timates previously reported.[6,8] Combining the new entropy values from this research with other data yields thermochemical values of interest. For example, the formation of uranium(IV) oxychloride from the elements may be written

$$U(c,\alpha) + {}^1/{}_2O_2(g) + Cl_2(g) = UOCl_2(c)$$

The standard entropies of $UOCl_2$ and of the elements involved,[11,12] when combined with the heat of formation of $UOCl_2$,[6,13] permit the calculation of molal values for the entropy and free energy of formation at 298.16°K.

$$\Delta S_f{}^\circ = -56.76 \pm 0.06 \text{ cal./deg.}$$
$$\Delta H_f{}^\circ = -261.7 \text{ kcal.}^{7,14}$$
$$\Delta F_f{}^\circ = -244.8 \text{ kcal.}$$

In a similar manner (with reference to liquid bromine as the standard state) we obtain the thermochemical values for the formation of a mole of uranium(IV) oxybromide at 298.16°K.

$$\Delta S_f{}^\circ = -35.3 \pm 0.4 \text{ cal./deg.}$$
$$\Delta H_f{}^\circ = -246.9 \pm 0.7 \text{ kcal.}^{9,14}$$
$$\Delta F_f{}^\circ = -236.4 \pm 0.7 \text{ kcal.}$$

Davidson and Streeter[14] studied the disproportionation of $UOCl_2$ to $UO_2$ and $UCl_4$ gas utilizing the effusion method, and Gregory[13] studied the analogous reaction for $UOBr_2$. Combination of the disproportionation data with values for the vaporization equilibrium of $UCl_4$[14,15] and $UBr_4$[16,17] allows the calculation of the enthalpy increments for the disproportionation reactions at 298.16°K. as 7 and

$$2UOCl_2(c) = UCl_4(c) + UO_2(c)$$
$$2UOBr_2(c) = UBr_4(c) + UO_2(c)$$

8 kcal., respectively.[13] These enthalpy increments, combined with the heats of formation of the oxyhalides determined by Barkelew[6,8,13] on rather impure samples, and the accurately known heats of formation of $UCl_4$[15] and $UBr_4$,[16] yield calculated values for the heat of formation of $UO_2$ which differ by about 14 kcal., suggesting that "either the equilibria data are in error or the calorimetrically determined heats of formation of $UOCl_2$ and $UOBr_2$ are greatly in error."[13] Huber, Holley and Meierkord[18] have determined the heat of formation of $UO_2$ by combustion of uranium metal. Using their value, together with the heats of formation of $UOCl_2$, $UCl_4$, $UOBr_2$ and $UBr_4$, one obtains $\Delta H^\circ_{298}$ = 13 kcal. for the disproportionation of $UOCl_2$, and $\Delta H^\circ_{298}$ = 23 kcal. for the $UOBr_2$ reaction. This again suggests the inconsistency of the equilibrium data.

Bozic and Gal[19] report that $UOCl_2$ is unstable, and on exposure to air is converted to $UO_2Cl_2$. During the course of this investigation, samples of $UOCl_2$ were frequently exposed to the air of a dry box, occasionally for several hours, but no evidence of the claimed oxidation was observed.

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[12] "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Govt. Printing Office, Washington, D. C., 1952.

[13] Reported in L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, "Thermodynamic Properties and Equilibria at High Temperatures of Uranium Halides, Oxides, Nitrides and Carbides," U. S. Atomic Energy Commission, MDDC-1543, Oak Ridge, Tenn., 1945, pp. 46–9.

[14] Ref. 13, pp. 33–6.

[15] Reported in J. J. Katz and E. Rabinowitch, ref. 6, pp. 476–483.

[16] Ref. 15, pp. 527–9.

[17] Reported in L. Brewer, *et al.*, ref. 13, p. 40.

[18] E. J. Huber, Jr., C. E. Holley, Jr., and E. H. Meierkord, THIS JOURNAL, **74**, 3406 (1952).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

# Lower Oxides of Samarium and Europium. The Preparation and Crystal Structure of $SmO_{0.4-0.6}$, SmO and EuO[1]

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A lower oxide of samarium whose oxygen to samarium ratio varied between 0.4 and 0.6 was prepared. This compound has the face centered cubic zinc blende-type structure; the lattice parameter varies between 5.3698 ± 0.0006 and 5.3790 ± 0.0008 Å. The lattice parameter of SmO is 4.9883 ± 0.0003 Å. Previously reported variations in the lattice parameter of SmO are believed to be due to nitride–oxide mixtures. EuO has a NaCl-type structure with a lattice parameter of 5.1439 ± 0.0005 Å.

## Introduction

Ellinger and Zachariasen[3] reported a phase which they believed to be SmO on some annealed samples of samarium metal and some metal preparations. They reported a lattice parameter varying from 5.015 to 5.050 ± 0.002 Å. No reason for the variation was known. An investigation was undertaken to examine the lower oxides of samarium, europium and ytterbium with the hope of explaining these systems. Part of this work is reported here.

## Experimental Part

**Materials.**—Samarium and lanthanum metals and $Sm_2O_3$ were obtained from Ames Laboratories, Ames, Iowa, and were labeled as greater than 99.9% pure. Europium ses-

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[1] The data presented here were included in a dissertation submitted by H. A. Eick to the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the Ph.D. degree. The work was supported in part by the Atomic Energy Commission Research Contracts Division.

[2] Allied Chemical and Dye Fellow, 1954–1955.

[3] F. H. Ellinger and W. H. Zachariasen, THIS JOURNAL, **75**, 5650 (1953).

quioxide was obtained from Research Chemicals, Inc., Burbank, California, and was labeled as 99.8% pure.

**Apparatus.**—A distillation apparatus which could be loaded and emptied in a dry-box was constructed. It consisted of a Vycor collection finger which could be cooled by passing air or water through it, and a tantalum heating shield 0.96 cm. in diameter and 5.1 cm. high, whose top was 0.63 cm. below the collection finger. This shield, made from 2 mil tantalum sheet, was forced onto a tantalum block which served as the bottom. A molybdenum radiation shield surrounded the heating shield which was heated by induction. The assembled unit was supported by a tungsten rod penetrating a Pyrex 29/42 standard taper joint. A Pyrex envelope surrounded these units and connected them to the vacuum system.

**Procedure.**—Samarium turnings and $Sm_2O_3$ were placed in a small (about 0.6 cm. × 0.2 cm.) tantalum crucible and set in the heating shield. The system was closed and evacuated to $10^{-5}$ mm. pressure on a liquid air trapped mercury high vacuum system while the shield was heated to about 800° for degassing. After a minimum of two hours at this pressure the system was filled with Airco welding grade argon to a pressure of 720 mm. and heated to 1100–1300°. If purified argon was used, the same products were obtained, but in reduced yields. A distillate was collected when the heating shield reached temperatures of 1125° and above. After no more sublimate was collected under 1300°, the system was evacuated to a $10^{-6}$ mm. pressure and taken into the dry-box whose argon atmosphere was purified by K-Na alloy and $MgClO_4$.

The distillate was removed from the cold finger; part of it was placed in a capillary for X-ray analysis while the remainder was prepared for chemical or gravimetric analysis.

**Analyses.**—The samples were found to be free from nitrogen as tested by the Kjeldahl method. There was no carbon containing vapor in the system, so a carbide could not have been formed. A spectographic analysis, performed by Dr. V. A. Fassel, Ames Laboratories, Ames, Iowa, indicated that the cation of the compound was greater than 99.8% samarium, thus eliminating heavy metal compounds.

X-Ray intensity data on reflections from planes (331) and (420), those most sensitive to the presence of anions, were obtained with a spectrometer using iron radiation. These data confirmed the presence of an anion, assumed to be oxygen, in the lattice.

X-Ray powder diagrams were taken with a 114.7 mm. Debye–Scherrer powder camera. Either Cu K$\alpha$ ($\lambda_{\alpha_1}$ = 1.54051 × $10^{-8}$ cm.) or Fe K$\alpha$ ($\lambda_{\alpha_1}$ = 1.93597 × $10^{-8}$ cm.) radiation was used. The intensity was calculated according to the formula $I = LPAjF^2T$ (where $LP = (1 + \cos^2 2\theta)/(\sin^2\theta \cos\theta)$; $A$ is the absorption factor calculated according to the method of Bradley[4]; $T$ is the temperature factor calculated from an estimated characteristic temperature, $\Theta$, equal to 350; $j$ is the multiplicity factor which is the same for both lines; $F$ is the structure factor[5] with the atom form factor for samarium corrected for dispersion with iron radiation according to the method of Dauben and Templeton.[6] The observed ratio of $I_{331}/I_{420}$ was 1.025 ± 0.002, indicating an anion deficient zinc blende-type face centered cubic structure of composition $SmO_{0.30\ \pm 0.05}$. (The limit of error in this case indicated the precision of the measurements.)

Two procedures of gravimetric analysis were followed. In the first method samples were sealed into small weighed micro-bulbs in the dry box. They were then removed from the dry box, reweighed and broken onto a tared platinum crucible which was then heated to constant weight forming the sesquioxide. The heated residue was carefully dissolved with concentrated nitric acid and the crucible washed and heated to constant weight. In this way a correction was made for any glass that was admitted with the sample. These weights were made on an Ainsworth F.D.J. optical lever microbalance (sens. 1.5 mcg./div.).

These analyses showed that the samples oxidized rather slowly upon exposure to air at room temperature and were not pyrophoric unless metal was present.

The other procedure was to place some of the sample directly onto a weighed platinum crucible, put the crucible into a weighing bottle, and close it. The weighing bottle was taken out of the dry box and the sample was removed and weighed on a quartz fiber balance (sens. 0.12389 mcg./div.) within one minute after exposure to the atmosphere. The samples were then carefully heated to constant weight.

Table I shows the composition as well as the lattice parameter (when available) of a series of preparations.

Table I

Data on Zinc Blende-Type Phase of Samarium Oxide

| Weight (mg.) | O/Sm | Lattice constant (Å.) |
|---|---|---|
| 4.884 | 0.49 | 5.3761 ± 0.0003 |
| 2.916[a] | .29 | |
| 4.909 | .40 | 5.3698 ± .0006 |
| 6.218 | .60 | 5.372 ± .002 |
| 4.872 | .49 | 5.3764 ± .0007 |
| 0.776[b] | .56 | 5.3790 ± .0008 |
| .2856[b] | .61 | 5.3725 ± .0008 |
| .5239[b] | .55 | |
| 1.7439[a] | .32 | |
| 0.6624[b] | .61 | |
| .7308[b] | .43 | |
| 1.0312[b] | .41 | |
| Av. | .48 | |

[a] Samarium metal observed to be present. [b] Only the initial portion of the distillate was analyzed.

## Discussion

**ZnS-type Lower Oxide of Samarium.**—The conditions for the preparation of this zinc blende-type phase were very exacting. The system had to be absolutely anhydrous and the temperature controlled carefully. On long distillation the resulting sublimate was not always monophasic, but sometimes contained two different oxide phases as well as metal. The initial portion of the distillate was always the zinc blende-type phase; therefore only this portion was analyzed in the later experiments. Consequently, the amount of material analyzed was very small in some cases.

The results show that this zinc blende-type phase varied in composition between $SmO_{0.4}$ and $SmO_{0.6}$. The lattice parameter varied between 5.3698 ± 0.0006 and 5.3790 ± 0.0008 Å. There was no linear correlation between lattice parameter and composition.

This compound appears to be an anion deficient oxide whose composition is determined by the specific conditions of preparation. It oxidized to the cubic form of the sesquioxide slowly at low temperatures and very rapidly at about 300° on exposure to air.

When this ZnS-type lower oxide is heated in vacuum, material is transported to the cold finger. X-Ray powder diffraction of the distilled material shows the ZnS-type lower oxide and another phase which on the basis of fragmentary analysis seems to correspond to a still lower oxide of samarium of composition near $SmO_{0.1}$.

**NaCl-type Lower Oxide of Samarium.**—The residue in some of the experiments reported above contained a reddish colored compound with a NaCl-type face centered cubic structure and a lattice parameter of 5.00 ± 0.02 Å. This phase resulted from the combination of samarium metal and $Sm_2O_3$ and possible residual oxygen in the argon atmosphere, and is believed to be SmO. The best value obtained was 4.9883 ± 0.0003 Å. However,

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(4) A. J. Bradley, *Proc. Phys. Soc. (London)*, **47**, 879 (1935).

(5) "Internationale Tabellen zur Bestimmung von Kristallstrukturen," V. 2, Gebruder Borntraeger, Berlin, 1935, pp. 571–573.

(6) C. H. Dauben and D. H. Templeton, *Acta Cryst.*, **8**, 841 (1955).

Eick, Baenziger and Eyring[7] have observed that SmN has a NaCl-type structure with a lattice parameter of 5.0481 Å. Using an argon atmosphere containing nitrogen and oxygen and a trace of water, NaCl-type phases varying in lattice parameter from 5.00 to 5.05 Å. were obtained. These phases were considered to be mixed nitride–oxides.

On the basis of these experiments it appears probable that the compound of varying lattice parameter reported by Ellinger and Zachariasen[3] is a samarium oxide–nitride whose upper limit is SmN. The compound obtained from the reaction of samarium and $Sm_2O_3$ is believed to be the pure monoxide. Many other powder diagrams (non-indexable because of small particle size) were obtained whose parameters were similar to this one. Oxide–nitride solutions in the vanadium system have been observed.[8]

**NaCl-type Lower Oxide of Europium.**—In order to prepare lower oxides of europium, $Eu_2O_3$ was added to filings of lanthanum metal in a way entirely analogous to the preparations using $Sm_2O_3$ and samarium metal described above except that the temperature range of treatment was 1300–1500°. In this procedure the lanthanum reduced the $Eu_2O_3$ to metal and/or the lower oxide. The lanthanum and $La_2O_3$ are not volatile, and hence do not contaminate the sublimate.

These europium preparations were found to contain a NaCl-type phase with a lattice parameter of 5.1439 ± 0.0005 Å. Kjeldahl determinations demonstrated that nitrogen was absent. From visual observations of the intensity of the reflections from planes (331) and (420) the compound was assumed to be EuO. Brauer and others[9,10] have reported preparing EuO·SrO, and Klemm and Senff[11] have reported the $Eu^{+2}$ ion to be 0.03 Å. smaller than the $Sr^{+2}$ ion. The lattice parameter of SrO (from kX. units) is 5.154 Å. The value reported above agrees very well with what would be expected from these data for EuO; therefore the compound is believed to be EuO.

When EuO was formed together with EuN in a few experiments by using nitrogen containing a trace of oxygen, a lattice constant as small as 5.1328 ± 0.0008 Å. was observed. This shrinking of the lattice parameter possibly resulted from the partial solution of EuO in EuN. The EuN parameter did not change.

**Comparison of NaCl-type Samarium and Europium Compounds.**—From the data on SmN ($a_0$ = 5.0481 ± 0.0004 Å.) and EuN ($a_0$ = 5.007 ± 0.004 Å.) recently absérved,[7] it is apparent SmO has a smaller lattice constant than SmN while the reverse is true for the europium compounds. SmN is larger than EuN as might be expected from the lanthanide contraction, but, in contrast, EuO is larger than SmO. This apparent anomaly in the case of the monoxide suggests a different type of bonding in the two compounds.

Another example analogous to the SmN–SmO system besides VN–VO is TiN[12]–TiO.[13] On the other hand there are examples such as the PuO[14]–PuN[15] system in which the oxide has a larger unit cell than the nitride as in the EuO–EuN system.

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[8] V. A. Epel'baum and A. Kh. Breger, *Z. Fiz. Khim. SSSR*, **20**, 459 (1946); *Acta Physicochim.* (*USSR*), **21**, 764 (1946).

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[10] G. Brauer, R. Muller and K. H. Zapp, *Z. anorg. allgem. Chem.*, **280**, 40 (1955).

[11] W. Klemm and H. Senff, *ibid.*, **241**, 259 (1939).

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