HELIUM RELEASE FROM $^{244}\text{Cm}_2\text{O}_3$

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Isotopes Division

NOVEMBER 1973

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	<u>Page</u>
ABSTRACT	1
INTRODUCTION	1
EXPERIMENTAL	3
Mathematical Model for Helium Release Experiments	3
Apparatus and Procedure	4
Material	4
RESULTS	5
Diffusion Parameters	5
Effect of Radiation Dose Rate	7
Times to Steady-State Helium Release	7
DISCUSSION	8
Hypothesis on Mechanism of Release	8
Low Activation Energy Release	9
Effect of Radiation	11
ACKNOWLEDGMENT	12
REFERENCES	12

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ABSTRACT

The release of helium from hot-pressed pellets and sol-gel microspheres of $^{244}\text{Cm}_2\text{O}_3$ was investigated under isothermal steady-state release at 900 to 1700°C. The release of helium from hot-pressed pellets of coprecipitated 75 mole % $^{244}\text{Cm}_2\text{O}_3$ -25 mole % Gd_2O_3 and 46 mole % $^{244}\text{Cm}_2\text{O}_3$ -54 mole % Gd_2O_3 was also investigated at 1300 to 1700°C. Release characteristics could be approximately described by diffusion models.

In this report rationally consistent mechanisms are postulated for the release of helium from $^{244}\text{Cm}_2\text{O}_3$.

INTRODUCTION

The alpha-emitting radioisotope ^{244}Cm is under development¹ as a fuel to supply energy for several types of systems which convert heat to electric power. The fuel compound currently favored is $^{244}\text{Cm}_2\text{O}_3$. The safe and efficient application of $^{244}\text{Cm}_2\text{O}_3$ as a heat source requires a knowledge of the pertinent characteristics of the fuel compound. The behavior of the helium, which is generated at a rate of $1.01 \times 10^{-7} \text{ cm}^3/\text{g}$ for $^{244}\text{Cm}_2\text{O}_3$ from alpha decay, must be known quantitatively. Other characteristics which must be known and a summary of the status of the characterization of $^{244}\text{Cm}_2\text{O}_3$ are given in ref. 2. This report describes the release of helium from monoclinic B-type and hexagonal A-type $^{244}\text{Cm}_2\text{O}_3$ bodies under steady-state conditions as a function of temperature.

The diffusion of helium in crystalline solids has received little attention as compared to the diffusion of krypton and xenon in nuclear reactor fuels. Angelini and McHenry³ have reported the initial phase of the investigation described in this report. Angelini *et al.*,⁴ Mound Laboratory,⁵ and Northrup *et al.*⁶ have studied the release of helium from plasma-fired $^{238}\text{PuO}_2$ microspheres. Stark⁷ and Williams⁸ have given correlations of the data in refs. 4 and 5. Clinard *et al.*⁹ have studied the release of helium from ThO_2 and Douglas and Bronesz¹⁰ have used the electron microscope to investigate alpha particle damage to several actinide oxides. Earlier work on the diffusion of helium as well as krypton and xenon in ceramic fuels and the effect of radiation on diffusion is comprehensively reviewed and interpreted by Bradbury and Frost.¹¹ Their conclusions concerning fission gases in ceramic oxides are summarized as follows:

1. Fission damage (and alpha radiation) produces lattice defects, dislocation loops, and dislocation networks. The dislocations are mobile at 800-1200°C while "light defects" migrate between 1200-1700°C. Most radiation damage anneals at temperatures above 1000°C. Single defects will be annihilated or form clusters at temperatures of 150-700°C.
2. Noble gases which are highly insoluble in oxides interact with radiation damage effects to produce bubbles. Gas bubbles precipitate on dislocation loops and grain boundaries. These bubbles move by some mechanism (or mechanisms) which is not understood. Several conflicting theories have been proposed.
3. From data on samples irradiated at levels of 3.5×10^{14} to 1.8×10^{18} fissions/cm³ and examined by postirradiation annealing, a trapping model was proposed by MacEwan and Stevens¹² to explain the decrease in fission gas release with increased irradiation. However, the work of Daniel *et al.*¹³ as interpreted by Ainscough¹⁴ indicates an increase in the diffusion coefficient of fission-product gases with irradiation at high dose rates (up to 3.6×10^{21} fissions/cm³). Bradbury and Frost¹¹ in their review observed that the diffusion coefficients were calculated assuming a constant diffusion path length but that the result could as easily have been explained by a shortening of the diffusion path by radiation damage. They state that at high burnup levels grain boundary porosity and a subgrain structure are often observed.
4. Bradbury and Frost¹¹ conclude that the only way fission gas release can be predicted is from data taken under conditions where the sample is undergoing irradiation and the dynamic effect of irradiation is present. They discuss the work of Carroll^{15,16,17} which was done in-pile. Carroll postulates a trapping model to explain his data.

An enormous amount of work by many authors has been expended during the last decade in attempts to quantitatively describe the behavior of the noble gas fission product in ceramic nuclear reactor fuels, and yet this goal has not been accomplished. With few exceptions, these studies have been conducted by postirradiation anneals or other experimental methods in which dynamic radiation effects are absent.

It is our belief that the large range of parameters and theories describing the noble gas diffusion in ceramic fuels is due to the varying degree to which radiation effects are present.

In this report rationally consistent mechanisms are postulated for the release of helium from $^{244}\text{Cm}_2\text{O}_3$.

EXPERIMENTAL

Mathematical Model for Helium Release Experiments

A classical diffusion model approach was employed in the present helium release work, and mathematical relations describing the release were derived under the following assumptions:

1. The basic helium-releasing unit is a sphere of effective radius, "a." This radius will probably be significantly smaller than the actual body dimensions because of open porosity, grain boundaries, defects, and dislocations in the body.
2. The concentration of helium at the external surface of each releasing unit is zero. This assumption is believed to be justified by the extremely low solubility of inert gases in actinide oxides.¹⁸
3. The helium motion can be described by Fick's law, with an effective diffusion coefficient, D, within each releasing unit. This coefficient is independent of position.

In the steady-state release experiments to determine the diffusion coefficient of helium in $^{244}\text{Cm}_2\text{O}_3$, it was assumed that generation of helium within the material occurred at a rate, P (cm^3 of gas)/(cm^3 of solid)(sec), independent of time and position. At steady state the release rate of helium will equal the generation rate, and under the foregoing assumptions the concentration distribution of helium within a releasing spherical unit is given by:¹⁹

$$c(r) = (P/6D)(a^2 - r^2) , \quad (1)$$

where

$c(r)$ = concentration of helium at radius r , cm^3/cm^3 ,
 a = effective radius of releasing unit, cm, and
 D = effective diffusion coefficient, cm^2/sec .

The average concentration within the sphere, C_{av} , may be calculated as:³

$$C_{av} = P/15D' , \quad (2)$$

where

$D' = D/a^2$ = effective diffusion-release parameter, sec^{-1} .

Experimentally, the sample is maintained at the required temperature in vacuum until the measured helium-release rate equals the known generation rate. The average helium concentration is then determined by degassing the sample to 1900°C , and an effective diffusion parameter, D' , can be calculated directly from Eq. (2).

The relation between D' and the time (t) to a given fraction (f) of steady-state helium saturation (for fractions of saturation above 0.77) is given by:

$$t = \frac{1}{D'\pi^2} \ln\left(\frac{6}{\pi^2(1-f)}\right) \quad (3)$$

which is derived from Fick's second law.

Apparatus and Procedure

The details of the apparatus and procedure have previously been described in ref. 4.

Material

The supply of curium oxide fuel was received from Savannah River Laboratory. The compound $^{244}\text{Cm}_2\text{O}_3$ was prepared by heating the oxide at 1350°C for 30 min in an argon atmosphere. The $^{244}\text{Cm}_2\text{O}_3$ powder was then vacuum hot-pressed in a graphite die at 1450°C and 4000 psi. The $^{244}\text{Cm}_2\text{O}_3$ pellets were heated in a tube furnace at 1000°C for 1 hr at an oxygen concentration of ~ 1000 ppm in order to remove the graphite adhering to the pellet surface. The mode of fabrication ensured a $^{244}\text{Cm}_2\text{O}_3$ product having a monoclinic B-type crystal structure.

The densities of the pellets were calculated from their weight and dimensions. The densities of the 10-, 5-, and 0.250-g $^{244}\text{Cm}_2\text{O}_3$ pellets used in this experiment were 10.8, 10.8, and 10.3 g/cm^3 , respectively. The fuel material contained ~ 6 mole % ^{240}Pu due to alpha decay of the ^{244}Cm . The elemental impurities in the as-received ^{244}Cm oxide are presented in Table 1.

Table 1. Spark-Source Mass Spectrometer Analysis of Elemental Impurities in the As-Received ^{244}Cm Oxide Powder Used in Fabricating the Hot-Pressed Pellets

Element	Concentration (wt ppm)	Element	Concentration (wt ppm)
Ag	<50	Mg	>100
Al	<200	Mn	200
Am	7000	Ni	200
Ca	>1000	P	300
Cd	<50	Pb	<50
Co	70	Pt	1000
Cr	300	Si	>1000
Cu	200	Ta	700
Fe	2000	Zn	400
K	200	Zr	8000

The density of the 46 mole % $^{244}\text{Cm}_2\text{O}_3$ –54 mole % Gd_2O_3 pellet was measured to be 8.4 g/cm^3 . The density of the 75 mole % $^{244}\text{Cm}_2\text{O}_3$ –25 mole % Gd_2O_3 pellet was calculated to be 9.6 g/cm^3 . The elemental impurities in the gadolinium oxide used in the oxalate coprecipitation of the above two oxide fuels are presented in Table 2.

Table 2. Spark-Source Mass Spectrometer Analysis of Elemental Impurities in the As-Received Gadolinium Oxide Powder

Element	Concentration (wt ppm)	Element	Concentration (wt ppm)
Al	20	Mn	1
B	0.3	Mo	2
Ba	<1	Na	15
Ca	30	Nd	10
Ce	10	Ni	2
Cl	800	P	<0.7
Co	<0.4	Pr	30
Cr	<1	S	5
Cu	2	Si	100
Dy	<4	Sm	30
Er	<4	Tb	<1
Eu	70	Ti	<1
Fe	100	Tm	<1
Gd	M	U	<2
Ho	<1	V	<0.3
K	10	Y	6
La	10	Yb	<4
Lu	<1	Zn	1
Mg	5		

The sol-gel microspheres were not made from the same batch of material from which the hot-pressed pellets were made. The percent of ^{240}Pu and the remainder of impurities were approximately the same as those for the pellets.

RESULTS

Diffusion Parameters

The results of steady-state helium release determinations from 900 to 1700°C are plotted in Fig. 1. The diffusion parameter, D' , is independent of the geometry of the sample, which indicates that the basic releasing unit is of constant dimensions.

Fig. 1. Helium Diffusion Parameter, D' , in $^{244}\text{Cm}_2\text{O}_3$ Versus Reciprocal Absolute Temperature.

At temperatures below 1615°C (the temperature of the monoclinic-hexagonal phase transition) the diffusion parameter, D' , was controlled by two different processes. The value of D' is obtained by adding the values calculated from

$$D' = 7.87 \times 10^{-4} \exp(-16,248/RT^\circ\text{K}) , \quad (4)$$

which is predominant at temperatures below 1300°C , and the values calculated from

$$D' = 68.0 \exp(-53,080/RT^\circ\text{K}) , \quad (5)$$

which is predominant from 1300 to 1615°C . At temperatures above 1615°C , the release of helium is significantly different from that below 1615°C . This effect was presumably due to the characteristics of the hexagonal structure or to changes in the sample produced during the monoclinic-hexagonal transition. Figure 2 shows the rapid transient release of helium at the monoclinic B-type to hexagonal A-type phase transition temperature in $^{244}\text{Cm}_2\text{O}_3$. The steady-state diffusion parameters in $^{244}\text{Cm}_2\text{O}_3$ above 1615°C are given by

$$D' = 4.65 \times 10^7 \exp(-102,780/RT^\circ\text{K}) . \quad (6)$$

Fig. 2. Helium Release Rate Versus Temperature (rate of temperature increase, $3.7^\circ\text{C}/\text{min}$).

The activation energies for the two processes predominant at temperatures between 900 and 1615°C, -16,248 and -53,080 cal/mole, respectively, are similar to those observed in $^{238}\text{PuO}_2$.⁴

Effect of Radiation Dose Rate

The effect of varying the radiation dose rate on the diffusion parameter (D/a^2) of helium in $^{244}\text{Cm}_2\text{O}_3$ was studied. To vary the radiation dose rate the $^{244}\text{Cm}_2\text{O}_3$ was diluted with Gd_2O_3 . The classical diffusion model indicates that the diffusion parameter is independent of helium concentration (or in this case the production rate of helium). The helium production rate, however, is a linear function of the radiation dose rate. Values of the steady-state helium concentration in the $^{244}\text{Cm}_2\text{O}_3$ - Gd_2O_3 samples (from which diffusion parameters are calculated) were determined on 75 mole % Cm_2O_3 -25 mole % Gd_2O_3 and 46 mole % Cm_2O_3 -54 mole % Gd_2O_3 in the temperature range 1300-1700°C. The data are plotted in Fig. 3. A power dependence of D' on radiation dose rate is inferred. This conclusion is consistent with the relative values of D' determined on $^{242}\text{Cm}_2\text{O}_3$, $^{244}\text{Cm}_2\text{O}_3$, and $^{238}\text{PuO}_2$. The assumption that Gd_2O_3 is inert is reasonable but not proven.

Fig. 3. Helium Diffusion Parameter, D' , in $^{244}\text{Cm}_2\text{O}_3$, 75 mole % $^{244}\text{Cm}_2\text{O}_3$ -25 mole % Gd_2O_3 , and 56 mole % $^{244}\text{Cm}_2\text{O}_3$ -54 mole % Gd_2O_3 Versus Reciprocal Absolute Temperature.

Times to Steady-State Helium Release

The relationship between D' , fraction of steady-state helium release attained (f), and time (t) can be derived from Fick's second law. The time can be approximated with good accuracy for values of $f > 0.77$ by the equation,

$$t = \frac{1}{D'\pi^2} \ln\left(\frac{6}{\pi^2(1-f)}\right) \quad (7)$$

where

f = ratio of helium concentration at any time, t , to the concentration at infinite time,

D' = diffusion parameter, sec^{-1} , and

t = time to fraction of saturation, f , in seconds.

Table 3 shows the calculated times required for $^{244}\text{Cm}_2\text{O}_3$ to attain $f = 0.95$ of helium steady-state saturation at several temperatures. To assure the experimental attainment of steady-state helium release, typical experiments were carried out for time periods several fold larger than those calculated to achieve $f = 0.95$.

Table 3. Calculated Times to 0.95 Saturation
for $^{244}\text{Cm}_2\text{O}_3$

Temperature ($^{\circ}\text{C}$)	Time to 0.95 Saturation
900	8.8 days
1100	1.2 days
1300	9.2 hr
1400	4.2 hr
1500	1.8 hr
1600	40 min
1700	14 min

DISCUSSION

Hypothesis on Mechanism of Release

A rational hypothesis which describes the mechanism(s) of the helium movement in monoclinic B-type $^{244}\text{Cm}_2\text{O}_3$ must be consistent with all of several experimental observations:

1. The high-temperature and low-temperature portions of a plot of $\log D'$ versus $1/T^{\circ}\text{K}$ have different slopes (activation energies).
2. The values of D' in the temperature region 1200 to 1700 $^{\circ}\text{C}$ show a logarithmic dependency at steady state on the radiation dose rate.
3. Values of D' are independent of the geometry of the sample.

A hypothesis on the general nature of the release of helium from $^{244}\text{Cm}_2\text{O}_3$ which is based on our experimental data and supported by the work of others follows:

Helium is released from $^{244}\text{Cm}_2\text{O}_3$ by two controlling mechanisms at steady state (steady state relative to both radiation effects and helium concentration). One mechanism predominates above 1300 $^{\circ}\text{C}$ and another predominates below 1300 $^{\circ}\text{C}$. At low temperature

(<1300°C) we believe the helium diffuses through the lattice of $^{244}\text{Cm}_2\text{O}_3$ to a dislocation network formed by alpha damage. (Some helium atoms will undoubtedly be ejected into the dislocation network.) The path length for this process is probably less than 200 Å. The helium diffuses via the dislocation paths with a characteristically low activation energy to the surface of the releasing unit. The releasing unit which is independent of geometry of the sample is probably the individual grains of the body. From the releasing units the helium moves with low resistance, probably along grain boundaries to the surface of the body.

The predominant mechanism for the movement of helium in $^{244}\text{Cm}_2\text{O}_3$ at high temperatures (>1300°C) appears to be similar to that of krypton and xenon in UO_2 . Although the mechanism of krypton and xenon in UO_2 is not known quantitatively, several qualitative observations have been drawn by Bradbury and Frost¹¹ in their review. At temperatures of 800 to 1200°C dislocation loops formed by radiation damage are mobile and form defect clusters. At temperatures above 1200°C observable bubbles are formed by coalescence of clusters. These bubbles migrate by some undefined mechanism to grain boundaries. A sufficiently high concentration of bubbles in the grain boundaries provides paths for the flow of noble gas to the surface of the body.

Low Activation Energy Release

Experimentally observed diffusion coefficients with low activation energies in the low temperature region are not uncommon. The low temperature enhancement of diffusion processes may be due to several factors. Two of these factors which could conceivably be present in helium diffusion in $^{244}\text{Cm}_2\text{O}_3$ will be discussed.

The effect of impurities on solid-solid diffusion has been studied extensively. Mapother, Crooks, and Maurer²⁰ have studied the effect of the cationic vacancies created by divalent impurity cations on the diffusion of Na^+ in NaCl . Shewman²¹ has examined the data of Mapother *et al.*²⁰ from a theoretical point of view. He shows that the slope of the Arrhenius plot times R (gas constant) in the low temperature (extrinsic) region is the energy (ΔH_m) required to mobilize an impurity vacancy. For Na^+ in NaCl a value of 17.7 Kcal/mole was obtained. The energy (ΔH_s) for the formation of a Na^+ vacancy derived from the high temperature slope of the Arrhenius plot $[(\Delta H_s/2) - (\Delta H_m)]/R$ was 47.4 Kcal/mole. In the extrinsic range the diffusion coefficient increases linearly with impurity concentration.

Lagerwall²² in work undertaken with the objective of elucidating the diffusion of xenon and krypton in UO_2 has studied the diffusion of argon in CaF_2 . His results indicated that impurity vacancies, cationic, or anionic, have no measurable effect on the diffusion parameter. In the

low temperature region (below $\sim 700^\circ\text{C}$) he observed a low activation energy diffusion process similar to that observed in $^{238}\text{PuO}_2$ and $^{244}\text{Cm}_2\text{O}_3$. The activation energy was 8.1 Kcal/mole. He attributes the low activation energy process to diffusion along dislocation produced by radiation damage rather than lattice diffusion. Lagerwall also studied the effect of radiation levels on the diffusion parameter. This will be discussed in the next section.

If it is assumed that helium diffuses in $^{244}\text{Cm}_2\text{O}_3$ by an impurity vacancy mechanism, then ΔH_m is 16.2 Kcal/mole and ΔH_s is 86 Kcal/mole. While the value of ΔH_s is comparable to that for the diffusion of cation vacancies in oxide, the value of ΔH_m is lower than the observed values in oxides by a factor of two. Kingery²³ states that expected values are 30-35 Kcal/mole.

The enhancement of diffusion processes at low temperatures in pure metal by dislocations is well established.²¹ Shewman²¹ states "for temperatures below half the melting point, the apparent lattice diffusion coefficient is entirely determined by the dislocation density" He also comments that there is no quantitative theory to predict the enhancement, but that it is easy to see qualitatively that the activation energy for self-diffusion in boundaries is less than in the lattice.

Whapham and Sheldon²⁴ have used transmission electron microscopy to study the effects of alpha irradiation on UO_2 . After irradiation with 65-keV alpha particles to a dose of 2×10^{16} alpha particles/cm², an interconnecting network of dislocation loops was observed. The average diameters of the interconnecting loops were ~ 200 -300 Å. Bronesz¹⁰ observed similar effects when several actinide oxides were irradiated to 10^{15} alphas (5.5 MeV/cm²). Defect densities of 5×10^{14} /cm³ were observed following an annealing cycle to agglomerate the defects into resolvable clusters.

The decay of $^{244}\text{Cm}_2\text{O}_3$ will produce an alpha dose of 6.35×10^{15} alphas/day·cm². A one-month decay gives a dose of 1.90×10^{17} alphas/cm², which is shown by previous workers to be sufficient to form a dislocation network similar to that observed by Whapham and Sheldon.²⁴

If the diffusion coefficient of helium in $^{244}\text{Cm}_2\text{O}_3$ lattice is assumed to be not less than 10^{-17} cm²/sec, the effect of helium lattice diffusion along a 200-Å path to the dislocation network can be shown to be a negligible contribution to the observed values of D' . The concentration of helium at the center of a 200-Å sphere at steady state is

$$\Delta C = PR^2/6D \quad (8)$$

where

P = helium production rate = 1.01×10^{-7} cm³/g·sec

R = radius of sphere = 1×10^{-6} cm

D = diffusion coefficient at 900°C $> 1 \times 10^{-17}$ cm²/sec

then at 900°C

$$\Delta C < 1.7 \times 10^{-3} \text{ cm}^3 . \quad (9)$$

The helium concentration at the center of a releasing unit of radius $R = 100 \text{ \AA}$ at steady state calculated from measured values of $(D/r^2)(D')$ at 900°C is

$$\Delta C = 2.6 \times 10^{-2} . \quad (10)$$

With the assumed small lattice diffusion coefficient the contribution to the helium concentration by lattice diffusion is only 7% of the total helium concentration observed.

The low temperature diffusion of helium via the dislocation network produced by alpha radiation in $^{244}\text{Cm}_2\text{O}_3$ may be compared to Barrer's mechanism²⁵ for the diffusion of helium in vitreous SiO_2 and silicate glasses. Barrer hypothesizes that helium diffuses through the open network structure of fused silica which has ring structures containing ~ 12 atoms. The activation energy for helium diffusion in fused silica is 5,700 cal/mole as compared to 16,248 cal/mole for the low-temperature diffusion of helium in $^{244}\text{Cm}_2\text{O}_3$.

Effect of Radiation

The diffusion parameters of helium in $^{244}\text{Cm}_2\text{O}_3$ under steady-state conditions were observed to decrease logarithmically with decreasing radiation dose rates. The radiation dose rates were varied by coprecipitating Gd_2O_3 and $^{244}\text{Cm}_2\text{O}_3$ to form solid solutions. Several workers have studied the effects of radiation on diffusion in ionic crystalline solids. Daniel *et al.*¹³ and MacEwan and Stevans¹² studied the effect of radiation dose on the diffusion of xenon in UO_2 . Lagerwall²² investigated argon diffusion in CaF_2 . Elleman²⁶ investigated xenon diffusion in CsI . Carroll *et al.*¹⁶ have determined the release characteristic of fission gas from UO_2 under in-pile irradiation conditions; the other authors (refs. 13, 16, 22, and 26) made measurements using postirradiation experiments. Extensive studies have been conducted on the fission damage in nuclear fuels. This work was summarized from a review¹¹ in the Introduction to this paper.

Most of the experimental work reported in the literature has been conducted using short-term irradiations and postirradiation anneals. We concur with the authors of ref. 11 that these experiments cannot be used to predict the behavior of noble gas in oxides which are undergoing the dynamic effect of irradiation. Further, we believe that the experiments have limited value since they do not generally approach saturation values for the noble gases. However, it seems abundantly clear from postirradiation anneal experiments that noble gases interact with radiation damage in oxides. Many authors have stated that irradiation deters the diffusion of noble gases in oxides. Our data indicate an irradiation enhancement of the steady-state release processes of helium from $^{244}\text{Cm}_2\text{O}_3$.

Carroll *et al.*¹⁶ in experiments done in-pile report that above a fission density of 3.2×10^{13} fissions/cm³·sec the release of ⁸⁵Kr is enhanced by the dynamic effects of irradiation. Daniels *et al.*¹³ have studied the effects of burnup on the diffusion of fission gases in UO₂ at 1000°C. They report that in the range of 1×10^{20} to 2.6×10^{21} the value of D increases experimentally from 10^{-17} cm² to 10^{-11} cm²/sec.

We conclude that alpha irradiation is an important factor in the release of helium from ²⁴⁴Cm₂O₃. We have previously observed much smaller values of D' in ²³⁸PuO₂ (ref. 4) than in ²⁴⁴Cm₂O₃.

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