EUROPIUM OXIDE AS A POTENTIAL LMFBR CONTROL MATERIAL

A. E. Pasto

OAK RIDGE NATIONAL LABORATORY

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ABSTRACT

Europium oxide has been suggested as a possible neutron absorber material for use in the control rods of LMFBRs. This document is a review of the available literature data for Eu_2O_3 concerning its physical properties and characteristics, and is an evaluation of the current status of the data regarding reactivity worth, compatibility, irradiation stability, and in-reactor heating rate. Preliminary fabrication experiments are also described.

It is concluded that the monoclinic form of Eu_2O_3 is an excellent candidate absorber material. It is readily fabricated into dense pellets by sintering or hot pressing, has an initial nuclear worth equivalent to that of natural B_4C , and retains a significant portion of this worth during burnup due to its "chain-type" neutron absorption behavior. However, few data are available regarding the fast neutron irradiation behavior of Eu_2O_3 pellets and their compatibility with structural materials and coolants.

A cursory evaluation of other oxides of europium is also included.

INTRODUCTION

Europium is a member of the family of elements that is commonly called the "rare earths." These elements constitute the group having atomic numbers from 57 (lanthanum) through 71 (lutetium). Two other elements, scandium and yttrium, exhibit properties similar to these and are commonly included in this family.

The first discovery of a "rare earth" was reported in 1794 by Johann Gadolin, who detected the existence of yttria in a rare Swedish ore from Ytterby. In the 1800's most of the rest of the "rare earths" were separated and reported. Since these occurred as oxides and exhibited properties resembling those of the common earths alumina and lime, they were called earths. In fact, of course, these elements are metals. The ores from which these "earths" were separated were quite rare, hence the name "rare earths." Actually, this is a misconception. These elements occur in low concentrations in many different and widely scattered minerals, with the result that they are as plentiful as the noble metal group, as is illustrated in Fig. 1. They constitute about one-sixth of all known elements — thus, the term "rare earth" is misleading. A more preferable term for these elements is "the lanthanides," a term that indicates the similarity of their properties to those of lanthanum. This terminology will be used throughout the remainder of this report.

Europium was discovered as a new element in 1886 by Boisbaudran and named by Demarcay in 1906. It occurs in minor quantities in several minerals and is readily obtained from monazite sand. This sand is a chief source of thorium, and as the demand for thorium increases, the supply of by-product lanthanides (including europium) will increase.

Monazite sand is commonly broken down by sulfuric acid treatment, which converts the lanthanides to soluble sulfates. These are then converted to hydroxides by boiling with excess sodium hydroxide. Calcination of this product yields a mixture of lanthanide oxides. These can be taken back into solution and the individual elements separated out by any of several techniques, including solvent extraction, ion exchange, etc. Europium can readily be obtained with 99.99% purity in this manner. The chemical procedures are reviewed in the books by Sinha,¹ Spedding and Daane,² and Eyring.³

Naturally occurring europium consists of two isotopes, ^{151}Eu and ^{153}Eu , of approximately equal abundance (47.8 and 52.2 at. % respectively). This mixture possesses certain characteristics that are desirable in a material to be used as a control element for both thermal and fast nuclear reactors. In thermal reactors, it has a very high neutron absorption cross section, and it retains a significant portion of this cross section as a function of time. Its long life as an absorber is due to "chain-type" absorption behavior. That

Fig. 1. Relative abundance of the elements. (Ref: L. H. Ahrens, "Aspects of the Geochemistry of the Rare Earths," in *Progress in the Science and Technology of the Rare Earths*, Vol. 1, ed. by LeRoy Eyring, Macmillan, New York, 1964) (Reprinted with permission from L. H. Ahrens and Pergamon Press, Inc.)

is, ^{151}Eu absorbs a neutron and produces ^{152}Eu , which can absorb a neutron and form ^{153}Eu , which can absorb a neutron to form ^{154}Eu , etc. This behavior is in sharp contrast to that of samarium and gadolinium, both of which exhibit higher initial cross-section values, but lose their reactivity worth rapidly due to lack of a chain-type absorption mechanism. This type of behavior for europium is well documented in reviews by Martin and Beaver,⁴ Ray,⁵ and Anderson.⁶

Current designs for fast breeder reactors call for a core containing control rods bunched together into "pin clusters." To yield the maximum absorber density without causing the absorber element to run at

excessively high temperatures requires the use of dense pellets stacked into rods. At present, B_4C is the absorber material designated for the FFTF, with Eu_2O_3 as a backup. Nevertheless, Eu_2O_3 is potentially an even better material than B_4C for this application. A recent article by Spenke⁷ discusses all the relevant factors involved in such a determination. Spenke's conclusions are:

1. Europium oxide is equivalent to natural boron carbide on a reactivity worth per unit volume basis.
2. Europium oxide will not produce helium gas on irradiation, as does B_4C .
3. The daughter products of europium are good neutron absorbers, leading to good retention of reactivity worth. The boron carbide daughter products do not absorb a significant number of neutrons.

Also, due to the retention of reactivity worth in Eu_2O_3 , the control rods should not require replacement as often as for the rapidly burned-out B_4C . Both materials, however, have the problem of internal heat generation. The (n,γ) reactions and subsequent decay of the europium isotopes may, in conjunction with the core gamma heating, generate substantial quantities of heat. (This aspect is discussed more fully in Supplement I.) The low thermal conductivity of Eu_2O_3 coupled with this heating effect may lead to high center-line temperatures in the pellets, thus limiting the size of pellets used.

Spenke notes that the afterheat of europium is dependent largely on the long half-lives of the ^{152}Eu and ^{154}Eu isotopes. Thus, after an initial rapid decrease (a few days time), the total decay energy varies only slightly over long periods. At this level, handling and storage of the elements present no special problems.

Concerning the reactivity worth of Eu_2O_3 in fast spectra, Spenke finds monoclinic Eu_2O_3 to possess a 33% better worth per volume than natural boron carbide. Early ORNL calculations⁸ have indicated that this number may range from 17 to 43%, while Atomics International calculations⁹ show Eu_2O_3 to be better by about 24%. These numbers vary mostly due to differences in the assumed neutron spectra, although there may also be a neutron self-shielding effect.

M. M. Martin of ORNL has made a preliminary assessment of probable changes in the reactivity worth of europium sesquioxide when exposed to a particular fast-neutron flux. For comparative purposes, he chose 94%-dense Eu_2O_3 containing 2.55×10^{22} atoms Eu/cm^3 and 98%-dense natural B_4C (2.134×10^{22} atoms $^{10}B/cm^3$). Because of available data^{10,48,49} and ease of calculation, a monoenergetic 50-keV flux of 1.8×10^{15} neutrons $cm^{-2} sec^{-1}$ was assumed to represent the average condition in an outer control position (row 7 of the FFTF) of a fast reactor.

The principal capture reactions, half-lives, and capture cross sections of the pertinent europium and boron isotopes are shown below:

Fig. 2. Relative worth of Eu and ^{10}B in-reactor.

The partial cross section of ^{151}Eu for formation of the 9.3-hr isomer of ^{152}Eu was taken to be 37% of the total capture cross section of ^{151}Eu (the factor used for exposure to thermal neutrons). Note also that the 9.3-hr isomer of ^{152}Eu does not decay to the ground state of ^{152}Eu and that the contribution of gadolinium and samarium decay daughter products was ignored.

The results of the various neutron capture and radioactive growth and decay processes given in Eqs. (1) through (6) and their effects on nuclear worth are presented in Fig. 2. This is, at best, a first approximation. However, it is tentatively concluded that natural B_4C and Eu_2O_3 , in which only ^{10}B , ^{151}Eu , and ^{153}Eu isotopes are considered, should exhibit nearly identical initial reactivity worth on an equal-volume basis in fast reactors. As shown in Fig. 2, the buildup of the principal europium capture products of ^{152}Eu and ^{154}Eu leads to a relatively slower rate of loss of reactivity worth with fluence and increases the useful life of Eu_2O_3 -bearing absorbers. For example, let us assume that the life of a fast-reactor neutron absorber is

established solely from a reduction in reactivity worth of 10%. From Fig. 2 it is readily observed that the life of an Eu_2O_3 -bearing absorber should be at least three times longer than that of a B_4C -bearing absorber.

A. M. Perry of ORNL has cursorily estimated the relative worth vs full-power years for Eu_2O_3 in row 7 of EBR-II. Although his assessment used conservative values for capture cross sections of ^{152}Eu and ^{154}Eu and somewhat different half-lives, the results given in Appendix A of Supplement I also indicate a long control-rod lifetime to achieve a 10% reduction in worth.

The absence of helium production coupled with the economical incentive of a possible significant increase in useful lifetime in comparison to natural B_4C makes Eu_2O_3 an extremely attractive control material for fast reactors. However, more work should be done to firmly establish the reactivity worth of Eu_2O_3 for anticipated neutron spectra in the FFTF and the demonstration LMFBR. This assessment should elucidate (1) pertinent nuclear data gaps (especially for the neutron capture cross sections of ^{151}Eu , ^{152}Eu , ^{153}Eu , ^{154}Eu , ^{152}Gd , and ^{152}Sm) and probable accuracy of the existing information, (2) the need for additional experimentally determined nuclear data, and (3) the total heating rates during operation and subsequent cooling periods. A few absorber design configurations should also be given a first look to assess probable heating rates.

EUROPIUM SESQUIOXIDE (Eu_2O_3)

Europium will not be used in a reactor in the metallic state, since the metal is extremely reactive toward water and atmospheric water vapor and oxygen, and fabrication is thus difficult. One of the most easily obtainable forms of the lanthanides has been the sesquioxide. This material is readily fabricated into shapes and requires no special handling. A further advantage of the oxide form of europium is that it possesses a higher europium density than the metal. Hence most of the nuclear applications of europium and the other lanthanides have involved use of the sesquioxide.

Physical and Chemical Properties

The product remaining after the extraction of the lanthanides from the raw ore and the separation of europium may be the oxalate, nitrate, carbonate, hydroxide, sulfate, fluoride, or chloride. Calcination of any of these salts in air will yield the sesquioxide, one of the most thermodynamically stable europium compounds. Stecura¹¹ has published thermograms of several europium salts along with data on times and temperatures required to yield Eu_2O_3 (see Table I). The thermograms are illustrated in Figs. 3 and 4.

The crystal form of Eu_2O_3 derived from calcination of europium oxalate, hydroxide, carbonate, and nitrate is body-centered cubic, analogous to the structure of Mn_2O_3 . It is commonly called the C form. The unit cell contains 16 molecules of Eu_2O_3 and has an edge length¹² of 10.869 Å. Using these values, the theoretical density can be calculated to be 7.28 g/cm³, with a corresponding europium density of 2.49×10^{22} atoms Eu/cm³. This cubic polymorph transforms on heating to a monoclinic form (the B form) through a diffusion-controlled reconstructive transformation.¹¹ Typical of this type of phase change, the kinetics are strongly temperature dependent. Complete conversion from cubic to monoclinic takes from several days at 1050°C to less than an hour at 1300°C. This behavior is illustrated in Fig. 5. The reverse reaction (transformation from monoclinic to cubic) has not been observed even after subjecting the monoclinic form to prolonged heat treatments at temperatures just below the transformation temperature.^{13,14} (For a further discussion, see Supplement II.) Warshaw and Roy¹⁵ have induced the monoclinic form to transform to the cubic by hydrothermal techniques. However, their technique brought the monoclinic form of europium oxide into contact with water at high temperatures. This could easily have converted the material to the hydroxide. The water was then removed at 974°C and the resulting

Table 1. Decomposition products of lanthanide salts^a

(Ref: S. Stecura, "Crystallographic Modifications and Phase Transformation Rates of Five Rare Earth Sesquioxides," U.S. Bureau of Mines Report of Investigations 6616)

Rare-earth salt	1st decomposition		2d decomposition		3d decomposition	
	Temperature (°C)	Product	Temperature (°C)	Product	Temperature (°C)	Product
Carbonates:						
La ₂ (CO ₃) ₃	500	La ₂ O ₂ CO ₃	830	La ₂ O ₃		
Nd ₂ (CO ₃) ₃ ·2H ₂ O	300	Nd ₂ (CO ₃) ₃	480	Nd ₂ O ₂ CO ₃	720	Nd ₂ O ₃
Sm ₂ (CO ₃) ₃ ·2H ₂ O	320	Sm ₂ (CO ₃) ₃	500	Sm ₂ O ₂ CO ₃	630	Sm ₂ O ₃
Eu ₂ (CO ₃) ₃ ·2H ₂ O	270	Eu ₂ (CO ₃) ₃	500	Eu ₂ O ₂ CO ₃	620	Eu ₂ O ₃
Gd ₂ (CO ₃) ₃ ·4H ₂ O	500	Gd ₂ O ₂ CO ₃	620	Gd ₂ O ₃		
Oxalates:						
La ₂ (C ₂ O ₄) ₃ ·4H ₂ O	320	La ₂ (C ₂ O ₄) ₃	530	La ₂ O ₂ CO ₃	800	La ₂ O ₃
Nd ₂ (C ₂ O ₄) ₃ ·10H ₂ O	280	Nd ₂ (C ₂ O ₄) ₃	510	Nd ₂ O ₂ CO ₃	670	Nd ₂ O ₃
Sm ₂ (C ₂ O ₄) ₃ ·8H ₂ O	250	Sm ₂ (C ₂ O ₄) ₃	510	Sm ₂ O ₂ CO ₃	630	Sm ₂ O ₃
Eu ₂ (C ₂ O ₄) ₃ ·5H ₂ O	290	Eu ₂ (C ₂ O ₄) ₃	330	Eu ₂ O ₂ C ₂ O ₄	450	Eu ₂ O ₂ CO ₃ ^b
Gd ₂ (C ₂ O ₄) ₃ ·8H ₂ O	250	Gd ₂ (C ₂ O ₄) ₃	600	Gd ₂ O ₂ CO ₃	670	Gd ₂ O ₃
Nitrates:						
La(NO ₃) ₃ ·6H ₂ O	220	La(NO ₃) ₃	420	LaONO ₃	670	La ₂ O ₃
Nd(NO ₃) ₃ ·6H ₂ O	260	Nd(NO ₃) ₃	410	NdONO ₃	660	Nd ₂ O ₃
Sm(NO ₃) ₃ ·6H ₂ O	300	Sm(NO ₃) ₃	400	SmONO ₃	490	Sm ₂ O ₃ -SmONO ₃ ^c
Eu(NO ₃) ₃ ·4H ₂ O	290	Eu(NO ₃) ₃	390	EuONO ₃	500	Eu ₂ O ₃ -EuONO ₃ ^d
Gd(NO ₃) ₃ ·6H ₂ O	290	Gd(NO ₃) ₃	410	GdONO ₃	520	Gd ₂ O ₃ -GdONO ₃ ^e
Sulfates:						
La ₂ (SO ₄) ₃ ·6H ₂ O	350	La ₂ (SO ₄) ₃	1150	La ₂ O ₂ SO ₄	1450	La ₂ O ₃
Nd ₂ (SO ₄) ₃ ·8H ₂ O	280	Nd ₂ (SO ₄) ₃	1000	Nd ₂ O ₂ SO ₄	1400	Nd ₂ O ₃
Sm ₂ (SO ₄) ₃ ·7H ₂ O	400	Sm ₂ (SO ₄) ₃	1000	Sm ₂ O ₂ SO ₄	1340	Sm ₂ O ₃
Eu ₂ (SO ₄) ₃ ·8H ₂ O	330	Eu ₂ (SO ₄) ₃	900	Eu ₂ O ₂ SO ₄	1330	Eu ₂ O ₃
Gd ₂ (SO ₄) ₃ ·8H ₂ O	200	Gd ₂ (SO ₄) ₃	900	Gd ₂ O ₂ SO ₄	1280	Gd ₂ O ₃
Chlorides:						
LaCl ₃ ·6H ₂ O	195	La ₂ OCl ₄ -LaCl ₃	580	LaOCl-La ₂ O ₃	1450	La ₂ O ₃
NdCl ₃ ·5H ₂ O	270	Nd ₂ OCl ₄	730	NdOCl-Nd ₂ O ₃	1450	Nd ₂ O ₃
SmCl ₂	450	SmOCl	1300	Sm ₂ O ₃		
EuCl ₃ ·5H ₂ O	190	Eu ₂ OCl ₄	420	EuOCl	1400	Eu ₂ O ₃
GdCl ₃ ·5H ₂ O	280	Gd ₂ OCl ₄	440	GdOCl	1200	Gd ₂ O ₃
Fluorides:						
LaF ₃	550	La ₄ O ₃ F ₆	1150	LaOF	1500	La ₂ O ₃
NdF ₂ ·1/2H ₂ O	300	NdF ₂	920	Nd ₃ O ₂ F ₅	1140	NdOF ^f
SmF ₂ ·1/2H ₂ O	900	SmF ₂	1000	Sm ₃ O ₂ F ₅	1200	SmOF ^g
EuF ₂ ·1/2H ₂ O	350	EuF ₂	1250	EuOF	1480	Eu ₃ O ₃
GdF ₂ ·1/2H ₂ O	330	GdF ₂	740	Gd ₃ O ₂ F ₅	1060	GdOF ^h

^aTemperatures correspond to the points on the thermogram at which the intermediate compounds are initially observed.^bEu₂O₂CO₃ at 630°C decomposes to Eu₂O₃.^cSm₂O₃-SmONO₃ at 680°C decomposes to Sm₂O₃.^dEu₂O₃-EuONO₃ at 670°C decomposes to Eu₂O₃.^eGd₂O₃-GdONO₃ at 670°C decomposes to Gd₂O₃.^fNdOCl at 1,500°C decomposes to Nd₂O₃.^gSmOF at 1,500°C decomposes to Sm₂O₃.^hGdOF at 1,490°C decomposes to Gd₂O₃.

Fig. 3. Europium carbonate, nitrate, and oxalate thermograms. (Ref: S. Stecura, "Crystallographic Modifications and Phase Transformation Rates of Five Rare Earth Sesquioxides," U.S. Bureau of Mines Report of Investigations 6616)

Fig. 4. Europium chloride, fluoride, and sulfate thermograms. (Ref: S. Stecura, "Crystallographic Modifications and Phase Transformation Rates of Five Rare Earth Sesquioxides," U.S. Bureau of Mines Report of Investigations 6616)

Fig. 5. Kinetic isotherms for Eu_2O_3 C to B transformation. (Ref: S. Stecura, "Crystallographic Modifications and Phase Transformation Rates of Five Rare Earth Sesquioxides," U.S. Bureau of Mines Report of Investigations 6616)

product was cubic Eu_2O_3 . This would be expected if the hydroxide had formed, since the hydroxide decomposes to the cubic form of the sesquioxide on calcination at this temperature. Thus their data, suggesting that the transformation is reversible, are questionable. Further data concerning the relative stability of the B and C forms suggest that perhaps the transformation from monoclinic to cubic does not occur because the cubic form is metastable. That is, the low-temperature cubic form is considered to be derived from the calcination process through a hindered or topotactic solid-to-solid reaction, which does not allow true thermodynamic equilibrium. The so-called transformation temperature, under this theory, is simply that at which the atoms in the lattice obtain sufficient energy to become mobile. This was deduced by Brauer,¹⁶ who precipitated europium sesquioxide from a sodium-potassium-europium nitrate melt. The precipitation commenced around 380°C and was completed at 420°C , the range in which the cubic phase should be formed. However, the melt-precipitated europium sesquioxide was the B-type monoclinic form, which was not supposed to occur below 1050°C . Even the addition of some "seed" C-type cubic powder to the melt did not prevent the appearance of the monoclinic form.

Judging from the latest free-energy data¹⁷ (Tables 2 and 3) the C form is thermodynamically more stable than the B form from room temperature up to about 1127°C . But the monoclinic form has not been observed to transform back to the cubic form in this temperature range, probably because there is insufficient mobility of the atoms in the lattice.

The unit cell of the monoclinic structure contains six molecules of Eu_2O_3 . Several different sets of lattice parameters have been reported from which one can calculate several values for the theoretical density. Some of these are listed in Table 4.

Per mole of oxygen atoms, the heat of formation of monoclinic europia (-132 kcal/mole O at room temperature) is comparable with those of other highly stable oxides (-134 for HfO_2 , -132 for ZrO_2 , and -135 for Al_2O_3).¹⁸ The melting point of Eu_2O_3 was originally reported to be near 2050°C ,¹⁹ but later measurements put it at 2330°C .²⁰ This value is more in line with the melting points of the neighbor compounds to europia (Sm_2O_3 , 2300°C ; Gd_2O_3 , 2330°C).¹⁹ Above 2000°C , europia undergoes phase

Table 2. Thermodynamic functions for the formation of cubic Eu_2O_3

[Ref: G. C. Fitzgibbon, E. J. Huber, Jr., and C. E. Holley, Jr.,
 "Enthalpy of Formation of Europium Sesquioxide,"
J. Chem. Thermo. 4, 349–58 (1972)]

Temperature		$\Delta H_f^\circ(T)$ (cal/mole)	$\Delta S_f^\circ(T)$ (cal K^{-1} mole $^{-1}$)	$\Delta G_f^\circ(T)$ (cal/mole)
$^\circ\text{C}$	$^\circ\text{K}$			
25.15	298.15	$-397,400 \pm 900$	-78 ± 2	$-374,000 \pm 1100$
27	300	$-397,400 \pm 900$	-78 ± 2	$-373,900 \pm 1100$
127	400	$-396,700 \pm 900$	-76 ± 2	$-366,100 \pm 1200$
227	500	$-395,900 \pm 900$	-75 ± 2	$-358,600 \pm 1400$
327	600	$-395,100 \pm 900$	-73 ± 2	$-351,100 \pm 1500$
427	700	$-394,400 \pm 900$	-72 ± 2	$-343,900 \pm 1700$
527	800	$-393,600 \pm 900$	-71 ± 2	$-336,700 \pm 1900$
627	900	$-392,900 \pm 900$	-71 ± 2	$-329,000 \pm 2100$
727	1000	$-392,400 \pm 900$	-70 ± 2	$-322,700 \pm 2300$
827	1100	$-396,400 \pm 900$	-73 ± 2	$-315,700 \pm 2500$
927	1200	$-393,800 \pm 900$	-73 ± 2	$-308,300 \pm 2700$
1027	1300	$-395,200 \pm 1000$	-72 ± 2	$-301,200 \pm 2900$
1127	1400	$-394,600 \pm 1000$	-72 ± 2	$-293,800 \pm 3100$

$\Delta G_f^\circ(T) = -399,600 - 16.3T \log_{10} T + 126T$ cal/mole, $0 < T < 1090^\circ\text{K}$

Table 3. Thermodynamic functions for the formation of monoclinic Eu_2O_3

[Ref: G. C. Fitzgibbon, E. J. Huber, Jr., and C. E. Holley, Jr.,
 "Enthalpy of Formation of Europium Sesquioxide,"
J. Chem. Thermo. 4, 349–58 (1972)]

Temperature		$\Delta H_f^\circ(T)$ (cal/mole)	$\Delta S_f^\circ(T)$ (cal K^{-1} mole $^{-1}$)	$\Delta G_f^\circ(T)$ (cal/mole)
$^\circ\text{C}$	$^\circ\text{K}$			
25.15	298.15	$-394,700 \pm 800$	-76 ± 2	$-372,000 \pm 1000$
27	300	$-394,700 \pm 800$	-76 ± 2	$-371,900 \pm 1000$
127	400	$-394,100 \pm 800$	-74 ± 2	$-364,400 \pm 1100$
227	500	$-393,400 \pm 800$	-73 ± 2	$-357,000 \pm 1300$
327	600	$-392,700 \pm 800$	-72 ± 2	$-349,800 \pm 1400$
427	700	$-392,000 \pm 810$	-70 ± 2	$-342,700 \pm 1600$
527	800	$-391,300 \pm 810$	-69 ± 2	$-335,700 \pm 1800$
627	900	$-390,600 \pm 810$	-69 ± 2	$-328,200 \pm 2000$
727	1000	$-390,100 \pm 820$	-68 ± 2	$-322,000 \pm 2200$
827	1100	$-394,100 \pm 840$	-72 ± 2	$-315,100 \pm 2400$
927	1200	$-393,600 \pm 850$	-71 ± 2	$-308,000 \pm 2500$
1027	1300	$-393,000 \pm 870$	-71 ± 2	$-301,000 \pm 2700$
1127	1400	$-392,500 \pm 900$	-70 ± 2	$-293,800 \pm 2900$

$\Delta G_f^\circ(T) = -396,600 - 14.2T \log_{10} T + 118T$ cal/mole, $0 < T < 1090^\circ\text{K}$

transformations to three other polymorphic forms. From about 2040 to 2140 $^\circ\text{C}$, Eu_2O_3 takes a hexagonal structure (the A form), which converts to another hexagonal form (the H form) from 2140 to about 2260 $^\circ\text{C}$, and it finally converts to an unknown structure (the X form) just before it melts.²¹ The $\text{A} \rightleftharpoons \text{H}$ transformation is probably of the "displacive" type, involving small thermal effects and no hysteresis. The $\text{H} \rightleftharpoons \text{X}$ transformation, on the other hand, is assumed to be more like the $\text{C} \rightleftharpoons \text{B}$ transformation, classified as "reconstructive." This is also true for the $\text{B} \rightleftharpoons \text{A}$ phase inversion. The phase stability relations of Eu_2O_3 and the other lanthanide oxides are illustrated on a plot of atomic number vs temperature, given as Fig. 6.

Table 4. Comparative values of lattice parameters and density of B-type Eu_2O_3

Lattice parameter				Theoretical density (g/cm^3) calculated ^a	Reference
a (Å)	b (Å)	c (Å)	β (deg)		
14.110	3.603	8.805	100.05	7.95	43
14.12	3.600	8.801	99.98	7.96	21
14.09	3.601	8.790	99.8	7.98	11
14.082	3.604	8.778	100.0	7.99	12
14.1133	3.6025	8.8080	100.026	7.951	ORNL measurement
13.944	3.581	8.676	98.5	8.18	13

^aTheoretical density calculated as follows:

$$\text{g}/\text{cm}^3 = \frac{351.92 \text{ g Eu}_2\text{O}_3}{1 \text{ mole Eu}_2\text{O}_3} \times \frac{1 \text{ mole Eu}_2\text{O}_3}{6.023 \times 10^{23} \text{ molecules Eu}_2\text{O}_3} \times \frac{6 \text{ molecules Eu}_2\text{O}_3}{1 \text{ unit cell}} \times \frac{1 \text{ unit cell}}{\text{volume (cm}^3\text{)}}$$

where unit cell volume (cm^3) = $(a)(b)(c)(\sin \beta) \times 10^{-24}$.

Fig. 6. Stabilities of lanthanide sesquioxides. Data taken from W. C. Mosley, "B-Type $^{244}\text{Cm}_2\text{O}_3$ - a Candidate Isotopic Power Fuel," DP-MS-67-104.

The thermal properties of monoclinic Eu_2O_3 have been thoroughly investigated. The specific heat, thermal expansion coefficient, and thermal conductivity values are given in Table 5, where they can be compared with those of B_4C . The thermal expansion data are plotted vs temperature in Fig. 7. Figures 8 and 9 illustrate the temperature dependence of thermal conductivity and show how it correlates with other materials. The thermal expansion is relatively high for a ceramic material, while the thermal conductivity is very low. This combination of properties is likely to lead to a low thermal shock resistance, since the low conductivity can cause high thermal gradients and the high expansion will then bring about large thermal stresses. Some evidence of this poor thermal behavior was noted during the sintering experiments described below, where cracking was observed if the dense materials were cooled too rapidly after firing.

Fabrication

The higher europium atom density for the monoclinic form as compared with the cubic form indicates that monoclinic Eu_2O_3 is the preferred material. Furthermore, in the event that the control-rod center-line temperature should attain 1050°C or over, the monoclinic form would not undergo a large volume shrinkage such as would occur if the rod utilized cubic Eu_2O_3 . For these reasons, europia has been incorporated into reactors in the monoclinic form.

Europia has been fabricated into many different neutron-absorber-element configurations, but these have nearly always been in the form of a powder dispersed in a metallic matrix for use in thermal reactors.

Fig. 7. Linear thermal expansion of several oxides, including Eu_2O_3 . (Ref: Z. B. Jastrzebski, *Nature and Properties of Engineering Materials*, p. 361, Wiley, New York, 1959; used with permission of publisher) Europia data from R. L. Wilfong et al., "Thermal Expansion of the Oxides of Yttrium, Cerium, Samarium, Europium, and Dysprosium," U.S. Bureau of Mines Report of Investigations 6180.

Table 5. Comparison of structure and properties of Eu_2O_3 and B_4C

Structure or property	Eu_2O_3			B_4C	Reference
	Form I	Form II	Reference		
Structure type	Body-centered cubic	Monoclinic	<i>a</i>	Rhombohedral	<i>b</i>
Lattice parameter, Å	$a_0 = 10.866$	$a_0 = 14.1133$ $b_0 = 3.6025$ $c_0 = 8.8080$ $\beta = 100.026^\circ$	<i>a</i>	$a_R = 5.167$	<i>b</i>
Theoretical density, g/cm^3	7.287	7.951	<i>c</i>	2.51	<i>d</i>
Absorber cation density, atoms/cm^3	2.49×10^{22}	2.72×10^{22}	<i>c</i>	2.17×10^{22}	<i>c</i>
Free energy of formation, kcal/mole					
at 25°C	-374	-372	<i>e</i>	-12.55 (527°C)	<i>f</i>
at 727°C	-322.7	-322	<i>e</i>	-8.68 (2227°C)	<i>f</i>
Melting point, $^\circ\text{C}$		~ 2300	<i>g</i>	2350-2500	<i>d</i>
Specific heat, cal mole $^{-1}$ ($^\circ\text{C}$) $^{-1}$					
0 to 800°C		33.3	<i>h</i>	16.6 (260°C)	<i>i</i>
Linear coefficient of thermal expansion, ($^\circ\text{C}$) $^{-1}$					
30 to 840°C		10.5×10^{-6}	<i>j</i>	4.5×10^{-6} ($25-800^\circ\text{C}$)	<i>i</i>
0 to 1000°C		10.35×10^{-6}	<i>k</i>	5.54×10^{-6} ($25-1000^\circ\text{C}$)	<i>d</i>
0 to 1200°C		10.3×10^{-6}	<i>h</i>	6.02×10^{-6} ($25-1500^\circ\text{C}$)	<i>d</i>
Thermal conductivity, W m^{-1} ($^\circ\text{C}$) $^{-1}$					
at 25°C		3.42	<i>l</i>	33.5 (25°C)	<i>m</i>
at 1000°C		2.38	<i>n</i>	12.6 (800°C)	<i>m</i>
Young's modulus, psi at 25°C		4.5×10^6	<i>h</i>	65×10^6	<i>d</i>
Transformation rate, $^\circ$					
at 1100°C	Several days		<i>p</i>		
at 1300°C	Less than 1 hr		<i>p</i>		

^aORNL measurements.^bJ. L. Hoard and R. E. Hughes, *The Chemistry of Boron and Its Compounds*, ed. by E. L. Muetterties, Wiley, London, pp. 25-154, 1967.^cORNL calculation.^dP. T. B. Shaffer, *Materials Index, Vol. 1, Plenum Press Handbooks of High Temperature Materials*, Plenum Press, New York, 1964.^eG. C. Fitzgibbon, E. J. Huber, Jr., and C. E. Holley, Jr., "Enthalpy of Formation of Europium Sesquioxide," *J. Chem. Thermo.* 4, 349-58 (1972).^fJANAF Thermochemical Tables 1960-65, P.B. 168, 370, Dow Chemical Company, New York.^gR. G. Bedford and E. Catalano, "Investigations into the Eu-Eu₂O₃, the Eu-Pt-Eu₂O₃, the Sm-Sm₂O₃, and the Yb-Yb₂O₃ Systems," *J. Solid State Chem.* 3, 112-24 (1971).^hC. E. Curtis and A. G. Tharp, "Ceramic Properties of Europium Oxide," *J. Amer. Ceram. Soc.* 42(3), 151-56 (1959).ⁱJ. C. Hodge, C. Kostenho, and J. I. Lang, *Thermal Properties of Refractory Alloys*, ASD-TDR-63-597 (June 1963).^jG. L. Ploetz, C. W. Krystyniak, and H. E. Dumas, "Sintering Characteristics of Rare Earth Oxides," *J. Amer. Ceram. Soc.* 41(12), 551-54 (1958).^kR. L. Wilfong et al., *Thermal Expansion of the Oxides of Yttrium, Cerium, Samarium, Europium, and Dysprosium*, U.S. Bureau of Mines Report of Investigations 6180.^lKiparisov et al., "Thermal Conductivity of Eu₂O₃," *I.A.N. Neorg. Mater.* 7, 1073 (1971).^mH. W. Deems and C. F. Lucks, *Thermal Conductivity of Boron Carbide from 100°C to 800°C*, BMI-713, Battelle Memorial Institute (December 10, 1951).ⁿGrünling and Schickflus-Borges, *Sintering and Thermal Conductivity of Eu₂O₃*, Siemens AG Bericht Nr. 112/70 (1970).^oCubic $\rightarrow$ monoclinic (time to obtain 100% monoclinic form at given temperature).^pS. Stecura, *Crystallographic Modifications and Phase Transformation Rates of Five Rare Earth Sesquioxides*, U.S. Bureau of Mines Report of Investigations 6616.

Fig. 8. Thermal conductivity of Eu_2O_3 . [Refs: Grünling and Schickfluss-Borges, "Sintering and Thermal Conductivity of Eu_2O_3 ," Siemens AG Bericht Nr. 112/70 (1970); Kiparisov et al., "Thermal Conductivity of Eu_2O_3 ," *I.A.N. Neorg. Mater.* 7, 1073 (1971)]

Fig. 9. Thermal conductivity of Eu_2O_3 relative to several other materials. (Ref: D. L. McElroy and J. P. Moore, "Radial Heat Flow Methods for the Measurement of the Thermal Conductivity of Solids," in *Thermal Conductivity*, Vol. 1, ed. by R. P. Tye, Academic Press, New York, 1969) Europa data from Grünling and Schickfluss-Borges, "Sintering and Thermal Conductivity of Eu_2O_3 ," Siemens AG Bericht Nr. 112/70 (1970); Kiparisov et al., "Thermal Conductivity of Eu_2O_3 ," *I.A.N. Neorg. Mater.* 7, 1073 (1971).

These elements have performed well, as will be discussed later; however, because the LMFBR operates with a fast-neutron spectrum, a higher concentration of europium atoms is required due to the rapid falloff of absorption cross sections with neutron energy. Hence, a solid pellet of Eu_2O_3 is the desirable form. ²¹

Dense pellets have been prepared by several investigators without much difficulty. Researchers at General Electric in 1967 conducted irradiation studies of lanthanide compounds for which they prepared monoclinic Eu_2O_3 pellets of 93 to 96% theoretical density.²² They cold pressed their powder at about

50,000 psi and sintered the resulting pellet at 1500°C for 16 hr in air. Grünling and Schickfluss-Borges²³ describe the fabrication of monoclinic Eu_2O_3 pellets by isostatically pressing and sintering. Using isostatic pressures of 73,500 to 147,000 psi, densities of 96 to 97% of theoretical were obtained on subsequent sintering at 1500°C in an oxidizing atmosphere. Their sintering times ranged from about 3.3 to 11 hr. It was stated by these authors that the fabrication conditions employed were far from optimum, and that higher densities could certainly be obtained by further work.

Pellets of monoclinic Eu_2O_3 of $94 \pm 2\%$ density (using 7.95 g/cm^3 as theoretical density for the B-type phase) were recently produced at ORNL for irradiation test purposes, and one objective of the test was to determine if there would be any behavior difference due to method of fabrication. Hence, both hot pressing and sintering were investigated. Initial cold pressing and sintering experiments yielded dense pellets, but these cracked quite extensively after sintering. The same effect was found in the hot-pressed pellets, which had been cooled by simply shutting off the furnace. The cracking behavior was similar to the type seen in other materials that have poor thermal shock resistance, so slower cooling rates were employed. This eliminated the problem completely.

The starting material was 99.99%-pure Eu_2O_3 powder in the cubic (C-type) form. Rods were isostatically pressed at 40,000 psi and sintered in a vacuum furnace. The heating rate was approximately 15°C/min to 1750°C , at which temperature the furnace was held for 1 hr under a vacuum of 2×10^{-5} torr. A cooling rate of about 3°C/min down to 850°C yielded uncracked rods with densities of 92 to 95% of theoretical. These rods were dark gray to black on removal from the furnace, probably due to a loss of oxygen from the Eu_2O_3 leading to a slightly reduced state. This small loss of oxygen has been documented²⁴ for Eu_2O_3 . To restore the oxygen and clean the surface, the rods were heated to 1000°C in air and held for 1 hr. The resulting pieces were yellowish-tan in color.

Hot pressing as a fabrication method has the advantage of producing a given density at either a lower temperature or a shorter time than the sintering technique. The hot-pressed product can then have a smaller grain size, which is usually desirable. Pellets of 93 to 95% density have been vacuum hot pressed by the author, utilizing cubic Eu_2O_3 as the starting material. The powder was prepressed in a steel die into pellets, which were subsequently loaded into a graphite die. Hot pressing was done at 1500°C under a vacuum of approximately 5×10^{-4} torr. Pressure was applied slowly and reached 5000 psi after about 45 min. Pressing was stopped when proper density was obtained. The furnace was then cooled slowly, keeping the pellets under pressure. The carbon layer adhering to the pellets was burned off at 1000°C in air, leaving a pale-pink pellet.

Both the hot pressed and the sintered pellets were then machined to final size. These are illustrated in Figs. 10 and 11. As expected, the lower temperature used for hot pressing resulted in a finer grained product, but in both samples the grains appear equiaxed. Figures 12 and 13 illustrate the microstructures of the europia pellets.

Further densification experiments have been continuing at ORNL. Both cubic and monoclinic forms have been hot pressed to greater than 90% density.

Researchers at HEDL have produced $90 \pm 2\%$ -dense C-form Eu_2O_3 by hot pressing under argon at 950 to 1000°C .²⁵ This work led the author to attempt densification of the monoclinic form by first pressing at around 1000°C to obtain high-density C form and then heating under pressure to 1300°C to convert to B form. This proved very successful. Preliminary results show that pressing the cubic powder at 1000°C for 1 hr and heating under pressure at 1300°C for 1 hr yields 96%-dense pellets. Initial pressing at 1050°C and then at 1300°C results in 97% density, while 98.8% density was obtained by first pressing at 1100°C . When this experiment was performed at 1125°C , a printout of the ram travel vs time showed that all of the densification was occurring at 1125°C , while no further density was gained at the subsequent 1300°C .

Fig. 10. Eu_2O_3 specimens isostatically pressed at 40,000 psi and sintered at 1750°C and 2×10^{-5} torr.

Fig. 11. Eu_2O_3 specimens vacuum hot pressed at 1500°C and 5×10^{-4} torr.

pressing. The pellets from this experiment yielded immersion densities of 7.89 to 7.95 g/cm^3 . This corresponds to 99 to 100% of a theoretical density of 7.95 g/cm^3 . Thus, 100%-dense monoclinic Eu_2O_3 , as illustrated in Fig. 14, can be prepared by vacuum hot pressing the cubic powder at 1125°C for 1 hr. As a matter of fact, the ram travel data indicate that this may be accomplished in even less time. This hot-pressing development, along with a sintering study, is continuing.

Irradiation Behavior

It is a recognized fact that Eu_2O_3 serves as an excellent control material for thermal reactors. Several reactors have made use of its high cross section and long lifetime, such as the High Flux Isotope Reactor at ORNL, the U.S. Army "SM" and "PM" reactors, and the High Flux Beam Reactor at Brookhaven. In these instances the oxide was incorporated into a metal matrix in the form of a cermet. This was done to protect the oxide from contact with high-temperature water, which severely attacks it²⁶ and which could cause swelling and loss of control-rod integrity. The cermet also exhibits good structural strength and prevents the

Fig. 12. Micrograph of sintered 93%-dense Eu_2O_3 . 100X.

Fig. 13. Micrograph of hot-pressed 93%-dense Eu_2O_3 . 100X.

Fig. 14. Micrograph of fully dense hot pressed Eu_2O_3 . 100X.

possible leaching of radioactive isotopes into the coolant.²⁷ Postirradiation inspection of these control-rod elements has indicated excellent dimensional stability, good retention of reactivity worth, and lack of particle degradation.²⁸⁻³³ Indeed, an Eu_2O_3 -Al dispersion-type control element from the HFIR that had undergone more than 48,000 MWd of irradiation showed no significant loss of nuclear worth.²⁹ This same element exhibited no core-cladding separation, matrix cracking, or chemical reaction between the Eu_2O_3 and the aluminum. Most of the other reports concern dispersion of Eu_2O_3 in stainless steel, and the results are essentially the same.

Irradiation performance data on dense pellets of pure Eu_2O_3 are scarce, as europia has not been used in reactors in this form. However, some U.S. data from researchers at General Electric and some Russian data have been published. The GE report is quite detailed, concerning several lanthanide oxides and borates.²² The Eu_2O_3 was sintered into pellets of 93 to 96% of theoretical density and irradiated in the GETR. The pellets received an integrated thermal neutron flux of from 1.2 to 1.9×10^{21} neutrons/cm² at a maximum operating temperature of 150°C. One pellet exhibited minor radial cracking, whereas the more dense pellet did not. No gross fracturing was observed, and dimensional changes were insignificant. Metallographic examination of pre- and postirradiation samples revealed that no significant changes had occurred during irradiation, yet x-ray diffraction indicated that gross damage had occurred in the crystal structure. The pellets gave no x-ray diffraction peaks, indicating that the monoclinic structure may have become amorphous. Goltsev et al.³⁴ reported identical observations, except that the pellet density had decreased by 1% after receiving an integrated flux of about 1×10^{22} neutrons/cm² at 350 to 600°C.

Materials Compatibility

Another important consideration in determining the suitability of a material for use in a reactor environment is its compatibility with cladding or other structural materials. Of prime importance is the occurrence or lack of occurrence of reactions that could lead to control-rod failure. Failure can be defined in several ways, such as cladding-absorber separation possibly leading to absorber thermal degradation, absorber-induced cladding swelling and resulting hot spots in the reactor, etc. The present fast reactor absorber design involves encapsulation of absorber pellets in type 316 stainless steel pins. This steel's composition is roughly 16 to 18 wt % Cr, 10 to 14 wt % Ni, and 2 to 3 wt % Mo, with 0.1% maximum carbon, 2% maximum manganese, and 1% maximum silicon.³⁵ Leitten³⁶ studied the compatibility of stainless steels with Eu_2O_3 in the temperature range 900 to 1250°C. He found that Eu_2O_3 reacted with the austenitic steel, resulting in swelling and the formation of a compound containing europium and silicon. The degree of reaction increased with time, temperature, and amount of silicon present in the steel. It was determined that Eu_2O_3 and stainless steels made from elemental powders containing less than 58 ppm Si were stable in contact at 1230°C. His tests were of quite short duration, however, from 1.5 to 16 hr.

Compatibility studies of lanthanide oxides with various metal powders were reported by Hoyt et al.²² Their data, given in Table 6, were obtained after 2 hr of heating in vacuum at the given temperatures. It can be seen that Eu_2O_3 reacts with iron (probably), nickel, and type 304 stainless steel at temperatures below 1200°C.

Table 6. Compatibility of
lanthanide oxides and various metals

[Ref: E. W. Hoyt et al., *Rare Earth Oxides and Rare Earth Borates: Corrosion, Compatibility, and Radiation Effects*, GEAP-3909 (April 17, 1962)]

Matrix	Oxide	Temp. (°C)	Reaction
Fe	Dy_2O_3	1150	No
Fe	Sm_2O_3	1150	No
Fe	Eu_2O_3	1150	Uncertain
Ni	Dy_2O_3	1150	Yes
Ni	Sm_2O_3	1150	Yes
Ni	Eu_2O_3	1150	Yes
SS-304	Dy_2O_3	1200	No
SS-304	Sm_2O_3	1200	No
SS-304	Eu_2O_3	1200	Yes
Hastelloy-B	Dy_2O_3	1120	No
Hastelloy-B	Sm_2O_3	1120	No
Hastelloy-B	Eu_2O_3	1120	Yes
Inconel-X	Dy_2O_3	1120	No
Inconel-X	Sm_2O_3	1120	No
Inconel-X	Eu_2O_3	1120	Yes
Mo	Dy_2O_3	1900	No
Mo	Sm_2O_3	1900	No
Mo	Eu_2O_3	1900	No
Nb	Dy_2O_3	1800	No
Nb	Sm_2O_3	1800	No
Nb	Eu_2O_3	1800	No
W	Dy_2O_3	2000	No
W	Sm_2O_3	2000	No
W	Eu_2O_3	2000	No

Longer-term compatibility tests of Eu_2O_3 have been conducted at ORNL by M. M. Martin. In these tests, pellets of 93%-dense monoclinic Eu_2O_3 were placed inside cylinders of various metals. The test conditions are as follows:

Couples

Eu_2O_3 - 316 stainless steel (annealed)

Eu_2O_3 - TZM (annealed)

Eu_2O_3 - W (annealed)

Types of Eu_2O_3

Hot-pressed: 1500°C - 4,000 psi - 45 min
Monoclinic - 93% dense

Isostatically pressed: R.T. - 40,000 psi, then sintered: 1750°C - 60 min
Monoclinic - 93% dense

Conditions

117 hr at 870°C - He bonded

118 hr at 980°C - He bonded

The results are listed below:

TZM and W couples:

No detected attack

316 stainless steel couple - 980°C:

Intergranular penetration of Eu_2O_3 into stainless steel (15 μ max)

Calculated penetration ($d \propto t^{1/2}$)	}	5.2 mils in 1 yr
		7.3 mils in 2 yr
		12.7 mils in 6 yr

Chromium deposit on surface of Eu_2O_3 - suspect formation of EuCrO_3

316 stainless steel couple - 870°C:

Surface roughing - minor subsurface crystal formation

After 118 hr at 980°C, both TZM (Mo-0.5 wt % Ti-0.1 wt % Zr) and tungsten in contact with Eu_2O_3 showed no interaction. This is in line with the data of Hoyt et al. (Table 6). The stainless steel- Eu_2O_3 couple, however, showed significant interaction. The Eu_2O_3 appears to have penetrated into the steel surface to a depth of about 15 μm . Further, a chromium-rich deposit is observed on the surface of the Eu_2O_3 . These interactions can best be shown by x-ray scans of the interface of a hot-pressed Eu_2O_3 -type 316 stainless steel couple that ran 118 hr at 980°C (Fig. 15). The europium can be plainly seen to have penetrated into the steel surface in the photograph on the left middle. The chromium deposit on the

Y-116256

Fig. 15. Electron beam scanning images of type 316 stainless steel-europium oxide interface after 118-hr exposure at 980°C, showing intergranular penetration of europium into the stainless steel and chromium deposition on the europium oxide surface.

europium surface is visible in the lower right photograph. Although the true significance of these tests in regard to the actual operating conditions of a sodium-cooled type 316 stainless-steel-clad europium absorber pin is not known, the presence of such reactions might suggest that perhaps the oxide pellets should be encapsulated with a layer of a nonreactive metal, such as tungsten or molybdenum. Further out-of-reactor compatibility tests, including Na—Eu₂O₃—type 316 stainless steel, are in process.

OTHER EUROPIUM OXIDES

Europium's ground-state electronic structure can be represented as (Xe)4f⁷6s², where (Xe) represents the core electrons of the europium atom, which take the xenon atom configuration. Loss of two outer-shell electrons leads to Eu²⁺ with the electronic configuration (Xe)4f⁷6s⁰. The half-filled *f* shell (4f⁷) is a highly stable state for the lanthanide compounds, and hence one might expect to be able to form Eu²⁺ ions readily. However, in combination with oxidizing substances such as oxygen, Eu²⁺ loses another electron and takes up the (Xe)4f⁶6s⁰ electronic configuration. This is the stable state found in Eu₂O₃. The 2+ state will form EuO under proper reducing conditions. The presence of both a 2+ and 3+ oxidation state allows the formation of yet another oxide, Eu₃O₄, or better Eu^{II}Eu^{III}₂O₄, in analogy to iron and manganese oxides. Under atmospheric pressure the most stable of these oxides with increasing temperatures is Eu₂O₃, as illustrated by their vaporization behavior. The reactions followed on heating have been given by Hashke and Eick^{37,38} as

These relationships and other thermodynamic considerations have led to the Eu-O phase diagram given by McCarthy and White³⁹ and reproduced here in Fig. 16. It will be noticed from this figure that Eu₂O₃ has the ability to lose small amounts of oxygen at elevated temperatures to form Eu₂O_{3-x}. This loss of oxygen was reported by Barrett and Barry²⁴ in 1965. Their experiments showed that Eu₂O₃ can readily be partially reduced by hydrogen gas at temperatures as low as 650°C to form oxygen-deficient compounds such as Eu₂O_{2.9856}. Fabrication experiments at ORNL have shown a change of color in Eu₂O₃ specimens on firing to temperatures around 1500°C in vacuum. This can be reversed by refiring in air at 1000°C, which leads to the possible explanation that the Eu₂O₃ is becoming oxygen deficient on firing in vacuum. The refired specimens lose their gray to black discoloration and gain a small amount of weight. Barrett and Barry further state that Eu₂O₃ cannot be induced to take up excess oxygen. One might expect this to be so, since it would require oxidation of some Eu³⁺ to Eu⁴⁺, a highly unlikely process in view of the high stability of the Eu³⁺ state.

The phase relations and preparation of compounds in the system Eu-Eu₂O₃ have recently been discussed in a paper by Bedford and Catalano.⁴⁰ They indicate that the monoclinic sesquioxide is stable over the composition range Eu₂O_{2.90} to Eu₂O_{3.00} at 1500°C. On the other hand, EuO exhibits a very narrow composition range. This compound was initially of some interest as a possible absorber material, since it is cubic (fcc) and possesses a higher density of europium atoms per unit volume than for the sesquioxide (2.94 × 10²² atoms/cm³ for EuO, 2.72 × 10²² atoms/cm³ for Eu₂O₃). This fact would give EuO a higher macroscopic neutron absorption cross section than that of Eu₂O₃. The reported melting point for EuO is high, in the neighborhood of 1900 to 2015°C.^{39,40} However, at approximately 1520°C, Reed⁴¹ has calculated that the pressure of Eu(g) over EuO will reach 1 atm and that EuO will dissociate into Eu₃O₄(s) + Eu(g). The presence of gaseous europium could have an adverse effect on absorber element performance if the element reached such operating temperatures. But this problem could probably be

Fig. 16. Portion of a possible Eu-O phase diagram at 1 atm pressure. [Ref: G. J. McCarthy and W. B. White, "On the Stabilities of the Lower Oxides of the Rare Earths," *J. Less-Common Metals* 22, 409-17 (1970); assembled from the literature and best estimates of what the diagram should look like. Used with permission of authors.]

controlled by suppressing the dissociation reaction. A more formidable obstacle to the utilization of EuO would be the fabrication of dense shapes of the oxide. Attempts to sinter EuO in vacuum would likely lead to dissociation into Eu_3O_4 or Eu_2O_3 ; sintering in oxidizing atmospheres would certainly lead to production of Eu_2O_3 . Perhaps it could be sintered under an atmosphere of controlled oxygen partial pressure. Hot pressing in graphite would yield carbon contamination, which could not be oxidized off without forming Eu_2O_3 . It might, however, be possible to line the die with a refractory metal such as tungsten to prevent carbon contamination.

The oxide Eu_3O_4 has not been seriously considered due to difficulty in preparation of the pure compound.⁴⁰ Furthermore, the material is nonisotropic, possessing an orthorhombic structure.⁴² The theoretical density calculated from Rau's lattice parameter is 8.11 g/cm^3 , which corresponds to a europium atom density of $2.818 \times 10^{22} \text{ Eu atoms/cm}^3$. This value is just slightly more than the 2.72×10^{22}

atoms/cm³ calculated for monoclinic Eu₂O₃ but less than the 2.94×10^{22} atoms/cm³ calculated for EuO.

Thus it appears at this time that Eu₂O₃ is the prime candidate of the europium oxides for use as a fast-reactor control material, particularly because of its stability under usual reactor operating conditions. A possible alternate is EuO, but much more research is required to determine its stability. That is, one must determine if it can be reproducibly formed, fabricated, and handled, and then determine its behavior in the reactor environment.

EVALUATION OF LITERATURE DATA ON PROPERTIES OF Eu₂O₃ PERTINENT TO PERFORMANCE IN-REACTOR

For Eu₂O₃ to be utilized as an absorber material in a fast breeder reactor, several critical properties must be well known. These include:

1. reactivity worth,
2. heating rate,
3. compatibility with cladding,
4. stability in a fast neutron flux.

Reactivity Worth

The available literature on nuclear cross sections for the isotopes involved is neither consistent nor complete. For example, the cross section for the ¹⁵¹Eu(*n*, γ) reaction at 10 keV is given as 8.5 b by Barr and Devaney,¹⁰ about 8 b by Liu,⁴³ and 4.65 b by Benzi et al.⁴⁴ For ¹⁵³Eu, the same authors give 6.5, 5, and 4.68 b. Another very important cross section involved in the Eu absorption chain is that of ¹⁵²Eu. Barr and Devaney¹⁰ indicate that this number may be between 9 and 20 b at 10 keV. Also, Barr and Devaney¹⁰ indicate that for the ¹⁵⁴Eu(*n*, γ) reaction, the cross section is near 6 b at 10 keV, while Liu⁴³ indicates this number to be near 18 b. Thus it becomes apparent that further cross-section determinations are required if the worth of Eu₂O₃ is to be accurately calculated. Perhaps a better way of obtaining the worth would be an actual reactivity worth measurement in a reactor mockup facility. However, this would only determine europa's initial worth and would tell little about its long-term life, since we could not determine the effect of ¹⁵²Eu, ¹⁵⁴Eu, and the other isotopes of Eu, Gd, and Sm which are built in during irradiation. The effect of these isotopes can be determined only by individual cross-section measurements or long-term reactivity worth measurements on irradiated Eu₂O₃. Also, Perry notes that the partial cross section of ¹⁵¹Eu for formation of the 9.3-hr isomer of ¹⁵²Eu is not well known for fast neutron spectra.

The fraction of ¹⁵¹Eu atoms forming this isomer decay to Gd and Sm isotopes which are thought to have low cross sections, whereas the long-lived isotope of ¹⁵²Eu has a substantial cross section and contributes significantly to long-term worth. For thermal neutrons the fraction of ^{152m}Eu from ¹⁵¹Eu is about 0.35. For 25-keV neutrons it appears that the fraction is closer to 0.7. Averaged over the EBR-II spectra, Perry guesses that the fraction might be in the range of 0.5 to 0.7, or even higher. In order to better estimate the long-term worth of Eu₂O₃, this partial cross section needs to be determined for fast neutrons.

Heating Rate

Another parameter which is important in the design of control rods is the core γ contribution to the heating rate in the assembly. In Eu₂O₃ the sum of the (*n*, γ) and decay γ heating is not the major contributor to total heating rate. A. M. Perry of ORNL [in a preliminary analysis (Supplement I)] calculates that the decay γ heating rate may be between 0.18 to 0.36 W/g in EBR-II, while HEDL⁴⁵ has calculated the (*n*, γ) heating rate in EBR-II to be about 1.2 W/g. This gives a total of about 1.4 to 1.6 W/g for decay γ and (*n*, γ) heating, while Perry indicates that the core- γ contribution may be between 2 and 6

W/g, most likely 2 to 2.5 W/g. Of course, a similar situation would prevail in the FFTF and the demonstration LMFBR. It is then apparent that this core γ heating rate should also be measured in order to properly design an absorber rod configuration.

Compatibility

The literature data^{36,22} concerning compatibility of Eu_2O_3 with stainless steel indicate that an interaction occurs at temperatures above 800°C . The extent and consequences of such an interaction in a control-rod configuration operating with a temperature gradient between the Eu_2O_3 and stainless steel cladding are not known and should be determined. However, if such interaction does prove to be a problem, the europia could be sheathed in tungsten or molybdenum, since no reaction is observed with these metals. The consequences of accidental sodium intrusion or the feasibility of utilizing sodium bonding in an Eu_2O_3 control-rod element is also unknown.

Irradiation Stability

Stability in the reactor environment includes possible polymorphic transformations, swelling, cracking, and the resultant effect on thermal conductivity.

The literature concerning phase stability has been considered in some detail by V. L. Burdick. Sections of his report are included here as Supplement II. His conclusion is that, in a fast neutron flux, the monoclinic modification would be more stable than the cubic form, but that this cannot be considered settled until actual reactor irradiation experiments are completed.

Swelling and cracking behavior cannot be predicted except in a qualitative manner. It may be expected that the europia lattice will swell as a result of defect formation arising from fast-neutron displacement effects, but this swelling may be at least partially offset by the conversion of europium atoms to gadolinium atoms, which have a smaller ionic radius. Thermal reactor irradiations described previously^{22,34} have indicated no more than a 1% density decrease ($\approx 1\%$ volume swelling) in europia pellets after receiving an integrated flux of about 1×10^{22} neutrons/cm² at 350 to 600°C .

Cracking is likewise unpredictable, but some radial and circumferential cracking is likely to be observed in at least some fraction of the pellets. This general conclusion is drawn from a radiation damage study involving ceramics such as MgO , Al_2O_3 , and Y_2O_3 .⁴⁶ Irradiation tests with Eu_2O_3 can be expected to provide data on this effect.

The literature data concerning the thermal conductivity of Eu_2O_3 have been examined by J. P. Moore of ORNL, and his observations are included in Supplement III of this report. He concludes that a good estimate of the (unirradiated) thermal conductivity for monoclinic Eu_2O_3 would be about $0.04 \text{ W cm}^{-1} (^\circ\text{C})^{-1}$ at room temperature, decreasing to about $0.028 \text{ W cm}^{-1} (^\circ\text{C})^{-1}$ at 900°C . These numbers can be expected to decrease by factors ranging from $1/2$ to $1/100$ after fast neutron irradiation, depending on the type of damage incurred. The worst possible case would be complete separation of the grains of Eu_2O_3 at the grain boundaries as observed in BeO .⁴⁷ Again, only a comprehensive irradiation test program will provide such data.

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SUPPLEMENT I

A PRELIMINARY ASSESSMENT OF Eu_2O_3 DECAY HEAT
AND BURNUP IN EBR-II

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A PRELIMINARY ASSESSMENT OF Eu_2O_3 DECAY HEAT*
AND BURNUP IN EBR-II

A. M. Perry

ABSTRACT

The amount of afterheat to be expected in Eu_2O_3 pins irradiated for one year in Row 7 of EBR-II is estimated to be in the neighborhood of 1.5 to 2 w/cm³ immediately after shutdown, decaying with a 9.3-hr half life to a much lower, long-lived afterheat level of about 0.1 w/cm³. In addition, gamma heating during operation from gamma rays originating outside the samples is estimated to be about 2 to 2.5 w/g. Loss of reactivity worth due to burnup of the europium is estimated to be roughly 3% per full-power year under conditions similar to those in EBR-II (Row 7); this result may be scaled for different flux levels in other reactors.

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INTRODUCTION

We have taken a first look at certain aspects of the testing of Eu_2O_3 in EBR-II (Row 7) as a possible control material for fast reactors. These aspects include:

1. Afterheat of Eu_2O_3 test specimens (as compared, for example, with Ta).
2. Probable gamma-heating rates in the specimens during operation.
3. Probable change in reactivity worth of irradiated Eu_2O_3 rods as a result of composition changes.

These aspects are discussed in the following sections.

1. AFTERHEAT IN Eu_2O_3 SPECIMENS IN EBR-II (ROW 7)

1.1 Calculation of Neutron Absorption Rate in Eu_2O_3 in Row 7 of EBR-II

George Ragan has calculated the rate of neutron absorptions in Ta rods at midplane in Row 7 of EBR-II¹ ($R = 30.9$ cm, $Z = -1.2$ cm) using fluxes recently obtained from Argonne National Laboratory² and using Ta cross sections, both shielded and unshielded ("infinitely dilute") as recently published by Tuttle and Springer.³ The result of this calculation was a neutron absorption rate, at full power, of 3.3×10^{13} neutrons/cm³sec with dilute (small-sample) cross sections (i.e., unshielded) or 2.5×10^{13} neutrons/cm³sec with shielded cross sections (for rods of about 0.67 in. diam).

About four years ago, Jerry Delene estimated that Eu_2O_3 should be worth about 1.6 times as much as Ta, on an equal volume basis, in either a "soft-spectrum" or a "hard-spectrum" LMFBR.⁴ Also, on the basis of the average cross-section ratio, $\bar{\sigma}(\text{Eu})/\bar{\sigma}(\text{Ta}) \sim 3.8$, and the atom-density ratio, $N(\text{Eu})/N(\text{Ta}) \sim 0.42$, we estimate a macroscopic cross-

section ratio $\Sigma(\text{Eu})/\Sigma(\text{Ta}) \sim 1.6$. We therefore assume, tentatively, that the neutron capture rate per unit volume in Eu_2O_3 in EBR-II would be 1.5 to 2 times as high as in Ta.* For purposes of the present calculations, we use the factor 2, and proceed on the assumption of 5×10^{13} neutrons/cm³sec absorbed in EBR-II, Row 7. The effect of changing this assumption is easily estimated, since the heating rates calculated below are directly proportional to this absorption rate.

Self-shielding in the Eu_2O_3 samples is neglected, and this neglect would appear to be justified, at least for the smaller EBR-II samples, by the results given in Ref. 3. (See Appendix A of this memorandum.)

As for the distribution of these captures between ^{151}Eu and ^{152}Eu , we note that the cross-section ratio (between ^{151}Eu and ^{153}Eu) is about 1.4-1.5 over the important neutron-energy range, 1-100 keV, and — pending more detailed calculation of average cross sections — we assume that the specific capture rate in ^{151}Eu is 1.5 times as great as in ^{153}Eu (the two species are about equally abundant in natural europium). Thus, 60% of the captures initially are in ^{151}Eu , and 40% in ^{153}Eu , i.e., 3×10^{13} and 2×10^{13} neutrons/cm³sec respectively.

Finally, we must assume something about the fraction of captures in ^{151}Eu that lead to the 9.3 hr isomer of ^{152}Eu , rather than to the 12 yr ground state. This isomer does not decay to the ground state of ^{152}Eu , but instead decays directly by electron capture to stable ^{152}Sm (23%) or by beta emission to 10¹⁴-year ^{152}Gd (77%). In a thermal-neutron spectrum, 35% of the ^{151}Eu captures produce the isomer. While we do not yet know what this percentage should be in a fast-neutron spectrum, we assume tentatively that it will lie in the range of 20 to 50%, and will subsequently test the sensitivity of our afterheat estimates to assumed variations in this percentage.

* This range is consistent with Ref. 3 (see Appendix A).

1.2 Decay Energetics

The principal radioactive processes relevant to a discussion of afterheat in irradiated Eu_2O_3 are shown below.

Note that the 9.3-hr isomer of ^{152}Eu does not decay to the ground state of ^{152}Eu . Also, we neglect the 96-min isomer of ^{152}Eu which is produced in very minor amounts (roughly 1% of the production rate of the 9.3-hr isomer⁵) and which decays entirely to the 9.3-hr state (not to the ground state); thus, production of the 96-min isomer is effectively equivalent to production of the 9.3h isomer. (If the production rate were much larger, and if the half-lives of the two isomers differed by a much larger factor, this neglect might not be acceptable for short cooling times; however, under the circumstances that actually prevail, the neglect is justified.)

These are the processes considered in the present analysis. Other activities that should be considered in a more detailed calculation, especially for long irradiations, include:

The gadolinium isotopes from 154 through 158 are stable.

The energy available for absorption from the decay of each species of nucleus is the average kinetic energy of all the beta particles emitted plus the energy of the ensuing gamma rays emitted as the product nucleus decays to its ground state. The ratio of the average beta energy to the maximum (end-point) energy, for each group of betas, depends both on the maximum energy of the betas, on the Z of the (product) nucleus, and on the spin and parity changes in the transition. For the $\text{Eu} \xrightarrow{\beta^-} \text{Gd}$ transitions ($Z = 64$), the ratio ranges (for allowed transitions) from 0.27 for 0.2 MeV end-point to 0.38 for 2 MeV end-point. (A plot of this ratio may be found, for example, in Ref. 6, and is reproduced here as Fig. 1.)

Decay schemes for the europium isotopes were taken from Ref. 7. The beta and gamma energy emitted (but not necessarily absorbed) per disintegration is shown in Table 1.

Table 1. Beta and gamma decay energy per disintegration in europium isotopes
(All energies in MeV)

Isotope	Half life	Decay ^a mode	Fraction of decays (%)	Q^b	E_β^c	E_γ^d	E_{total}^e	$\bar{E}_\gamma^f$
^{152m}Eu	9.3h	EC	23	1.907	0	1.907	1.907	~0.9
^{152m}Eu	9.3h	β^-	77	1.87	0.690	0.036	0.726	~0.3
^{152g}Eu	12y	EC	72	1.857	0	1.857	1.857	~1.3
^{152g}Eu	12y	β^-	28	1.82	0.324	0.876	1.200	~0.5
^{154}Eu	16y	β^-	100	1.978	0.208	1.341	1.549	~1.0
^{155}Eu	1.8y	β^-	100	0.248	0.047	0.076	0.123	~0.08

^aEC = orbital electron capture.

^b Q = total transition energy = mass difference between initial and final systems.

^c E_β = total kinetic energy of all beta particles emitted, on the average, in the decay of this nuclide, taking into account the abundance of the beta groups and the factors $\bar{E}/E_{\text{max}}$ from Fig. 1.

^d E_γ = total gamma energy per decay.

^e $E_{\text{total}} = E_\beta + E_\gamma$ = absorbable energy released per disintegration (but not necessarily absorbed in emitting body). ($Q - E_{\text{total}}$ = energy carried off by antineutrinos.)

^f $\bar{E}_\gamma$ = average gamma energy, MeV/photon. (Very approximate.)

1.3 Self-Absorption Factors for Gamma Rays

While the beta particles are absorbed essentially at their point of origin, the gamma rays are more penetrating, and may escape from the body in which they are produced. We have estimated the absorption probabilities for europium decay gammas for uniform cylindrical rods of europium oxide of varying size and density, representing either single pins or — in an approximate way — clusters of pins. Gamma-ray absorption coefficients are given in many places; we used the graphs in Ref. 8. Escape probabilities are given in Ref. 9, as a function of μr , the dimensionless product of the gamma-ray absorption coefficient times the radius of the cylinder; the complement of this function is reproduced here as Fig. 2, and strictly speaking applies only to a uniformly distributed source. However, in the present case the source is not expected to be far from uniform, and we believe that the curve of Fig. 2 is a reasonable approximation to use here.

Perhaps a more serious question, in using Fig. 2, is whether the total gamma cross section (including scattering) or only the energy-absorption cross section should be used in calculating the parameter μr . Depending on the material and on the gamma-ray energy, these may differ by a factor of 2 or more. Use of the total cross section presumably leads to an underestimate of the escape fraction (an overestimate of the absorption fraction) since Compton-scattered gammas can subsequently escape, having left only part of their energy in the body. On the other hand, use of the energy-absorption cross section (which includes the photo-electric and pair-production cross sections and part of the scattering cross section) undoubtedly underestimates the absorption fraction because the scattered gammas (especially in high- Z materials) have a greatly increased probability of absorption, relative to the uncollided gammas. (This statement may not be true for gammas with energies appreciably above the pair-production threshold, ~ 1 MeV, but pair production is not a significant process for most of the decay gammas with which we are concerned here.)

The absorption fractions calculated here are based on the total cross section, but we also indicate the sensitivity of results to this

choice for the important cases (compare, for example, Figs.4 and 5, pages 17 and 18).

Gamma-ray absorption fractions are shown in Table 2, for clusters of Eu_2O_3 pins, simulated by single cylindrical rods as described in Table 3.

Table 2. Gamma-ray absorption factors for simulated Eu_2O_3 clusters^a

ϵ_γ (MeV) σ (cm ² /g)		$\rho = 6.85 \text{ g/cm}^3$			$\rho = 3.43 \text{ g/cm}^3$		
		30 cm ²	40 cm ²	50 cm ²	60 cm ²	80 cm ²	100 cm ²
0.1	μ_r	>21.2	>24.4	>27.3	>15.0	>17.3	>19.3
>1	FA	~1.0	~1.0	~1.0	~1.0	~1.0	~1.0
0.5	μ_r	3.2	3.7	4.1	2.3	2.60	2.90
0.15	FA	~0.9	~0.9	~0.9	~0.8	~0.8	~0.8
0.9	μ_r	1.63	1.71	1.91	1.05	1.21	1.35
0.07	FA	0.72	0.73	0.76	0.61	0.64	0.67
1.0	μ_r	1.27	1.46	1.64	0.90	1.04	1.16
0.06	FA	0.65	0.69	0.72	0.56	0.60	0.63
1.3	μ_r	1.06	1.22	1.37	0.75	0.87	0.97
0.05	FA	0.61	0.64	0.67	0.51	0.55	0.58
1.0	μ_r	0.64	0.73	0.82	0.45	0.52	0.58
0.03 ^b	FA	0.47	0.50	0.54	0.38	0.41	0.44

ϵ_γ (MeV) σ (cm ² /g)		$\rho = 6.85 \text{ g/cm}^3$			$\rho = 1.5 \text{ g/cm}^3$		
		0.755 cm ²	2.26 cm ²	5.28 cm ²	3.5 cm ²	10 cm ²	24 cm ²
0.5	μ_r	0.50	0.87	1.33	0.23	0.41	0.62
0.15	FA	0.40	0.55	0.67	0.23	0.35	0.46
1.0	μ_r	0.20	0.35	0.53	0.09	0.16	0.25
0.06	FA	0.21	0.32	0.42	0.10	0.17	0.25
1.0	μ_r	0.10	0.17	0.27	0.05	0.08	0.13
0.03 ^b	FA	0.11	0.18	0.27	0.06	0.09	0.14

^aSee Table 3 for details of geometrical representation.

^bEnergy-absorption cross section; all others are total cross sections.

Table 3. Simulated Eu_2O_3 pin clusters and equivalent uniform circular rods

Pins simulated		Equivalent uniform cylindrical rod				
Number	Diameter ^a (in.)	Density ^b (g/cm ³)	Rod diameter		Area (cm ²)	ρr (g/cm ²)
			(in.)	(cm)		
61	0.31	6.85	2.43	6.18	30.0	21.2
61	0.36	6.85	2.81	7.136	40.0	24.4
61	0.40 ₂	6.85	3.14	7.98	50.0	27.3
61	0.31 ₂	3.43	3.44	8.74	60.0	15.0
61	0.36	<u>3.43</u>	3.97	10.09	80.0	<u>17.3^c</u>
61	0.40 ₂	<u>3.43</u>	4.44	11.29	100.0	<u>19.3</u>
1	0.386	<u>6.85</u>	0.386	0.980	<u>0.755</u>	<u>3.36^c</u>
3	0.386	<u>6.85</u>	0.669	1.697	2.26	<u>5.81</u>
7	0.386	6.85	1.021	2.593	5.28	8.89
1	0.386	<u>1.50</u>	0.825	2.094	3.45	1.57
3	0.386	<u>1.50</u>	1.430	3.627	10.32	<u>2.72^c</u>
7	0.386	<u>1.50</u>	2.182	5.54	24.1	<u>4.16^c</u>

^aDiameter of oxide pellet.

^b Eu_2O_3 (BCC) density = $7.28 \times 0.94 = 6.85 \text{ g/cm}^3$. Volume fraction of Eu_2O_3 in clusters of pins is assumed to be ~ 0.5 in large FTR C.R. assemblies, ~ 0.2 in small experimental EBR-II assemblies.

^cWe consider these cases to be the most reasonable simulations of the actual cases they are intended to represent.

1.4 Saturation Factors, Duty Factors

For an irradiation period that is not long compared to the half-life of the induced radioactive species, the disintegration rate is less than the production rate by the saturation factor

$$S \equiv (1 - e^{-\lambda t}) ,$$

where λ is the decay constant.

The following table lists saturation factors for the three principal Eu activities considered here.

Table 4. Saturation factors for irradiated europium

Irradiation period (years)	^{152m}Eu	^{152g}Eu	^{154}Eu
1	1.0	0.0561	0.0424
2	1.0	0.109	0.083
3	1.0	0.159	0.122
4	1.0	0.206	0.159

For the results that follow, we have used the saturation factors for a one-year irradiation period. We calculate the disintegration rate for each active species as the product of this saturation factor, the production rate discussed in Section 1.1, and a reactor duty factor appropriate to each nuclide. For the 9.3-hr ^{152m}Eu isomer, we use a duty factor of 1.0; for 12-yr ^{152g}Eu and 16-yr ^{154}Eu we use a duty factor of 0.7.

This procedure does not take into account any reduction in the activity of ^{152g}Eu or ^{154}Eu owing to neutron capture by these nuclides (which would lead in the first case to stable ^{153}Eu , and in the second to 1.8-yr ^{155}Eu , whose decay energy is much less than that of ^{154}Eu). While we have also neglected the contribution of such active products as ^{153}Sm , ^{153}Gd , and ^{155}Eu , we would not expect these entirely to compensate for the above reduction because their decay energy is much lower than that of ^{152}Eu and ^{154}Eu , as shown in Table 5.

Thus, the decay heat that we calculate is somewhat high. However, the burnup lifetime of all these nuclides is long compared to the irradiation period (see Section 3), so the error caused by this approximation cannot be more than a few percent.

Table 5. Decay energy of some rare-earth isotopes

Isotope	Half-life	Transition energy (MeV)
^{152m}Eu	9.3 hr	$Q_{\beta^-} = 1.87, Q_{\text{EC}} = 1.907$
^{152g}Eu	12 yr	$Q_{\beta^-} = 1.82, Q_{\text{EC}} = 1.857$
^{152}Sm	Stable	
^{152}Gd	Stable	
^{153}Sm	47 hr	$Q_{\beta^-} = 0.80$
^{153}Gd	242 d	$Q_{\text{EC}} = 0.24$
^{154}Eu	16 yr	$Q_{\beta^-} = 1.978$
^{155}Eu	1.81 yr	$Q_{\beta^-} = 0.248$

1.5 Results of Afterheat Calculations

Results of the afterheat calculations, carried out as described in the preceding sections, are shown in Figs. 3 through 8. Cases A, B, C, and D (Figs. 3 through 6 respectively) are intended to represent various clusters of Eu_2O_3 pins, as follows:

- A: single 0.386 in. diam pin, density = 6.85 g/cm^3 ;
- B: three such pins, smeared density = 1.5 g/cm^3 ;
- C: seven such pins, smeared density = 1.5 g/cm^3 ;
- D: 61-0.36 in. diam pins, smeared density = 3.43 g/cm^3 .

(See Tables 2 and 3 for additional data.)

The independent variables for the straight-line graphs of Figs. 3 through 7 are the ratio $r \equiv \bar{\sigma}(^{151}\text{Eu})/\bar{\sigma}(^{153}\text{Eu})$ and the fraction $f_{11} = \bar{\sigma}(^{151}\text{Eu} \rightarrow ^{152g}\text{Eu})/\bar{\sigma}(^{151}\text{Eu})$, i.e., the fraction of neutron captures in ^{151}Eu that produces the 9.3 hr isomer. On the basis of data from various sources (see Appendix B), we believe that probable values of these variables in the EBR-II neutron spectrum (Row 7) are:

$$r \sim 1.5 ,$$

$$f_{11} \approx 0.5 .$$

More work is needed to determine these cross-section ratios more closely.

Figures 3 through 6 show the decay heat (in w/cm^3) due to the 9.3 hr ^{152m}Eu , that due to the long-lived isotopes ^{152g}Eu and ^{154}Eu together, and the totals. The decay heat due to ^{152m}Eu dominates for short cooling times; it is quite sensitive (i.e., directly proportional) to the poorly known ratio f_{11} , but of course dies away with the 9.3 hr half-life. The remaining contribution from ^{152g}Eu and ^{154}Eu is essentially constant for reasonable cooling times (half-lives 12, 16 years); it is much less sensitive to f_{11} and is quite insensitive to the ratio r , since the decay energies ^{152g}Eu and for ^{154}Eu are not very different.

Figure 7 merely repeats some of the graphs of Figs 4 through 6 for different values of the gamma-ray absorption fraction, and for the most probable value of r , $r = 1.5$. (Note that in each of these figures, the combined contribution of ^{152g}Eu and ^{154}Eu is multiplied by 10 for ease of reading on the same scale as the dominant contribution from ^{152m}Eu .)

In Fig. 8, the energy absorbed is shown for each nuclide, per disintegration of that nuclide, as a function of the gamma-ray absorption fraction. Thus, the effect of varying assumptions concerning both production rates and the gamma absorption fraction can readily be deduced.

2. GAMMA HEATING DURING OPERATION

Estimates of the gamma-heating to be expected in Eu_2O_3 pins irradiated in EBR-II, during reactor operation, were obtained by adjusting data for iron and uranium, as given in the EBR-II Experimenters Guide¹⁰, to account for the difference in gamma-ray cross sections between these materials and europium.

2.1 Energy-Absorption Cross Sections

Gamma-ray energy-absorption coefficients, from Ref. 8, are shown in Table 6 as a function of photon energy. Also shown are ratios of these coefficients, useful in making the needed adjustments. (The coefficients for Eu were estimated by interpolation of a cross-plot of $\log \mu$ vs Z for each photon energy.)

Table 6. Energy-absorption coefficients
($\mu - \text{cm}^2/\text{g}$)

		$E_\gamma - \text{MeV}$						
		0.3	0.5	0.6	0.7	0.8	0.9	1.0
1.	Fe (Z=26)	0.037	0.029	0.028	0.027	0.027	0.026	0.026
2.	U (92)	0.46	0.16	0.115	0.090	0.074	0.063	0.056
	U/Fe	12	5.5	4.1	3.3	2.7	2.4	2.2
3.	Ta (73)	0.26	0.091	0.067	0.054	0.046	0.041	0.036
	Ta/Fe	7.0	3.1	2.4	2.0	1.7	1.6	1.4
4.	Ag (47)	0.088	0.040	0.039	0.030	0.028	0.027	0.026
	Ag/Fe	2.4	1.4	1.4	1.1	1.0	1.0	1.0
5.	Al (13)	0.029	0.029	0.029	0.029	0.028	0.028	0.027
	Al/Fe	0.8	1.0	1.0	1.1	1.0	1.1	1.0
6.	Eu ^a (63)	0.185	0.067	0.052	0.043	0.037	0.034	0.030
	Eu/Fe	5.0	2.3	1.9	1.6	1.4	1.3	1.2
	Eu/Ta	0.71	0.74	0.78	0.80	0.80	0.83	0.83

^aEstimated by interpolation between curves for Sn (Z=50) and Ta (Z=73).

2.2 Gamma Heating

From Ref. 10, Table C-V, we obtain data for gamma-heating rates in uranium and iron, reproduced in part in the following table:

Distance, reactor centerline to S/A centerline (cm)	Grid Position	Gamma-heating rate (w/g)		
		U	Fe	U/Fe
30.62	7N4	11.9	3.9	3.05
31.18	7N3,5	10.8	3.7	2.92
32.81	7N2,6	9.2	3.4	2.71
35.36	7N1(T)	5.8	2.0	2.90
32.81	7N6(T)	5.2	1.6	3.25
35.84	8N4,5	7.4	1.7	4.35
36.80	8N3,6	7.1	1.5	4.7
38.64	8N2,7	6.1	1.3	4.7
41.25	8N1	5.6	1.1	5.1

Presumably the reason that the ratio of heating in uranium to that in iron increases with increasing distance away from the core centerline is that the gamma spectrum gets softer, due to scattering, at greater distances from the source. We note that the ratio in Row 7 is about 3, and from Table 6 we may infer an "effective" gamma energy of about 0.7-0.8 MeV. For this same energy range (again from Table 6), the ratio of heating (per gram) in Eu to that in Fe would be about 1.5. Thus, if the heating rate in Fe is about 3.5-4 w/g, we might expect that in Eu to be 5-6 w/g. If the low figure for position 7N6(t) is used, i.e., 1.6 w/g for Fe, we might expect about 2.5 w/g for Eu. The latter figure would be more consistent with the figure of 2.772 w/g (at the reactor midplane) that Dale Dyslin gives for Ta in capsule 027.¹¹ Using the ratio 0.8 from Table 6, we would scale this to 2.2 w/g for Eu_2O_3 at the midplane. This is at best an approximate first estimate of gamma heating in Eu_2O_3 .

3. BURNUP OF Eu_2O_3

We estimate the change in Eu_2O_3 neutron-capture rate, as a function of irradiation time, on the basis of data given in the following table:

Isotope	Atom density (atoms/cm ³)	Neutron absorption (neutrons/cm ³ sec)	Isotope burnup rate (fraction/yr)
¹⁵¹ Eu	1.12×10^{22}	2.9×10^{13}	0.0814
¹⁵³ Eu	1.22×10^{22}	2.1×10^{13}	0.0543

We assume that the capture products (¹⁵²Eu or ¹⁵⁴Eu) or their decay products (¹⁵²Sm, ¹⁵²Gd) have on the average half the neutron-absorption cross section of their neutron-capture precursors (see Appendix B).

Thus, assuming an initial capture rate of 5×10^{13} neutrons/cm³sec in Eu_2O_3 , and with time measured in equivalent full-power years, we would expect, as a first approximation, the following variations of reactivity worth with irradiation time:

Relative reactivity:

$$^{151}\text{Eu}: 0.58 \exp(-0.0814t)$$

$$^{152}\text{Eu}: 0.29\{1 - \exp(-0.0814t)\}$$

$$^{153}\text{Eu}: 0.42 \exp(-0.0543t)$$

$$^{154}\text{Eu}: 0.21\{1 - \exp(-0.0543t)\}$$

Individual reactivity contributions, as well as the total, are shown in Fig. 9. If a different neutron-absorption rate or a duty-factor less than 1.0 would seem appropriate to any particular case (e.g., FTR) the curves of Fig. 9 can be used by a direct transformation of the abscissa.

While the assumptions underlying this calculation are quite approximate, it would seem that the reactivity of Eu_2O_3 control rods should hold up well in a fast reactor for an exposure of several years.

Fig. 9 Relative Reactivity vs Time

ORNL DWG 73-1006

APPENDIX A

Self-Shielding and Volumetric Reactivity Worths

Tuttle and Springer³ found that the reactivity of tantalum specimens was more affected by neutron self-shielding than were those of either europium or boron absorbers. The effect may be illustrated by tabulating (or plotting) the reactivity worth (in cents/gram) as a function of the "optical thickness" $N\bar{\ell}$ of the absorber, where N is the number of absorber atoms/cm³ and $\bar{\ell}$ is the mean chord length of the absorbing body. (For example, for a long cylinder, $\bar{\ell} = d$, the diameter.) Self-shielding factors, derived from Ref. 3, are given in Table 7.

Table 7. Relative reactivity worth vs $N\bar{\ell}$

$N\bar{\ell}$	Ta	Eu
0	1.00	1.00
0.01	0.83	0.95
0.02	0.77	0.93
0.04	0.70	0.91
0.06	0.65	0.89
0.10	0.60	0.86

Optical thicknesses of single rods approximately equivalent to Eu_2O_3 pins or clusters of pins are shown in Table 8.

Table 8. Optical thicknesses of Eu_2O_3 rods

Pin diameter (in.)	Number of pins	Equivalent rod		N (atoms/b-cm)	$N\bar{\ell}$ (atoms/b)
		$\bar{\ell}$ (cm)	density (g/cm ³)		
0.386	1	0.98	6.85	0.023	0.023
0.386	3	1.70	6.85	0.023	0.040
0.386	3	3.63	1.5	0.005	0.018
0.386	7	5.54	1.5	0.005	0.028
0.36	1	0.95	6.85	0.023	0.021
0.36	61	10.5	3.43	0.0115	0.12

Thus, with Tuttle and Springer's results as shown in Table 7, we would expect self-shielding factors of about 0.9 for EBR-II test specimens and approximately 0.8 for 61-pin clusters in the FTR.

Tuttle and Springer's results may also be used to relate the volumetric reactivity worths of typical Eu_2O_3 and Ta specimens. For the Eu_2O_3 rods of Table 8, Ref. 3, gives worths of about 19.4 m¢/g Eu. For the large Ta rod of Ref. 1 (0.67 in. in diameter) a value of 3.27 m¢/g Ta is indicated. Hence, we have, for this case,

$$R_1 \equiv \frac{(\text{worth/cm}^3 \text{ Eu}_2\text{O}_3)}{(\text{worth/cm}^3 \text{ Ta})} = \frac{(19.4 \text{ m¢/g Eu}) (5.92 \text{ g Eu/cm}^3 \text{ Eu}_2\text{O}_3)}{(3.27 \text{ m¢/g Ta}) (16.6 \text{ g Ta/cm}^3 \text{ Ta})}$$

$$= 2.12 \frac{\text{m¢/cm}^3 \text{ Eu}_2\text{O}_3}{\text{m¢/cm}^3 \text{ Ta}}$$

Corresponding values for small (unshielded or infinite-dilution) samples are:

$$R_0 = \frac{(20.6)(5.92)}{(5.83)(16.6)} = 1.26 \frac{\text{m¢/cm}^3 \text{ Eu}_2\text{O}_3}{\text{m¢/cm}^3 \text{ Ta}} .$$

These results are consistent with the range 1.5 to 2 given in Section 1.1, and the value 2 chosen there is to be compared to the value $R_1 = 2.12$ given here.

APPENDIX B

Cross Sections

Information concerning neutron cross sections of europium has been drawn from several sources (Ref. 5, 12-14). We have not undertaken a careful review of these cross sections, nor have we undertaken to average them carefully over the spectrum to be expected in EBR-II. Both of these tasks should probably be undertaken.

The (n,γ) cross sections of ^{151}Eu and ^{153}Eu relative to that of ^{181}Ta and to each other are shown in Table 9, based on data from Ref. 12 (shown here in Fig. 10). As a rough average over the EBR-II spectrum, $\sigma(^{151}\text{Eu})/\sigma(^{153}\text{Eu}) \sim 1.5$ and $\sigma(\text{Eu})/\sigma(\text{Ta}) \sim 3.4$.

Table 9. Approximate relative (n,γ) cross sections of Ta and Eu¹²

Neutron energy (keV)	$\frac{\sigma(^{151}\text{Eu})}{\sigma(^{181}\text{Ta})}$	$\frac{\sigma(^{151}\text{Eu})}{\sigma(^{153}\text{Eu})}$	$\frac{0.5 \sigma_{151} + 0.5 \sigma_{153}}{\sigma_{181}}$
0.2	3.0	1.9	2.3
0.5	3.4	1.4	2.9
1.0	4.4	1.5	3.7
3	4.1	1.5	3.4
10	4.5	1.4	3.9
30	4.7	1.4	4.1
50	4.4	1.3	3.9
100	(3.8)		

The partial cross section of ^{151}Eu for formation of the 9.3 hr isomer of ^{152}Eu is even more difficult to determine. For thermal neutrons, the fraction, f_{11} , is about 0.35.¹² For 25 keV neutrons (using the partial cross section from Ref. 5 and the total cross section from Ref. 12) it appears that the fraction is closer to 0.7. This would be consistent with the increase in the ratio $\sigma(151 \rightarrow 152m_2)/\sigma(151 \rightarrow 152m_1)$ also noted by comparison of data from Ref. 5 and Ref. 12. We just don't know what the fraction f_{11} should be, averaged over the EBR-II spectrum, but guess that it might be in the range of 0.5 to 0.7, or even higher.

Fig. 10

The cross sections of ^{152}Eu and ^{154}Eu are not well determined. From Fig. 2 of Ref. 14, we might conclude that $\sigma_{152}/\sigma_{151} \sim 1-2$, and $\sigma_{154}/\sigma_{153} \sim 0.5-1$. From Ref. 13, we might conclude $\sigma_{152}/\sigma_{151} \lesssim 1$. The cross sections of ^{152}Sm and ^{152}Gd are also relevant (especially the latter). Judging solely from the fact that the cross section of natural gadolinium is about one-third that of natural europium (gleaned from Fig. 10) we might expect $\sigma(^{152}\text{Gd}) < \sigma(^{151}\text{Eu})$, but this is hardly a proof. In order to estimate the reactivity loss of Eu_2O_3 control rods, due to burnup, with some initial margin of conservatism, we tentatively assume that $\sigma_{152}/\sigma_{151} \approx \sigma_{154}/\sigma_{153} \approx 1/2$, where "152" includes some mix of ^{152}Gd , ^{152}Eu , and ^{152}Sm .

More work can and should be done on these cross sections.

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SUPPLEMENT II

CONSIDERATIONS ON THE PHASE STABILITY OF EUROPIUM SESQUIOXIDE

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CONSIDERATIONS ON THE PHASE STABILITY OF EUROPIUM SESQUIOXIDE

V. L. Burdick*

INTRODUCTION

The cubic structure (C-type) of Eu_2O_3 has been observed by many investigators and studied extensively by Rau¹ and Stecura.² Preparation of the C-type has been accomplished by decomposition of various europium compounds including carbonates, oxalates, hydroxides, nitrates, and sulfates and through oxidation of fluorides and chlorides. Whenever the decomposition or oxidation reactions are carried out at temperatures below about 1000°C, the C-type structure is found. When the oxide is heated above about 1100°C a crystallographic transition from C-type to B-type (monoclinic) occurs.² This transition appeared to be irreversible to some investigators¹⁻³ and reversible to others.^{4,5} The transformation involves a density change of about 10% and a change in cation coordination from 6 in the C-type to 7 in the B-type.

OBSERVATIONS ON THE STABILITY OF C-TYPE Eu_2O_3

Unpublished long-term tests at ORNL (700 hr) at 900°C in vacuum have not caused any C $\rightarrow$ B transformation. In addition to this observation on the apparent irreversibility of the C $\rightarrow$ B transition, Brauer⁶ cites other evidence for the metastability of cubic europia. In addition, Bärnhausen's⁷ results on oxidizing EuO and Eu_3O_4 in air at 300 to 400°C were considered surprising. He produced B-type Eu_2O_3 at these low temperatures. Brauer concluded that the lower density C-type europia

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resulted from lower density starting materials, such as the salts mentioned above, while the denser B-type resulted from the high density EuO and Eu_3O_4 . Topotactic tendencies in the decomposition reactions could be responsible for the C-type product. This idea seems consistent with a simplified picture of the decomposition of $\text{Eu}(\text{OH})_3$ as follows:

The basic structural unit in the hydroxide is ninefold coordinated cations, while in cubic europia it is sixfold coordinated cations. If one takes the average of three water molecules from two structural units of the hydroxide, then six oxygen ions are left for each cation and a simple collapse of this unit leaves the correct coordination for the formation of C-type oxide.

Brauer⁸ has prepared B-type europia at 400°C through precipitation of oxides from anhydrous rare earth nitrates dissolved in molten mixtures of alkali nitrates. Seed crystals of C-type europia added to the solution did not nucleate C-type precipitates at 400°C . It was concluded that the B-type structure must be the stable one at 400°C . However, no mention was made of further heat treatment (above 400°C) of the precipitates to observe possible transformation to the C-form at elevated temperatures.

Recently revised thermochemical data⁹ on Eu_2O_3 indicate that the C-type is stable up to about 1100°C . The free energy difference between the two phases is small [i.e., ΔG transition C $\rightarrow$ B is given as 1.94 ± 0.38 (kcal/mole) at room temperature, 1.16 ± 0.59 at 427°C , and 0.70 ± 0.70 at 827°C]. It is possible that small impurity concentrations, strain energy, and surface energy could affect the transition drastically since these effects could become more important than the free energy of transition. Similarly, these effects could

have been operative during the thermochemical measurements and affected ΔG values obtained.

OTHER EXAMPLES OF METASTABLE OXIDE PHASES

The formation of metastable oxide phases by decomposition or oxidation reactions is not uncommon. For example,¹⁰ $\gamma\text{-Al}_2\text{O}_3$ forms upon decomposition of the monohydrate $\text{AlO}\cdot\text{OH}$ at about 400°C . This phase is cubic and consists of a defect spinel structure. Further heating results in the formation of the θ phase at about 1000°C and finally the stable rhombohedral phase, $\alpha\text{-Al}_2\text{O}_3$, is formed at about 1200°C . These transitions are irreversible and represent changes which increase the density of alumina. The formation of the metastable phases is apparently controlled by topotactic effects since decomposition of the trihydrate does not produce the same reaction scheme.

In zirconia, which is structurally related to fluorite just as C-type europia is, the high-temperature tetragonal form cannot be quenched in. The structure of the pure oxide reverts to the monoclinic form below about 850°C . However, tetragonal zirconia can be produced by decomposing zirconium nitrate and alkoxide or by oxidizing the chloride at low temperatures.¹¹ This metastable phase remains until the oxide is heated to about 500 to 600°C , whereupon the monoclinic form is produced. With further heating, the monoclinic form transforms to tetragonal at about 1100 to 1200°C . This transition to a more symmetrical structure involves an increase in density and a change in cation coordination from 7 to 8.

Thus, it is apparent that metastable or unstable oxide phases can be produced rather readily and with the high activation energy normally associated with atomistic processes in oxides, some of these phases can persist

up to reasonably high temperatures. It is possible that C-type Eu_2O_3 is really metastable below about 1100°C but if it is stable, the activation energy required to make the transition $\text{B} \rightarrow \text{C}$ is just not available below the transition region.

One further consideration of the $\text{B} \rightarrow \text{C}$ transition should be made. That is the possibility of a hysteresis in the transition similar to that in the zirconia transition. In the literature surveyed thus far, only Hoekstra⁵ has heat treated monoclinic europia well below the 1100°C range. His experiments where the monoclinic type was held at 950°C for three weeks showed partial transformation to the C-type structure. These results suggest that further studies of the transition should be undertaken to determine if the hysteresis effect is present and, if so, to examine the mechanism of the transition to determine if it is one of the continuous type as proposed for ZrO_2 by Grain and Garvie.¹² For zirconia, they found that the transformation could be accounted for by small motions of oxygen ions (less than an interatomic distance) rather than a wholly reconstructive process. Although the coordination number of zirconium ions changes, the diffusionless process can prevail when rotation of certain oxygen ions is considered. The continuous transformation develops by means of domains of tetragonal zirconia growing in the monoclinic matrix. The formation of the domain need not be nucleated. Considerable strain energy is involved for the domain interfaces are coherent and there is a large volume difference (about 10%) between the two phases. The strain energy can halt the transition at any point in the transition region, and then the temperature must be changed to cause further transformation. For the reverse reaction, a different amount of strain would be associated with growing monoclinic domains in a tetragonal matrix. Thus, the origin of the hysteresis. A crystallite size effect was observed where grains smaller than a domain would contain no strain energy and

thus the heat of transition and therefore the rate of transition would be size dependent.

A similar mechanism could prevail in Eu_2O_3 although Stecura² has proposed a reconstructive type. It is possible that only small rearrangements of the lattice need to be made rather than a gross diffusional-type rearrangement. Detailed analysis of the relationships between the B- and C-types should be made to determine the possible transition mechanisms.

An assessment of the literature cited concerning the stability of the C- and B-modifications of Eu_2O_3 leads to the following conclusions:

1. C-type Eu_2O_3 is stable at temperatures up to about 1100°C. Observations of the monoclinic form prepared below this temperature are considered to be in the metastable region.

2. The $\text{C} \rightarrow \text{B}$ transition appears to be irreversible because: (a) the activation energy for the $\text{B} \rightarrow \text{C}$ transition is too high and the kinetics too slow in the temperature range required, or (b) there is a hysteresis in the transition and that most attempts to observe the transition have been made at temperatures too high for it to occur, or (c) impurities have impeded the transition.

CONSIDERATIONS FOR IRRADIATION BEHAVIOR

One primary consideration of the behavior of Eu_2O_3 under fast neutron irradiation is the stability of the different crystallographic modifications. The transformation between cubic and monoclinic forms is of most interest because of the temperature range at which it supposedly occurs and the rather drastic change in density during the transition.

Studies of radiation-induced phase transitions in oxides are confined mostly to zirconia. Wittels et al.¹³ concluded from irradiation experiments on

pure and doped zirconia that fission fragment fluxes associated with 10^{15} to 10^{16} fissions/cm³ produce a monoclinic to face-centered cubic phase change in zirconia. Additionally, the presence of uranium in ZrO₂ in concentrations less than 0.38 wt % does not act as a nucleation or stabilization agent. Fast neutrons alone did not appear to induce the transition in doses up to 6.3×10^{20} neutrons/cm². In contrast, Adam and Cox¹⁴ reported that either fast neutrons or fission fragments could induce the phase transition only if the zirconia contained impurity atoms that could nucleate and/or stabilize the cubic phase. The cubic phase was determined to be of the fluorite type and its density appeared to be about 6 to 7% greater than that of the monoclinic phase.

Adam and Cox¹⁴ found 100% transformation to the cubic phase for ZrO₂ films on alloy substrates but only partial transformation in bulk oxides. Wittels and Sherrill¹⁵ found that regions on the order of 100 Å radius resulted from the radiation-induced transition and in other work¹³ considerable strain was obviously present in transformed material. These observations suggest some correlations to the mechanism of phase transitions in zirconia discussed above. Thus, the question of microstructural effects, especially the shape, size, and size distribution of zirconia, still remains. Additionally, the difference in behavior of films and bulk samples suggests a microstructural effect.

It is interesting to note the similarity in the spacing of lattice planes in the cubic zirconia produced by irradiation by Wittels et al.¹³ and in cubic zirconia prepared by Mazdidasni et al.¹⁶ by decomposing zirconium alkoxides. Using the lattice parameter 5.09 Å from Wittels et al.¹³ and indexing the d-spacings from Mazdidasni et al.,¹⁶ the following

interplanar spacings for a fluorite-type cell are found (rounded to three figures):

<u>hkl</u>	<u>Wittels et al.</u>	<u>Mazdiyasni et al.</u>
111	2.94 Å	2.95 Å
002	2.55 Å	2.53 Å
220	1.80 Å	1.81 Å
311	1.53 Å	1.54 Å

Without accounting for lattice defects, the density of the cubic phase calculated from these data is 6 to 7% greater than that of the monoclinic phase, which is stable at low temperatures. Apparently the cubic form can more easily accommodate the strain introduced by fast neutron irradiation or alternatively the effect of strain energy and surface energy is such that the more symmetrical structure prevails. It should be noted that the decomposed alkoxide¹⁶ produced zirconia particles less than 50 Å in average particle size and that the cubic form transformed to tetragonal at about 300°C in powders with an average size of 50 Å. The particle size of these decomposed alkoxides are of the same order as the 100 Å "regions" noted by Wittels and Sherrill in irradiation-induced cubic zirconia.

A radiation-induced transformation in BaTiO₃ from tetragonal to cubic has been observed by Wittels and Sherrill.¹⁷ The lattice of the cubic (perovskite-type) phase induced by radiation was considerably expanded over the cubic structure produced by heating tetragonal BaTiO₃ to above 120°C. The results from the ZrO₂, BaTiO₃, and UO₂ radiation behavior led Wittels et al.¹³ to conclude that if several allotropic forms of a given nonmetallic material can exist, then the structures with highest symmetry will be the most stable under irradiation. This conclusion is drawn irrespective of classical thermodynamic behavior of the materials. The effects of high temperature

during irradiation are not known for ZrO_2 , but it was concluded that the zirconia transition was probably not thermally induced.

Radiation effects on other oxides, Al_2O_3 and MgO , have not induced phase transitions.¹⁸ Other macroscopic effects observed were lattice expansion, lower density, lower thermal conductivity, and grain boundary cracking in some cases. High-purity, fine-grained materials performed the best. For Al_2O_3 above 1100°C , in-reactor annealing was rapid enough to reduce damage but above 1230°C damage increased.

Heavily irradiated crystalline quartz (SiO_2) has nearly the same density as highly irradiated fused silica¹⁹ (vitreous). Upon annealing, the quartz becomes vitreous indicating that the quartz lattice has been subjected to so many atomic displacements that thermodynamically it is equivalent to the glassy state. No mention is made as to whether the quartz transforms to glass via high cristobalite (cubic form of SiO_2) or simply quartz to glass.

In order to predict the behavior of a material under irradiation, the macroscopic changes discussed in the foregoing must be examined on an atomistic scale. In general, the macroscopic changes are related to the phenomena of irradiation-induced vacancies and interstitials, spikes, ordering and clustering of atoms or defects, and to enhanced diffusion processes.

Thermally induced phase transitions can be thought of as processes which occur in order to decrease the free energy of the system by relieving strain energy caused by increased defect concentrations or anisotropic thermal dilation and by gaining configurational entropy. These processes in oxides often involve transformation to structures of higher symmetry and higher cation coordination. Additionally, there is often a small change in internal energy and a high activation energy for oxide transitions.

Irradiation-induced phase transitions in zirconia and barium titanate have proceeded in the direction of high temperature modifications. Apparently the irradiation has an effect similar to thermal treatment (i.e., a defect concentration and lattice strain energy develops such that the high temperature modification becomes more stable). Annealing effects under high temperature irradiation are not reported.

For Eu_2O_3 then, the predicted behavior under fast neutron irradiation is that the monoclinic modification would be more stable than the cubic form and that the higher temperature hexagonal form should be the most stable. The behavior could be analogous to that of Cm_2O_3 under self-radiation from α -decay of ^{244}Cm as reported by Mosley.²⁰ The C-type Cm_2O_3 exhibited lattice swelling, phase transformation, and apparent formation of amorphous oxide, while under similar conditions the monoclinic (B-type) showed little change in lattice parameters; however, loss of structure increased gradually with time.

There is no way to assess the degree to which the predicted phase transitions will occur since annealing effects are unknown. For europia, the only way to determine this is by irradiation experiments.

PROPOSED THERMAL STABILITY EXPERIMENTS

1. Long-term, carefully controlled heat treatments on high-purity monoclinic europia should be carried out at temperatures ranging from 750 to 950°C to confirm the reversibility (irreversibility) of the C $\rightarrow$ B transition.
2. Monoclinic Eu_2O_3 prepared by oxidizing EuO at 400°C should be checked for metastability by heat treatments as in Item 1 above.
3. The crystallite size effects should be checked on C-type and B-type Eu_2O_3 . Samples of various grain sizes (e.g., 100 Å up to 100 μm) should be prepared and then the temperature and rates of transitions should be studied.

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SUPPLEMENT III

CRITIQUE OF THERMAL CONDUCTIVITY DATA

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CRITIQUE OF THERMAL CONDUCTIVITY DATA*

The thermal conductivity data available^{1,2} has been obtained from samples of less than theoretical density. Work at ORNL on oxides has indicated that the appropriate term for correction of such data is

$$\lambda_{\text{meas}} = \lambda_{\text{T.D.}} \left[\frac{1 - P}{1 + \frac{1}{2} P} \right] \quad (1)$$

where $\lambda_{\text{T.D.}}$ is the thermal conductivity of theoretically dense material and λ_{meas} is the thermal conductivity of material with P closed volume fraction porosity works well.³ It is quite possible that the 89% dense sample of Kiparisov et al.¹ had some open porosity which would cause a small error in this equation. The data from references 1 and 2 as corrected to theoretical density are plotted in Fig. III(1).

The high-temperature data of Grünling and Schickfluss-Borges were obtained at the European Transuranium Institute which has an electron-beam thermal diffusivity device⁴ which has generated good data on UO_2 . To determine λ from diffusivity (α) one uses

$$\lambda = \alpha \rho C_p \quad (2)$$

where ρ is the density and C_p is the specific heat at constant pressures; and although the α data is probably correct, the C_p input is definitely wrong and possibly badly wrong. They are using C_p values from drop calorimeter⁵ data at lower temperatures and assuming C_p does not change with T . Actually

$$C_p = C_v [1 + \gamma \alpha_v T] \quad (3)$$

*Adapted from a study by J. P. Moore.

where C_v is the specific heat at constant volume, α_v is the volumetric expansion coefficient, and γ is the Gruneisen constant. Since C_p does increase with T , λ calculated from Eq. (2) would be expected to be higher than Grnling and Schickfluss-Borges indicate so that the conclusion is that their λ data are too low at the higher T values. There are other effects which cause C_p to increase as the melting point (2330°C) is approached which make this problem even more severe. In addition to the problems of using low T data on C_p at high T , it appears that the existing low T data on C_p is somewhat suspect based on the imprecision in the results⁵ and the fact that they were from enthalpy measurements.

The technique of Kiparisov et al.¹ which generated the lower T data appears to be better than most longitudinal heat flow systems which have been used unwisely at high T on low λ materials. Their paper where the device is described in detail has not been examined closely, but since they were monitoring T at many positions and were apparently checking radial flow in some manner, maybe it can be assumed that they also did a good job of getting the heater in uniform contact with the specimen. Even if they did everything correctly, the system will be in error because the thermal conductivity of the insulation is only about 2 orders of magnitude lower than the sample λ and perfect guarding still is not adequate. Since λ of the insulation and λ of the specimen converge with increasing T , the problem and hence the error becomes more severe with increasing T .

Figure III(1) includes data from references 1 and 2 as corrected to theoretical density using Eq. (1) and error bands are included about the data. The band about the data of Kiparisov et al. was calculated from their stated maximum error of 9% which is probably not too high in view of

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Fig. III(1). Thermal Conductivity of Monoclinic Eu_2O_3 .

the problems involved with their technique. The band about the data of Grünling and Schickfluss-Borges includes a 5% uncertainty on the α determination and a 5% uncertainty on the C_p at 800°C which increases to 15% at 1700°C. Keeping in mind that the low T data are probably in error most at the high T end of its range and that the high-temperature data is probably most nearly correct where some C_p data exist, a "best-guess" line has been drawn through the results. This line is probably representative of unirradiated fine-grain polycrystalline Eu_2O_3 in the monoclinic form to within about $\pm 20\%$, but in view of the spread in λ among the rare-earth oxides it appears that the thermal conductivity of Eu_2O_3 should be measured with a radial heat flow technique.

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