MASTER

X-RAY POWDER DIFFRACTION OF EINSTEINIUM COMPOUNDS*

R. G. Haire

Transuranium Research Laboratory, Oak Ridge National
Laboratory, Oak Ridge, TN 37830

and

J. R. Peterson

Department of Chemistry, University of Tennessee,
Knoxville, TN 37916 and Transuranium Research Laboratory,
Oak Ridge National Laboratory, Oak Ridge, TN 37830.

ABSTRACT

X-ray powder diffraction (XRPD) analysis has proven to be extremely valuable in the study of the transplutonium elements. The high specific activity and the thermal energy associated with the radioactive decay of einsteinium isotopes make XRPD analysis of einsteinium samples very difficult. The major problems are destruction of the samples' crystallinity and alteration of their chemical composition. Blackening of the X-ray film also compromises the analyses. By applying certain guidelines given here, a limited amount of success has been achieved in obtaining diffraction data on einsteinium and some of its compounds.

INTRODUCTION

XRPD has proven to be a valuable tool for studying the transplutonium elements; a considerable amount of data on these elements

* Research sponsored by the Division of Nuclear Sciences, Office of Basic Energy Sciences, U. S. Department of Energy under contracts W-7405-eng-26 with Union Carbide Corporation and EY-76-S-05-4447 with the University of Tennessee (Knoxville).

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy nor any of their employees, nor any of their contractors, subcontractors, or their employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

were obtained by XRPD when the total amount of material that existed was less than one milligram. The classic work of B. B. Cunningham using a single ion exchange resin bead to concentrate initially the actinide element is a prime example [1]. Very often XRPD is the only method available to characterize these scarce actinide elements and their compounds. Even with the availability of greater quantities of these elements, XRPD still remains one of the most used means of establishing that a particular compound or phase has been prepared.

One of the major reasons for interest in einsteinium and its compounds is that it is the last of the actinide elements expected to be available in greater than picogram quantities. Knowledge of its chemistry is therefore useful for extrapolation to higher members of the series, especially since there is a tendency for greater stability of lower valence states ($< III$) in going across the second half of the actinide series.

The scarcity of einsteinium isotopes and the high specific activity of the most available isotope, ^{253}Es ($5.6 \times 10^{10} \alpha \cdot \text{min}^{-1} \mu\text{g}^{-1}$, 6.6 MeV α) require that microtechniques be used for preparing and studying einsteinium. The thermal energy associated with the radioactive decay ($1 \text{ watt} \cdot \text{mg}^{-1}$) is also detrimental to a sample's composition. The blackening of X-ray film poses an additional problem. Thus, XRPD analysis of einsteinium materials creates a situation more difficult than previously encountered with the other actinides. The particular preparation and handling procedure used for an einsteinium sample will determine whether or not useful X-ray data can be obtained from it.

EXPERIMENTAL

Many of the microtechniques used for handling einsteinium have been described elsewhere [2-4] as applied to other transplutonium elements. As with any research problem, the investigator desires to work with the purest samples that can be obtained. With einsteinium the task is most difficult since in one day after purification the Es-253 already contains $\sim 3\%$ of its daughter, Bk-249.

The oxides and halides of a new element are usually the first compounds that are prepared and studied. Further, many of the synthetic routes to other compounds start with the oxide. Our early attempts to prepare einsteinium oxide by the resin-bead technique [1] failed for one of two reasons: (1) the einsteinium decomposed the resin before it could be calcined; or (2) the exchange sites in the resin were occupied to only $\sim 20\%$, and upon calcination, very small, fragile pieces of oxide were formed. In

recent years, we have used a microprecipitation method, that provides upon calcination in air individual Es_2O_3 particles 2-10 μg in size [4]. In principal, these Es_2O_3 particles could be studied by XRPD; but in practice X-ray patterns have not been obtained from these samples, the analyses always indicating the samples were not crystalline.

These oxide particles have also been used as starting materials for the synthesis of other einsteinium materials, notably the anhydrous halides, oxyhalides and the metallic state. The anhydrous trihalides of einsteinium (chloride, bromide, iodide) are prepared in quartz capillaries by reacting Es_2O_3 with the respective hydrogen halide [4]. Reduction of these trihalides with hydrogen yields the dihalides [5,6]. Recently we have prepared EsF_3 by treating the Es_2O_3 with ClF_3 or F_2 in a monel system. The trihalides, excluding the trifluoride, can be melted or sublimed in the quartz capillaries to provide well-crystallized samples for X-ray and/or absorption spectrophotometric analyses [4]. Einsteinium metal can be prepared by reducing Es_2O_3 with lanthanum metal, distilling the volatile einsteinium metal and condensing it on a quartz fiber or a tungsten wire. The fiber or wire is then placed in a quartz capillary and examined by XRPD. Because it is necessary to make the above transfers in an inert-atmosphere gloved box, the time elapsed between preparation and X-ray analysis is much greater for the metal than for the halides. Further, the reactivity of the metallic state precludes extensive heating of it in a quartz capillary. Thus, re-crystallization of a sample in an X-ray capillary is best achieved with the halide preparations.

DISCUSSION

Five guidelines are given in Table I for XRPD of einsteinium metal and einsteinium compounds. One of the most important is the

Table I

Guidelines for XRPD of Einsteinium and Its Compounds

1. XRPD analysis must begin immediately after preparation or annealing of the sample.
2. Exposure times should be limited to 1/2-1 hour.
3. Sample sizes must be kept between 1-3 μg of Es.
4. Shielding of the film with nickel foil is important (Cu radiation).
5. Thin deposits of the sample are preferred over bulk forms.

examination of the sample as soon as possible after preparation, to minimize destruction of the material and/or its crystallinity due to self-irradiation and/or the associated thermal energy. In absorption spectrophotometric studies of einsteinium halides, we have shown that the loss of crystallinity begins in 5-15 minutes after annealing. Since exposure times for XRPD usually take greater than 30 minutes, even without considering handling time before the analysis, the sample's crystallinity can be destroyed before the end of the X-ray examination. If the material is resistant to decomposition, or can be re-synthesized in the X-ray capillary, then the crystallinity can be restored by annealing immediately prior to or during the XRPD analysis. The annealing can take the form of a single heat treatment, be pulsed allowing for cooling time between pulses (for ambient temperature measurements), or the sample can be held at elevated temperatures during XRPD. The first X-ray diffraction data on einsteinium compounds were obtained for EsCl_3 and EsOCl by continuously resynthesizing and annealing the materials at 430°C during the X-ray analysis [7]. Annealing the sample (at 400°C for 3 min) immediately prior to X-ray analysis provided sufficient crystallinity to collect limited diffraction data on EsBr_3 [8].

The use of a 57.3 mm Debye-Scherrer camera modified with a small heating coil [3] permitted annealing the EsBr_3 sample only seconds before collecting X-ray data. Annealing of Es_2O_3 or einsteinium metal samples in the quartz capillaries has not been as successful. The reactivity of the metal prohibits annealing it in the X-ray capillary, and the higher temperature ($\sim 900^\circ\text{C}$) required to recrystallize the oxides poses experimental problems (capability of the miniature heating coils plus possible reaction of the sample and the quartz). To date, XRPD data have not been obtained for einsteinium oxide or metal.

Protecting the X-ray film from the einsteinium's radioactivity is also necessary. Whereas the radioactivity of other trans-plutonium elements used in research work can be tolerated in 57.3 mm cameras for 2-8 hours, 1-3 μg samples of ^{253}Es require limiting exposures to 1/2-1 hour. The ideal quantity of sample used for X-ray work is a balance between the sample's radiation and the amount of material necessary to give suitable XRPD data, utilizing a fine focus or microfocus X-ray source. Although a longer-lived Es isotope (Es-254) is known, sufficient quantities of it are not available, and in addition, the short-lived ^{250}Bk daughter in equilibrium with it would also irradiate the film significantly. The use of a beryllium cup around the sample [9] protects the capillary during the film loading and unloading and also affords protection from any alpha particles escaping the thin glass walls of the capillary. The use of 0.008 mm thick nickel foil (for $\text{CuK}\alpha$ radiation), either around the beryllium

cup or immediately in front of the film, offers the best protection from gamma irradiation. In this case, the usual nickel filter (to remove $\text{CuK}\beta$ radiation) for the X-ray source is not needed, and thus a greater intensity of X rays reach the sample. Unfortunately, the Es-253 isotope emits a number of gamma rays, ranging up to ~ 1 MeV in energy, which are not significantly attenuated by the nickel foil.

The last guideline in Table I was determined through experience, where it was found that samples in the form of their sublimates or thin films retained their crystallinity longer than those in bulk. From the standpoint of making micro-transfers, it is necessary to have samples of 1-10 μg in mass; if additional transfers of the material being synthesized are not required, then thin films or deposits are acceptable for analysis by X rays. XRPD data on EsI_3 [10] were recently obtained by analyzing sublimates, made by heating one portion of sealed capillaries, each containing ~ 4 μg of EsI_3 , and allowing the sublimed EsI_3 to condense in the cooler part of the capillaries. The crystallinity of these samples was retained for longer periods of time than that observed for bulk forms of EsI_3 . This aspect of thin samples was also demonstrated in the case of Es_2O_3 , where 2-3 μg pieces yielded no XRPD data, but 50-100 ng samples, consisting of individual 400-800 Å Es_2O_3 particles, were readily analyzed by electron diffraction [11] and remained crystalline for many hours. Similarly, 100-200 ng samples of einsteinium metal in the form of 200-400 Å films remained crystalline for a few hours [12], whereas thicker films appeared amorphous by XRPD.

An explanation for the observed difference in behavior of thin deposits and bulk forms of samples is that a significant fraction of the einsteinium's alpha particles escape the small crystallites in the thin deposits, releasing the major part of their energy outside of the crystallites themselves. Damage due to recoiling nuclei would still be encountered, although this process may produce some self-annealing by localized thermal spikes. Thus, by using thin deposits made up of very small crystallites, a large portion of the radiation damage to the sample may be avoided.

It is beyond the scope of this paper to discuss in detail electron diffraction or to compare the advantages/disadvantages of electron and X-ray diffraction analyses. It is worthwhile to note, however, that with regard to einsteinium samples, electron diffraction analysis has three advantages: (1) very short exposure times (10 sec) for diffraction patterns; (2) the possibility of analyzing samples in ~ 10 minutes after preparation; and (3) blackening of the film is avoided due to the greater distance between the film and sample (~ 1 meter). There are also

some general disadvantages to electron diffraction analysis: these are the need for repeated calibration of the electron's wavelength; the need to examine many different portions of a sample to assure the areas examined are representative of the entire material; and the need for very thin samples, since the penetrating power of the electron is low. For einsteinium samples, the wavelength calibration creates an interesting problem. Normally when precise electron diffraction measurements are desired, an internal standard is used. However, with einsteinium samples, one must not only contend with radiation damage to the einsteinium itself, but also that damage which may be done to the internal standard used for calibration!

In Table II are summarized the einsteinium materials for which X-ray or electron diffraction data have been collected. Hopefully, this list will be expanded in the future. We are continuing to use XRPD for analyzing einsteinium samples, especially for Es(II) halide compounds, where their extreme hygroscopic nature and reactivity with oxygen present major difficulties for electron diffraction analysis.

It is also planned to attempt the rapid analysis of einsteinium compounds by energy-dispersive XRPD. This technique, amenable to our present preparative and handling procedures, may afford the capability of attaining diffraction data on a sufficiently short time scale to allow monitoring structural changes in an einsteinium sample brought about by its intense self-irradiation.

Table II

Diffraction Data on Einsteinium and Its Compounds

<u>Material</u>	<u>Method</u>	<u>Date</u>	<u>Reference</u>
EsCl ₃ EsOCl	XRPD	1969	7
Es ₂ O ₃	Electron Diffraction	1973	11
EsBr ₃	XRPD	1975	8
EsI ₃	XRPD	Unpublished	10
Es Metal	Electron Diffraction	1978	12

REFERENCES

1. B. B. Cunningham, "Submicrogram Methods Used in Studies of the Synthetic Elements," *Microchem. J. Symp. Ser.*, **69-93** (1961).
2. J. R. Peterson, "Chemical Identification and Phase Analysis of Transplutonium Elements and Compounds via X-ray Powder Diffraction," *Advances in X-Ray Analysis*, Vol. 20, H. F. McMurdie, C. S. Barrett, J. B. Newkirk and C. O. Ruud, Editors, Plenum Pub. Corp., New York (1977), p. 75.
3. J. N. Stevenson and J. R. Peterson, "Some New Microchemical Techniques Used in the Preparation and Study of Transplutonium Elements and Compounds," *Microchem. J.*, **20**, 213 (1975).
4. J. P. Young, R. G. Haire, R. L. Fellows, and J. R. Peterson, "Spectrophotometric Studies of Transcurium Element Halides and Oxyhalides in the Solid State," *J. Radioanal. Chem.*, **43**, 477 (1978).
5. J. R. Peterson, D. D. Ensor, R. L. Fellows, R. G. Haire and J. P. Young, "Preparation, Characterization and Decay of Einsteinium(II) in the Solid State," *Proc. 3rd International Conf. on Electronic Structure of the Actinides*, Grenoble, France, Aug. 30-Sept. 1, 1978; to be publ. in *J. de Physique*.
6. R. L. Fellows, J. R. Peterson, J. P. Young and R. G. Haire, "The First Preparation of an Einsteinium(II) Compound, EsCl_2 ," *The Rare Earths in Modern Science and Technology*, G. J. McCarthy and J. J. Rhyne, Editors, Plenum Press, New York (1978), p. 493.
7. D. K. Fujita, B. B. Cunningham and T. C. Parsons, "Crystal Structures and Lattice Parameters of Einsteinium Trichloride and Einsteinium Oxychloride," *Inorg. Nucl. Chem. Lett.*, **5**, 307 (1969).
8. R. L. Fellows, J. R. Peterson, M. Noé, J. P. Young and R. G. Haire, "X-ray Diffraction and Spectroscopic Studies of Crystalline Einsteinium(III) Bromide, $^{253}\text{EsBr}_3$," *Inorg. Nucl. Chem. Lett.*, **11**, 737-742 (1975).
9. R. L. Sherman and O. L. Keller, "Modified Debye-Scherrer X-Ray Diffraction Camera for Radioactive Compounds," *Rev. Sci. Instrum.*, **37**, 240 (1966).
10. R. G. Haire, J. P. Young, J. R. Peterson and R. L. Fellows, "Spectrophotometric and X-ray Data of $^{253}\text{EsI}_3$," to be published, *Inorg. Nucl. Chem. Lett.*
11. R. G. Haire and R. D. Baybarz, "Identification and Analysis of Einsteinium Sesquioxide by Electron Diffraction," *J. Inorg. Nucl. Chem.*, **35**, 489-496 (1973).
12. R. G. Haire and R. D. Baybarz, "Studies on Einsteinium Metal," *J. de Physique* (in press; see ref. 5).