

GMELIN REFERENCE NUMBER

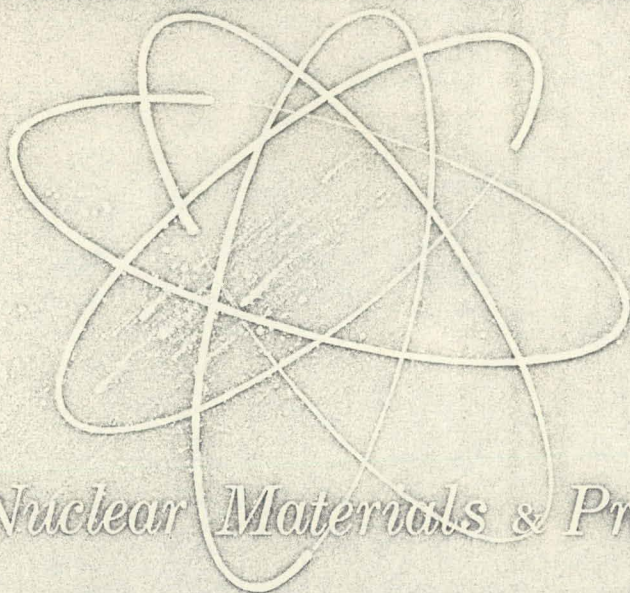
AED-Conf-

63-040-18 ✓

RECEIVED MAY 2 1963

TM 63-2-8 ✓

MASTER



Nuclear Materials & Propulsion Operation

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe of privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

CONF-20-18

X-RAY CRYSTALLOGRAPHIC STUDIES OF
EUROPIUM OXIDES AND HYDROXIDES

by

Eu

Robert C. Rau

3rd Rare Earth Conference
Clearwater, Florida
April 21-24, 1963

For presentation at

Third Rare Earth Conference
Grand Bahama Island

April 22-24, 1963

FLIGHT PROPULSION LABORATORY DEPARTMENT

GENERAL  ELECTRIC

Facsimile Price \$ 1.60

Microfilm Price \$.80

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

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.

X-RAY CRYSTALLOGRAPHIC STUDIES OF EUROPIUM OXIDES AND HYDROXIDES

Robert C. Rau

ABSTRACT

X-ray diffraction methods have been employed to study the phases occurring in the europium-oxygen system and in the europium hydroxide decomposition process. Europium sesquioxide, Eu_2O_3 , containing trivalent europium ions, occurs in two forms, body-centered cubic and monoclinic. Divalent europium forms a monoxide, EuO , which is face-centered cubic. Both divalent and trivalent ions are combined in the compound Eu_3O_4 , which is orthorhombic. Another orthorhombic compound of unknown composition has been obtained which is also believed to contain divalent and trivalent ions.

Studies on the thermal decomposition of europium hydroxide to the sesquioxide have yielded data on two hydroxide phases. The starting material, $\text{Eu}(\text{OH})_3$, is hexagonal and decomposes into an intermediate phase, EuOOH , which is believed to be orthorhombic.

INTRODUCTION

Over the past several years, a number of europium compounds have been studied for their possible use as nuclear control materials. During this period, a significant amount of crystallographic data has been collected for a number of europium oxides and hydroxides. It is the purpose of this paper to report on the crystallographic studies and to present the X-ray diffraction data for the known oxides and hydroxides of europium. In addition, brief descriptions of the methods of preparation of these compounds will be given.

PREPARATION OF SAMPLES

X-ray diffraction studies have been carried out on four europium oxides with known compositions, as well as an unknown phase which is also believed to be an oxide of europium. In addition, two europium hydroxide compounds have been investigated. Brief descriptions of the methods of preparing these compounds are given below.

Cubic Eu_2O_3 and Monoclinic Eu_2O_3

Europium sesquioxide, Eu_2O_3 , containing trivalent europium ions, occurs in two crystallographic forms, the body-centered cubic C-form and the monoclinic B-form(1). The body-centered cubic phase is the normal low-temperature form of Eu_2O_3 and can be produced by the dehydration of $\text{Eu}(\text{OH})_3$ in air atmosphere(2). At temperatures above 1050°C , this cubic sesquioxide transforms irreversibly to the high-temperature monoclinic modification(3). Powders of both of these Eu_2O_3 phases, and single crystals of the monoclinic form, were used for X-ray studies.

Cubic Eu_2O_3 powder, as obtained from the vendor, produced poor X-ray diffraction patterns with broad lines. Since it was believed that small crystallite size was responsible for this line-broadening, the material was heated for 20 hours in air at 1000°C to induce crystallite growth. This treatment gave a powder which produced sharp, well-defined diffraction patterns. Similar heat treatment was not required for the monoclinic Eu_2O_3 since the thermal treatment necessary to convert cubic Eu_2O_3 to the monoclinic form was sufficient to promote crystallite growth.

Several single crystals of monoclinic Eu_2O_3 were obtained during 100 hour compatibility tests of Eu_2O_3 and various metals at 1200°C in a helium atmosphere. These crystals, which were transparent to light, were in the shape of thin, flat needles, about $1/4$ inch in length.

EuO

Divalent europium forms a monoxide, EuO , which can be prepared by several methods. Eick, Baenziger, and Eyring(4) reduced Eu_2O_3 with lanthanum metal to form La_2O_3 , europium metal, and/or EuO , and Achard(5) reduced Eu_2O_3 with carbon to form both EuO and Eu_3O_4 . For the present work, a method similar to that of Matthias, Bozorth, and VanVleck(6) was used. In this method, Eu_2O_3 powder was blended in inert atmosphere with a slightly greater than stoichiometric amount of europium metal powder and pressed into compacts. These compacts were heated in argon at 1000°C for four hours, and then heated to 1450°C to drive off any unreacted europium metal. The EuO produced by this method was essentially a single-phased, microcrystalline powder, dark black-brown in color, which sometimes contained minor amounts of Eu_3O_4 . No crystals suitable for single crystal X-ray analysis were obtained.

Eu₃O₄

Eu₃O₄ exists as a distinct europium oxide phase containing both divalent and trivalent europium ions, and can thus be written EuO·Eu₂O₃. This compound has been produced in a number of ways. Bärnighausen and Brauer⁽⁷⁾ formed Eu₃O₄ by heating an equimolar mixture of EuO and Eu₂O₃ at 900°C in inert atmosphere. For the present study, two methods involving the reduction of Eu₂O₃ were used.

Based on the method of Achard⁽⁵⁾, Eu₃O₄ was first produced by heating compacts, composed of stoichiometric amounts of Eu₂O₃ and spectrographic grade carbon powders, for two hours at 1300°C and then five minutes at 1700°C in argon atmosphere. The product thus formed contained some unreacted carbon. More recently, single phase Eu₃O₄ has been consistently prepared by reducing Eu₂O₃ in hydrogen at 1650°C. Similar results have been obtained by melting Eu₂O₃ in hydrogen and by heating Eu(OH)₃ in hydrogen at 1650°C. The Eu₃O₄ produced by these methods occurred as black chunks, which, when ground, gave a red-brown powder. Under the polarizing microscope, individual dark red crystals could be picked out for single crystal X-ray studies.

Ortho I

Work on the europium-oxygen system has produced a new phase, designated Ortho I because of its orthorhombic crystal structure. Although this phase has not yet been identified, it is believed to be a reduced oxide of europium, possibly including both divalent and trivalent europium ions. Ortho I was first produced as a crystalline deposit on Eu₂O₃ during Eu₂O₃ - noble metal compatibility tests conducted in hydrogen at 1425°C. Subsequently, well-formed orange-yellow crystals of Ortho I have been reproduced a number of times by heating Eu₂O₃ powder in flowing dry hydrogen for periods of 60 to 120 hours at temperatures between 1425° and 1650°C. Weight gain by ignition in air indicated an approximate oxygen-to-europium ratio of 1.1 for Ortho I.

Eu(OH)₃ and EuOOH

Recent studies of the thermal decomposition of Eu(OH)₃ yielded crystallographic data for that compound and EuOOH⁽²⁾. Both of these phases were produced only as microcrystalline powders, therefore no single crystal studies were performed.

$\text{Eu}(\text{OH})_3$ was prepared by reacting europium metal with water at room temperature, evolving hydrogen during the process. After the reaction ceased, the solution was evaporated to dryness, yielding the $\text{Eu}(\text{OH})_3$ as a white residue. EuOOH was then produced by thermal decomposition of $\text{Eu}(\text{OH})_3$ at temperatures between 300° and 425°C in an air atmosphere. Heating above 425°C caused cubic Eu_2O_3 to form. Both $\text{Eu}(\text{OH})_3$ and EuOOH were found to be stable in room atmosphere.

X-RAY METHODS

X-ray crystallographic analysis of the europium oxides and hydroxides was carried out using powder and single crystal methods. In general, powder data was used to determine the lattice parameters of the compounds and for routine identification of phases after various heat treatments. Single crystal data was used to determine crystal symmetries and to aid in indexing the powder patterns. Further analysis of the single crystal data is contemplated for defining the complete crystal structures of several of the compounds.

Powder patterns were obtained by both film and diffractometer techniques, using iron $\text{K}\alpha$ radiation. Debye-scherrer photographs were obtained in standard 114.6mm.diameter Norelco powder cameras with the sample powders mounted on thin glass fibers. Chart recordings of the diffraction patterns were obtained on a Norelco diffractometer, with the powders packed in standard aluminum sample holders.

Interplanar d-spacings were determined from both the photographs and the chart recordings. Broad or strong diffraction lines could be read more easily and accurately from the diffractometer charts, but very weak lines were usually observable only in the photographs. Thus the final tabulations of d-values were composites of both types of patterns. Diffraction line intensities were determined directly from the chart recordings whenever possible.

An IBM-7090 computer program⁽⁸⁾ was used to calculate the lattice parameters of most of the europium compounds, utilizing data from indexed lines in the back-reflection region of the powder patterns. For the more complicated structures, the correctness of the powder pattern indexing was checked by computing a theoretical set of d-values with the 7090⁽⁹⁾, using the previously calculated lattice constants as input.

Single crystal X-ray studies were confined to crystals of monoclinic Eu_2O_3 , Eu_3O_4 , and Ortho I. Data was obtained from rotation and Weissenberg photographs, using copper radiation, and from precession photographs, using molybdenum radiation. This single crystal data was used to determine the approximate unit cell dimensions and to aid in indexing the rather complicated powder patterns of these compounds. It is hoped that further work can be done with the single crystal data of Eu_3O_4 and Ortho I to completely elucidate their structures.

In addition to X-ray data, optical crystallographic data was also obtained for some of the europium compounds, using calibrated immersion oils and a standard flat-stage polarizing microscope.

RESULTS AND DISCUSSION

The crystallographic data obtained for the europium oxides and hydroxides is summarized and presented in Table I. A discussion of the results for each compound follows.

Cubic Eu_2O_3

The low-temperature form of europium sesquioxide has the body-centered cubic Th_2O_3 structure common to all of the rare earth sesquioxides from Nd through $\text{Lu}^{(10)}$. The rather complex unit cell is large, with $a = 10.869 \text{ \AA}$, and contains 16 molecules of Eu_2O_3 . Its density, calculated on the basis of this cell, is 7.28 g/cc . Petrographic examination showed the material to be isotropic with an index of refraction of 1.92.

Monoclinic Eu_2O_3

The high-temperature monoclinic form of Eu_2O_3 has a crystal structure isomorphous with that of monoclinic Sm_2O_3 recently described by Cromer⁽¹¹⁾. Similar monoclinic forms of sesquioxides for the rare earths from Nd through Dy have variously been reported in the literature. The unit cell dimensions of monoclinic Eu_2O_3 are; $a = 14.082 \text{ \AA}$, $b = 3.604 \text{ \AA}$, $c = 8.778 \text{ \AA}$, and $\beta = 100^\circ 00'$. These parameters were hand-calculated from four well-defined lines in the back-reflection region of the powder pattern, since the lattice parameter computer program⁽⁸⁾ could not be used for crystals of symmetry lower than orthorhombic. The given parameters predict a theoretical powder pattern which agrees well with the observed pattern, and also agree with the rough parameters measured from single crystal films. Monoclinic Eu_2O_3 has six formula units per unit cell, leading to a calculated density of 7.99 g/cc . Crystals of monoclinic

Table I: Crystallographic Data for Europium Oxides and Hydroxides

Phase	Color ^a	Crystal Structure	Space Group	Lattice Parameters(Å)	Density (g/cc)	Optical Properties
Cubic Eu ₂ O ₃	White	Body-centered cubic	Ia ₃	a = 10.869	7.28 ^c	Isotropic N = 1.92
Mono. Eu ₂ O ₃	White	Monoclinic	C2/m	a = 14.082 b = 3.604 c = 8.778 β = 100°00'	7.99 ^c	Biaxial negative 2V = 20° N _x = 2.07 N _z = 2.10
EuO	Black-brown	Face-centered cubic	Fm ₃ m	a = 5.142	8.11 ^b 8.21 ^c	Opaque
Eu ₃ O ₄	Black	Orthorhombic	Pnam	a = 10.085 b = 12.054 c = 3.502	8.03 ^b 8.11 ^c	Biaxial N's near 2.12
Ortho I	Orange	Orthorhombic	-	a = 9.71 b = 49.5 c = 5.63	6.74 ^b	Biaxial positive 2V = 25° N _x = 1.89 N _z = 1.92
Eu(OH) ₃	White	Hexagonal	C6 ₃ /m	a = 6.365 c = 3.645	5.10 ^b 5.27 ^c	Uniaxial positive N's near 1.76
EuOOH	White	Orthorhombic ^d	-	a = 8.235 ^d b = 11.626 ^d c = 7.453 ^d	5.85 ^b	Biaxial N's near 1.82

^a Color of bulk material.^b Measured density.^c Theoretical density calculated from cell constants.^d Crystal structure and lattice parameters deduced from best available X-ray data.

Eu_2O_3 are optically biaxial negative, having high and low refractive indices near 2.10 and 2.07 and an optic angle of about 20° .

EuO

Europium monoxide is face-centered cubic, having a NaCl-type lattice. This structure has also been reported for SmO ⁽⁴⁾, and occurs for many simple divalent metal oxides. The lattice constant calculated for EuO from the back-reflection lines of the powder pattern is 5.142 Å. This unit cell contains four EuO molecules and has a theoretical density of 8.21g/cc, in good agreement with the 8.11g/cc measured value. No optical data was obtained for EuO since it was optically opaque.

Eu₃O₄

Eu_3O_4 crystallizes in the orthorhombic system, and is isomorphous with the compound Eu_2SrO_4 , where strontium is substituted for the divalent europium in the lattice⁽⁷⁾. The lattice parameters computed from the back-reflection region of the powder pattern of Eu_3O_4 are, $a = 10.085 \text{ Å}$, $b = 12.054 \text{ Å}$ and $c = 3.502 \text{ Å}$, and the unit cell contains four formula units. The theoretical density of 8.11g/cc calculated from these parameters is in good agreement with the 8.03g/cc value measured from small, single-phased Eu_3O_4 fragments. This measured density was obtained by the liquid displacement technique, using a 25 mg. capacity torsion balance which was modified to allow weighing of specimens in air and in liquid⁽¹²⁾.

The crystal structure of Eu_3O_4 has not yet been completely determined, but Weissenberg data indicate that the space group is Pnam with the atoms located in the positions $x, y, 1/4$; $\bar{x}, \bar{y}, 3/4$; $\frac{1}{2}-x, \frac{1}{2}+y, 3/4$; $\frac{1}{2}+x, \frac{1}{2}-y, 1/4$. Although the x and y coordinates are still unknown, Barnighausen and Brauer⁽⁷⁾ have pointed out that this structure is probably similar to those of Bi_2PbO_4 and Fe_2CaO_4 .

Complete optical data could not be determined for Eu_3O_4 due to its very dark color and its high refractive indices. However, examination in polarized light showed crystal fragments to be biaxial with indices near 2.12.

Ortho I

The still-unidentified Ortho I phase appears to have a very unusual structure. Single crystal diffraction photographs of this material show the crystal system to be orthorhombic, with approximate lattice parameters of $a = 9.71\text{\AA}$, $b = 49.5\text{\AA}$, and $c = 5.63\text{\AA}$. The unusually long b-axis is of particular interest. On first examination of the rotation photograph along this axis, strong layer lines were seen which corresponded to a lattice spacing of about 7.07\AA . However, close examination showed the presence of two weak layer lines between each pair of strong lines. These weak layers could only be indexed if each strong layer was designated $7n$ and each weak layer was designated $7n \pm 2$. Thus, the observed layer lines satisfy the numerical sequence 0, 2, 5, 7, 9, 12, 14, - - - -, and the true repeat distance along the b-axis is seven times 7.07\AA , i.e., 49.5\AA . Subsequent Weissenberg photographs taken of crystals rotating about the a-axis have also shown spots lying on the weak $7n \pm 2$ rows. The significance of this unusual layering is not yet understood, but will be pursued in further studies to determine the identity and crystal structure of Ortho I.

Optical properties and measured density have been determined for Ortho I. Petrographic analysis of the orange-yellow crystals showed them to be biaxial positive with an optic angle of about 25° and high and low refractive indices of 1.92 and 1.89. Micro-density measurements on several crystals of Ortho I gave a density of about 6.74g/cc .

Eu(OH)₃

Eu(OH)₃ has the hexagonal UCl₃-type structure which has been reported to exist for the trihydroxides of many of the other rare earths (13). Its lattice parameters calculated from the powder pattern are, $a = 6.365\text{\AA}$, and $c = 3.645\text{\AA}$, and its unit cell contains two formula units. The theoretical density calculated from these dimensions is 5.27g/cc , which compares fairly well with the value of 5.10g/cc determined pycnometrically on tengerams of the powder.

Since Eu(OH)₃ was available only as a microcrystalline powder, accurate indices of refraction could not be determined. However, measurements on oriented aggregates of the microcrystals showed Eu(OH)₃ to be uniaxial positive with indices near 1.76.

EuOOH

The crystal structure of EuOOH is not yet known. However, powder data indicate that it is probably isomorphous with the reported basic oxides of several other rare earths⁽¹⁴⁾. In the absence of single crystal data, an attempt was made to index the powder pattern of EuOOH so that lattice parameters could be determined. This effort resulted in an indexing which gave an orthorhombic unit cell having $a = 8.235\text{\AA}$, $b = 11.626\text{\AA}$, and $c = 7.453\text{\AA}$. These parameters gave a set of calculated d-values which agreed very well with the observed powder pattern. However, this cell is probably not the true unit cell, since 14 EuOOH groups would be required per cell to give a calculated density (6.03g/cc) in reasonable agreement with the pycnometrically measured value of 5.85g/cc. Since orthorhombic crystals usually contain multiples of four formula units per cell, it is probable that the chosen unit cell is a pseudo cell, possibly a submultiple of the true cell. Additional data, preferably from single crystals, would be required to positively describe EuOOH.

Due to the microcrystalline nature of the EuOOH, complete optical properties were not obtained. However, petrographic examination of the powder showed the material to be biaxial, with low birefringence, and having an average refractive index of 1.82.

ACKNOWLEDGEMENTS

The author is indebted to J. R. Miller, F. A. Martin and W. J. Glover, Jr. for preparing the many samples used for this work, and to Dr. T. N. McVay for providing much of the optical data.

This work was performed under contracts AT(11-1)-171 and AT(40-1)-2847 with the United States Atomic Energy Commission.

References

- (1) V. M. Goldschmidt, F. Ulrich, and T. Barth,
Skrifter Norske Videnskaps - Akad. Oslo,
I, Mat. - Naturv. Kl., No. 5, 5 (1925).
- (2) R. C. Rau and W. J. Glover, Jr., to be published.
- (3) C. E. Curtis and A. G. Tharp, J. Am. Ceram. Soc.
42, 151 (1959).
- (4) H. A. Eick, N. C. Baenziger, and L. Eyring, J. Am.
Chem. Soc. 78, 5147 (1956).
- (5) J. C. Achard, Comptes Rendus 250, 3025 (1960).
- (6) B. T. Matthias, R. M. Bozorth, and J. H. Van Vleck,
Phys. Rev. Letters 7, 160 (1961).
- (7) H. Bärnighausen and G. Brauer, Acta Cryst. 15,
1095 (1962).
- (8) M. H. Mueller, L. Heaton, and K. T. Miller, Acta
Cryst. 13, 828 (1960).
- (9) M. H. Mueller, E. F. H. Meyer, and S. H. Simonsen,
Argonne National Laboratory Report ANL - 6519,
April, 1962.
- (10) I. Warshaw and R. Roy, J. Phys. Chem. 65, 2048 (1961).
- (11) D. T. Cromer, J. Phys. Chem. 61, 753 (1957).
- (12) H. Berman, Amer. Min. 24, 434 (1939).
- (13) R. Roy and H. A. McKinstry, Acta Cryst. 6, 365 (1953).
- (14) M. W. Shafer and R. Roy, J. Am. Ceram. Soc. 42,
563 (1959).