by spark-source mass spectrometry) was prepared by reduction of americium dioxide with thorium metal, followed by the distillation and condensation of the americium metal. Small portions (20-100 μg) of the resulting metal foil, together with 200-300% stoichiometric excess of doubly-sublimed iodine, were flame sealed under vacuum (10^{-6} mm) in quartz capillaries

75-100 mm in length. These capillaries were then heated at 300°C for 14-30 hours. A variable-gradient, micro furnace was then employed to sublime the unreacted iodine to the larger end of the capillary (cooler zone). The end of the capillary containing the actinide product was then flame sealed and removed to provide a sample suitable for both absorption spectrophotometric and X-ray powder diffraction analyses.

When the americium tri-iodide was prepared using the dioxide on the starting material, the oxide was treated (with two or more cycles) above 600°C with gaseous hydrogen bromide or hydrogen chloride to yield the corresponding anhydrous trihalide. The resulting anhydrous trihalide was then melted to confirm conversion before treating it with hydrogen iodide vapor above 600°C to form the tri-iodide. The reaction of the oxide with hydrogen iodide does not proceed quantitiatively to the tri-iodide. A description of the general synthesis procedure has been reported [2].

Absorption Spectrophotometry. Absorption spectrophotometric data were obtained with a single-beam microscope spectrophotometer (quartz optics) which has been described [2]. The spectrometer system is designed such that spectra can be obtained at either ambient or elevated temperatures; a small platinum heating coil is employed for the latter application. A mini-computer associated with the spectrophotometer collects the data, corrects for background asorption (separate scan of capillary without the sample) and provides a plot of the sample's spectrum.

X-ray Powder Diffraction. X-ray powder diffraction data were obtained from the samples using Debye-Scherrer type cameras and Ni-filtered Cu radiation. Theoretical line intensities and positions used for indexing the experimental data were refined by the LCR-2 program [4]. Errors are reported as one standard deviation.

RESULTS AND DISCUSSION

X-ray Diffraction. Analysis of the X-ray powder diffraction data on americium tri-iodide prepared from metal and iodine at 300°C showed the products existed in an orthorhombic form ($PuBr_3$-type structure [5]). However, americium tri-iodide samples prepared from oxides and hydrogen halides at temperatures above 600°C exhibited hexagonal symmetry (BiI_3-type structure [5]). Approximate lattice parameters for the orthorhombic form of americium tri-iodide were reported many years ago by Zachariasen [6]; details of the preparation were not published. Subsequently, Asprey et al. [1] reported a hexagonal form of americium tri-iodide, but they were unable to prepare the orthorhombic form. Our lattice parameters for orthorhombic americium tri-iodie compared favorably with the values of Zachariasen [6] (see Table I). In contrast, our lattice parameters for the hexagonal form of americium tri-iodide are not in accord with those of Asprey et al. [1]. The disagreement may be due to differences in indexing the diffraction data.

The lattice parameters and the calculated molecular volume for the orthorhombic form of americium tri-iodie are in accord with the corresponding values for the uranium through plutonium tri-iodides [6], allowing for the expected gradual decrease when progressing to the heavier members. Our calculated molecular volume of the hexagonal form of americium tri-iodide is considerably larger than that of the orthorhombic form, but this volume difference is comparable to that observed between molecular volumes for the light and heavy lanthanide tri-iodides [1]. The lattice parameters and the dimorphic behavior of americium tri-iodide are quite similar to those of neodymium tri-iodide [7], in accord with the similar trivalent ionic radii of these two elements [8]. Our lattice parameters

for the hexagonal form of americium tri-iodide are slightly larger than those reported by Wild et al. [9] for hexagonal californium tri-iodide and the approximate values of Fried et al. [10] given for hexagonal berkelium tri-iodide. Thus, our parameters for americium tri-iodide are in accord with those obtained by extrapolation from the values for berkelium and californium tri-iodides.

The oxyiodide of americium was also obtained in this work by heating the tri-iodide in the presence of a gaseous water-hydrogen iodide mixture. Our lattice parameters for americium oxyiodide, tetragonal (PbFCl-type structure), are in excellent agreement with those reported previously by Baybarz et al. [11] and are similar to the reported values for neodymium [7] and samarium [12] oxyiodides (Table I).

Absorption Spectra. We have also examined americium tri-iodide and oxyiodide by solid-state absorption spectrophotometry, and the spectra obtained from 2-25 ™g sized samples are shown in Figure 1. These spectra were obtained at 25°C with the purpose of using them to differentiate between the two crystal forms of the tri-iodide, to monitor the phase transition and to determine the level of oxyiodide contamination in sample preparations. Spectral studies for assigning energy levels are best carried out at low temperatures, and such measurements have been made previously on thin films of the trichloride, tribromide, and tri-iodide of americium at liquid helium temperature by Pappalardo et al. [13]. The differences between our spectra (Figure 1) arise from the changes in the metal ion's environment and coordination number in the compounds, and the resulting effect they have on these f-f transitions. In the orthorhombic form, the americium has a coordination number of eight; in the hexagonal structure the metal ion is six coordinated. In the tetragonal

oxyiodide, the americium has a coordination number of eight. Once the absorption spectrum for each material had been correlated with results obtained from X-ray powder diffraction analysis, then the absorption spectrum became a useful and reliable means to identify and differentiate between the two forms of americium tri-iodide and/or americium oxyiodide.

The absorption spectra of the two forms of americium tri-iodide and americium oxyiodide (Figure 1) differ mainly in the fine structure of the absorption envelopes and in the relative intensities of the different absorptions. Examination of the absorptions at 9.2×10^5 m^{-1} shows that the orthorhombic form of the tri-iodide has three peaks, as opposed to a single peak for the hexagonal form, and a doublet for the oxyiodide. The relative intensities at 10.7 and 11.3×10^5 m^{-1} are also useful for identification. Additionally, the absorption at 11.8×10^5 m^{-1} was found to be quite intense in the orthorhombic form of the tri-iodide, while in the other two spectra the intensity of the absorption at this same energy is more similar in intensity to those of the other major absorptions in each spectrum. Absorptions at 19.1 and 21.5×10^5 m^{-1} in the three spectra also show differences.

During the course of this work, a few 150 μg sized samples of americium tri-iodide were prepared via the oxide-hydrogen halide synthesis. One of these preparations was an exceptional sample for spectral work (highly transparent, jewel-like crystal, in the hexagonal form). In its spectrum two additional peaks of medium intensity were observed at 22.8 and 23.2×10^5 m^{-1}, and very weak absorptions were observed at 17 (also barely visible in two of the spectra in Figure 1), and at 15.2, $\times 10^5$ m^{-1}. All of these absorptions have been observed and assigned by Pappalardo *et al.* [13] in spectra obtained from thin films of an undefined crystal form of americium tri-iodide.

Phase Transition. In this work we have determined from both absorption spectrophotometric and X-ray powder diffraction analysis that the transition temperature for converting the orthorhombic form of americium tri-iodide to the hexagonal form is 400 ! 30°C. This transition was found to be reversible, but conversion of the high-temperature form (hexagonal) to the orthorhombic structure was difficult, probably due in part to slower kinetics at 300°C. Thus, the low-temperature, orthorhombic form of americium tri-iodide was obtained when the compound was prepared by direct reaction of the elements at 300°C, and could be prepared when the hexagonal form was annealed for several hours (8-14 hr) at this temperature. The hexagonal form of americium tri-iodide was maintained at room temperature in samples that avoided very slow cooling from above 500°C. Thus, when americium tri-iodide is prepared by reacting americium oxide with hydrogen halides at elevated temperatures, the hexagonal structure is normally obtained. The fact that Asprey et al. [1] observed only the hexagonal form of americium tri-iodide in the temperature range 400-900°C is in agreement with our findings.

The absorption spectra of the two structure types of americium tri-iodide were very useful in confirming the orthorhombic to hexagonal transition temperature; the reverse reaction was too slow to monitor. Although spectra of the tri-iodides were obtained at the elevated temperatures, as well as at room temperature, the spectra at the higher temperatures exhibited less detail and much broader absorption bands. Thus, the best technique was to heat the samples to a particular temperature, quench the sample, and then obtain a spectrum at room temperature. By using a small heating coil around the sample in the spectrophotometer beam [2], this process could be carried out without altering the sample area being examined.

The phase behavior of americium tri-iodide was found to be very similar to that of neodymium tri-iodide [7] and each element may be the only member of their respective series where dimorphism can be readily investigated by thermal treatment. This can be rationalized by considering the transition temperatures as a function of trivalent ionic radii, where Pr > Nd > Am > Sm [8]. The transition temperatures for the orthorhombic-to-hexagonal phase transformation are > 600°C for neodymium tri-iodide [7] and 400°C for americium tri-iodide. Further, a hexagonal form of praseodymium tri-iodide could not be obtained by quenching from high tempeatures, and the preparation of samarium tri-iodide at temperatures as low as 250°C produced only the hexagonal form [7]. In essence, the transition temperature changes rapidly from being close to the melting point for neodymium tri-iodide (784°C, [14]) to 400° for americium, and to below 250°C for samarium tri-iodide, if a transition even exists here. Examination of transamericium actinide t: iodides, especially curium tri-iodide, for an orthorhombic form will be of interest.

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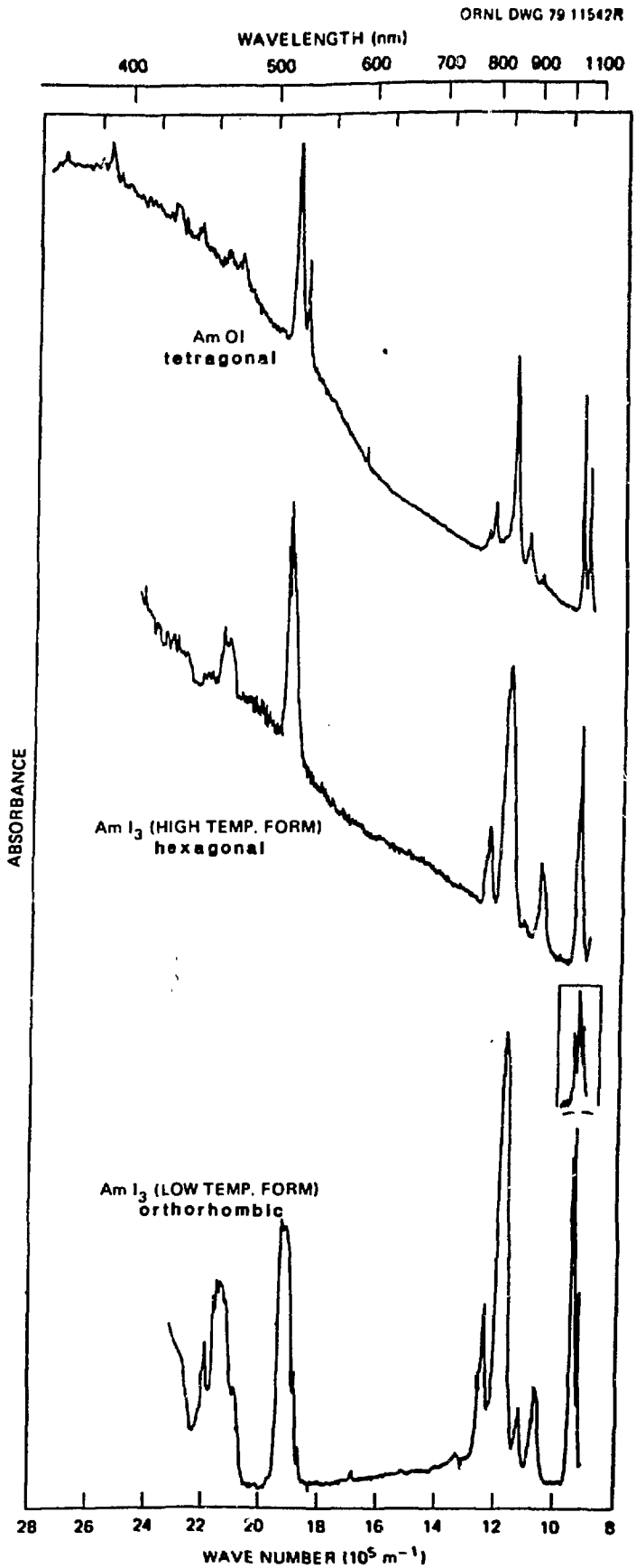
Table I. Lattice Parameters for Selected Lanthanides and Actinide Tri-iodides and Oxyiodides

Compound	Structure Type	Lattice Parameters, nm			Molecular Volume nm^3	Reference
		a_o	b_o	c_o		
PrI_3	$PuBr_3$	0.4309(8)	1.398(1)	0.9958(8)	0.1500	1
PrI_3	$PuBr_3$	0.4309(2)	1.3969(10)	0.9978(9)	0.1501	7
NdI_3	$PuBr_3$	0.4284(4)	1.3979(8)	0.9948(4)	0.1489	1
NdI_3	$PuBr_3$	0.4293(2)	1.3986(11)	0.9952(8)	0.1494	7
NdI_3	BiI_3	0.7610(7)	--	2.089(3)	0.1746	7
SmI_3	BiI_3	0.7490(8)	--	2.080(4)	0.1684	1
SmI_3	BiI_3	0.7590(10)	--	2.088(6)	0.1736	7
AmI_3	$PuBr_3$	0.430(5)	1.40(1)	0.99(1)	0.15	6
AmI_3	$PuBr_3$	0.428(4)	1.394(10)	0.9974(7)	0.1490	This work
AmI_3	BiI_3	0.742(2)	--	2.055(8)	0.1633	1
AmI_3	BiI_3	0.7637(4)	--	2.091(2)	0.1760	This work
AmOI	PbFCl	0.4011(5)	--	0.9042(5)	0.1455	11
AmOI	PbFCl	0.4010(4)	--	0.9038(5)	0.1453	This work
NdOI	PbFCl	0.4015(4)	--	0.9197(6)	0.1483	7
SmOI	PbFCl	0.4008(5)	--	0.9192(8)	0.1477	12

Figure Caption

1. Absorption Spectra for the Two Crystal Forms of Americium Tri-iodide and Americium Oxyiodide as Obtained at 25 ^{o} C.


ORNL DWG 79 11542R
WAVELENGTH (nm)
400
500
600
700
800
900
1100
Am OI
tetragonal
Am I3 (HIGH TEMP. FORM)
hexagonal
Am I3 (LOW TEMP. FORM)
orthorhombic
ABSORBANCE
28
26
24
22
20
18
16
14
12
10
8
WAVE NUMBER (10^5 m^-1)

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