

AUG 15 1966

[Reprinted from the Inorganic Chemistry, 5, 754 (1966).]

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Phase Relationships in the Rare Earth Sesquioxides at High Pressure^{1,2}

By HENRY R. HOEKSTRA

Received December 13, 1965

Phase relationships in the rare earth sesquioxides have been studied at pressures from 15 to 60 kbars at 550, 1000, and 1450°. No measurable shift is observed in the boundary between the hexagonal (A) and monoclinic (B) phases, but stability of the monoclinic phase relative to the cubic phase is enhanced by increased pressure as well as higher temperature. The C-B phase transformations are shown to be reversible. Lattice parameters are given for 11 monoclinic sesquioxides—Y₂O₃ and Sm₂O₃ through Lu₂O₃. The entropy increase involved in the transformation from the cubic to monoclinic structure is estimated to be 1.5 eu.

The rare earth sesquioxides were first investigated systematically by Goldschmidt and his co-workers³ in

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

1925. The great similarity in the chemical properties of the individual lanthanides had effectively prevented the isolation of sufficiently pure samples for any de-

(3) V. M. Goldschmidt, F. Ulrich, and T. Barth, *Skrifter Norske Videnskaps-Akad. Oslo, I: Mat. Naturv. Kl.* No. 5 (1925).

tailed study of the sesquioxides to that date. Goldschmidt's work showed that, despite the relatively small variation in cation radius between lanthanum (1.06 Å) and lutetium (0.85 Å),⁴ one encounters three distinct structure types in the sesquioxide series. During the past 40 years the lanthanide oxides have been studied by numerous workers who have determined the crystal structures of the three sesquioxide phases and have investigated the phase relationships among them. Goldschmidt's original designations for the phases (A, B, and C) are still in use today.

Type A⁵ is hexagonal, space group $P\bar{3}m1$, and contains one molecule per unit cell. Each trivalent cation is bonded to seven oxygen atoms (four short bonds and three long bonds), while the two types of oxygen atoms are bonded to five and four metal atoms, respectively.

Type B,⁶ space group $C2/m$, is monoclinic, contains six molecules in each unit cell, and also shows a seven-fold coordination of the cation. The crystal lattice has three different cation sites and five different anion sites which bond to four, five, or six metal ions.

Type C⁷ is cubic, space group $Ia\bar{3}$, with 16 molecules per unit cell. It is derived from the simple fluorite lattice by doubling the lattice parameter and by leaving one-fourth of the anion sites vacant. The resulting coordination is 6:4.

The stability fields of the three structure types, as established by recent studies, are outlined in Figure 1.⁸ The A $\leftrightarrow$ B boundary line is vertical or nearly so between neodymium and samarium. Recent studies by Weigel⁹ indicate that Pm_2O_3 may be the only rare earth sesquioxide to crystallize in all three structural modifications. Since the A-B phase boundary is virtually independent of temperature, there is little opportunity to study reversibility between these phases. The C $\leftrightarrow$ A transformation does not appear to be reversible, except through a hydration-dehydration step. Location of the B $\leftrightarrow$ C phase boundary line has been fairly well established; further extension of the line to higher temperatures is prevented by fusion of the sesquioxides. Thus, Y_2O_3 and the five heaviest rare earth oxides exist in only the cubic form at ambient pressure. The B $\leftrightarrow$ C transformation has been shown to be reversible for pure Dy_2O_3 , Tb_2O_3 , and Gd_2O_3 and for Sm_2O_3 and Eu_2O_3 in the presence of water as a catalyst.

The preceding investigations have been carried out at atmospheric pressure or in hydrothermal studies to 24,000 psi (~ 1.6 kbars). A comparison of molar volumes of the three structure types suggested that high pressure should lead to a shift in phase boundaries. The B-type structure should be favored over the C-type, and the hexagonal (A) type over both of the other structure types. The shift from 6:4 coordination with oxygen vacancies to the 7:(4, 5, 6) coordination of the monoclinic form produces a substantial ($\sim 8\%$)

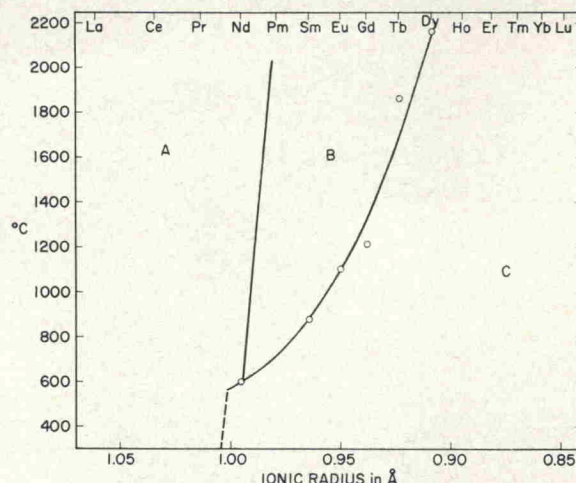


Figure 1.—Stability relationships of rare earth sesquioxides.

volume decrease, while the monoclinic to hexagonal phase change produces only a minor volume change. Since the phase transformations are of the reconstructive type, which involve rearrangement of the atoms or ions in the solid, rather than a minor displacement in their positions, it would be expected that any change brought about at high pressure and temperature would be retained upon release of pressure.

In a recent preliminary note Hoekstra and Gingerich¹⁰ reported the preparation of the monoclinic (B) form of six rare earth oxides which had previously been known only in the cubic (type C) form—namely, Ho, Er, Tm, Yb, Lu, and Y sesquioxides. The phase changes were shown to be reversible. The present report represents a continuation of the high-pressure work on the lanthanide sesquioxides; it outlines the B $\leftrightarrow$ C phase equilibrium surface as a function of ionic radius, temperature, and pressure. Entropy and enthalpy changes in the cubic-to-monoclinic phase transformations are estimated.

Experimental Section

Materials and Methods.—Rare earth sesquioxides (99.9+ % purity) were annealed in air at 1000° for several hours to remove water and CO₂. Terbium and praseodymium sesquioxides were prepared by reduction of Tb_4O_7 and Pr_6O_{11} with hydrogen at 900°. X-Ray diffraction studies indicated the existence of La_2O_3 , Pr_2O_3 , and Nd_2O_3 in the hexagonal (A) form, the remaining sesquioxides (Sm_2O_3 through Lu_2O_3) were obtained in the type-C form.

High-Pressure Technique.—A 2000–8000-ton, tetrahedral-anvil, high-pressure apparatus of the type designed by Hall¹¹ was used in this study. Pyrophyllite was employed as the solid pressure-transmitting medium. The pyrophyllite tetrahedra were 5.5 cm on an edge and contained a cylindrical sample cavity measuring about 1 cm in diameter and 1.5 cm in length. Figure 2 illustrates a typical sample assembly in cross section, with graphite heater and end caps, pyrophyllite liner, spacers, and prisms, molybdenum tabs, and sample disks. From one to four sesquioxide samples were treated in each high-pressure run. The oxide powders were placed in 2-mil Pt-foil cups, covered with a Pt-foil disk, and given a preliminary pressure treatment at 0.4 kbar in a steel die. The platinum envelope effectively isolated the oxide samples from any possible reaction with the pyrophyllite liner and spacers.

Electrical power was supplied to the high-pressure apparatus

(4) Ionic radii taken from D. H. Templeton and C. H. Dauben, *J. Am. Chem. Soc.*, **76**, 5237 (1954).

(5) L. Pauling, *Z. Krist.*, **69**, 415 (1929).

(6) D. T. Cromer, *J. Phys. Chem.*, **61**, 753 (1957).

(7) L. Pauling and M. D. Shappel, *Z. Krist.*, **75**, 128 (1930).

(8) I. Warshaw and R. Roy, *J. Phys. Chem.*, **65**, 2048 (1961).

(9) F. Weigel, private communication.

(10) H. R. Hoekstra and K. A. Gingerich, *Science*, **146**, 1163 (1964).

(11) H. T. Hall, *Rev. Sci. Instr.*, **29**, 267 (1958).

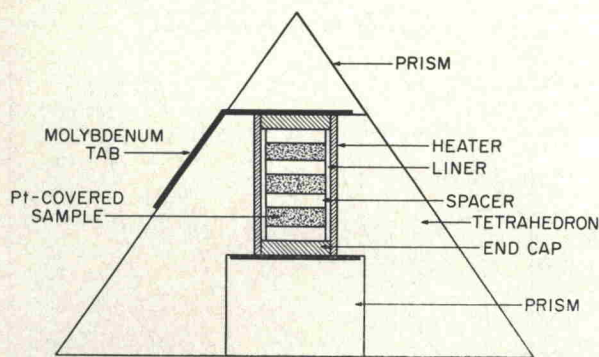


Figure 2.—High-pressure sample assembly.

by a 20-kw transformer for heating currents to 1500 amp and voltages to 10 v. Power was fed to the graphite heater by means of molybdenum tabs which contacted the two anvil faces to which power leads from the transformer were attached. Temperature measurements were made with a ceramic-coated Pt—Pt-13% Rh thermocouple sheathed in stainless steel. The thermocouple bead was located at the midpoint of the pyrophyllite liner surrounding the sample disks. Temperatures could be read to $\pm 1^\circ$. The high-pressure experiments were run principally at three temperatures: 550° (the lowest temperature at which equilibration occurred at a reasonable rate), 1000° , and 1450° . Temperatures were maintained within $\pm 5^\circ$ at 550° , $\pm 10^\circ$ at 1000° , and $\pm 25^\circ$ at 1450° . Heating times were generally 1 hr at 550° , 30 min at 1000° , and 5 min at 1450° .

The range of pressures investigated was from 15 to 60 kbars in intervals of 5 kbars. Calibration points used were 25.3 kbars for the Bi(I $\rightarrow$ II) transition,¹² 40 kbars for the Yb transition,¹³ and 59 kbars for the Ba transition.¹² The sequence of operations in a typical run included application of the desired pressure, heating to high temperature, maintenance of high temperature and pressure to allow approach to equilibrium, quenching to room temperature (a few seconds), then gradual release of pressure over a 5–10-min period. Samples were then removed for investigation by X-ray diffraction. X-Ray data were obtained with a Phillips 114.59-mm diameter powder camera using Ni-filtered Cu radiation.

Results

Unit Cell Parameters and Molar Volumes.—The monoclinic (B) form of Ho, Er, Tm, Yb, Lu, and Y sesquioxides was prepared at each of the temperatures investigated. Complete conversion to the B modification could be achieved in 1 hr at 550° only when the pressure was maintained 10–15 kbars above the “equilibrium” pressure, as established by the first appearance of the monoclinic phase in the cubic oxide. The B-type sesquioxides which can be synthesized at ambient pressure and high temperature (Sm_2O_3 through Tb_2O_3) were also prepared at each of the three temperatures in the high-pressure experiments. No evidence was obtained, however, for any shift in the A $\leftrightarrow$ B phase boundary line at pressures to 60 kbars. Unit cell parameters were calculated for each of the monoclinic oxides (Table I). The $\sin^2 \theta$ values were corrected for absorption by using a working graph obtained from a plot of the A values against $\sin^2 \theta$, where the A values are quantities proportional to the reciprocal lattice constants. New values for the hexagonal sesquioxides were also obtained. The data on the new monoclinic

TABLE I

RARE EARTH SESQUIOXIDE CELL PARAMETERS

Hexagonal	a (± 0.003), Å	c (± 0.005), Å		
La_2O_3	3.938	6.128		
Pr_2O_3	3.857	6.016		
Nd_2O_3	3.829	6.002		
Monoclinic	a (± 0.01), Å	b (± 0.003), Å	c (± 0.008), Å	β (± 0.05), deg
Sm_2O_3	14.18	3.636	8.841	99.92
Eu_2O_3	14.12	3.600	8.801	99.98
Gd_2O_3	14.08	3.571	8.764	100.03
Tb_2O_3	14.04	3.541	8.725	100.06
Dy_2O_3	13.97	3.519	8.661	100.00
Ho_2O_3	13.90	3.492	8.592	99.98
Y_2O_3	13.91	3.483	8.593	100.15
Er_2O_3	13.87	3.470	8.555	100.17
Tm_2O_3	13.81	3.447	8.505	100.20
Yb_2O_3	13.73	3.425	8.452	100.17
Lu_2O_3	13.70	3.410	8.425	100.22

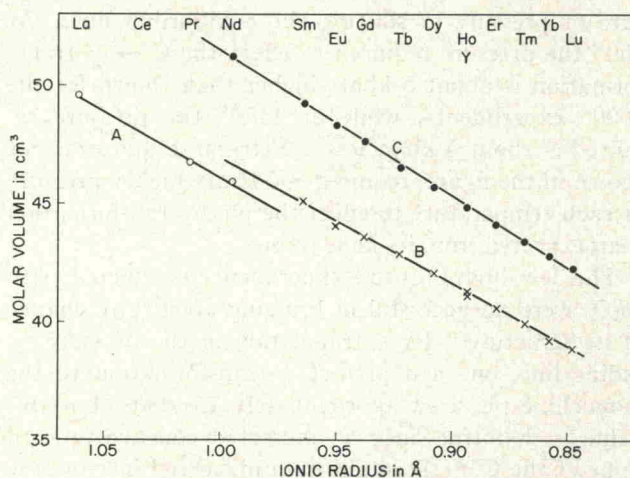


Figure 3.—Molar volumes of rare earth sesquioxide phases.

phases were found to be in good agreement with an extrapolation of results reported previously by Roth and Schneider¹⁴ for the ambient pressure-stable members of the series. The single exception is the fact that the angle β is shown to increase slightly in going from samarium to lutetium sesquioxide, while the earlier data had indicated a gradual decrease in the angle.

These results now permit a more extensive comparison of molar volumes among the three structure types in the lanthanide sesquioxides. Within the limits of error, the observed lanthanide contractions in the A- and B-type phases as shown by Figure 3 are identical, while the C-type structure shows a somewhat greater decrease in volume with decreasing cation radius.

Phase Relationships.—As indicated earlier, location of the B $\leftrightarrow$ C equilibrium line as a function of pressure and cation radius has been studied at three temperatures. Figure 4 illustrates the results obtained at 1000° . One observes that the shape of the pressure-ionic radius curve resembles the temperature-ionic radius plot shown in Figure 1. Thus, both high pressure and high temperature tend to stabilize the monoclinic phase relative to the cubic phase. The effect of ionic radius is, however, much greater than tempera-

(12) R. H. Wentorf, "Modern Very High Pressure Techniques," Butterworth Inc., Washington, D. C., 1962.

(13) P. C. Souers and G. Jura, *Science*, **140**, 481 (1963).

(14) R. S. Roth and S. J. Schneider, *J. Res. Natl. Bur. Std.*, **A64**, 309 (1960).

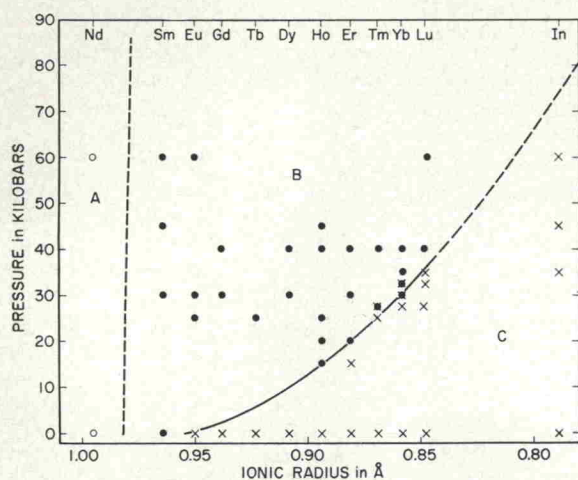


Figure 4.—Rare earth sesquioxides: 1000° isotherm.

ture or pressure in shifting the equilibrium line. At 550° the pressure required to effect the $C \rightarrow B$ transformation is about 5 kbars higher than shown for the 1000° experiments, while at 1450° the pressure required is about 5 kbars less. Yttrium sesquioxide, not shown in the figure, required ~ 5 kbars higher pressure at each temperature to effect the phase transformation than expected from its ionic radius.

The few high-pressure experiments conducted with In_2O_3 were unsuccessful in bringing about any change in its structure. By extrapolation of the pressure *vs.* radius line, one can predict a transformation to the monoclinic phase at approximately 75 kbars, but this value is doubtful since an increased concave upward slope of the $C \leftrightarrow B$ equilibrium line could increase the pressure required by a significant amount.

Figure 5 illustrates how high pressure alters the location of the $C \leftrightarrow B$ equilibrium in a cation radius *vs.* temperature plot. The equilibrium shift is noticeably greater in the interval between 1 atm and 20 kbars than it is in the 20 to 40 kbars interval.

Reversibility of the $C \leftrightarrow B$ phase transformation in the six new monoclinic sesquioxides was confirmed by annealing the B phases in air at ambient pressure and 900° for several hours. The cubic phase was obtained as a product in all experiments. Reversibility was also checked in several high-pressure experiments operated

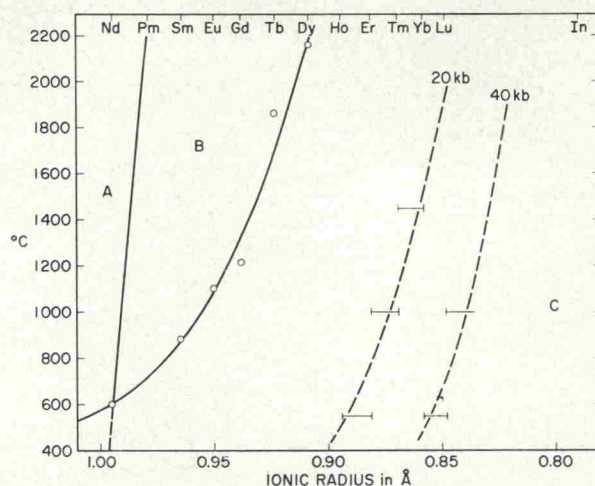


Figure 5.—Pressure effect on sesquioxide phase equilibria.

on the C-stable side of the equilibrium line. In each instance the conversion from monoclinic to cubic phase was confirmed.

Annealing experiments were run to study the phase equilibrium in Gd_2O_3 , Eu_2O_3 , and Sm_2O_3 . After 3 weeks at 950°, both the gadolinium and europium monoclinic sesquioxides showed partial conversion to the cubic phase. Reversibility of the $B \leftrightarrow C$ phase transformation has now been established for all sesquioxides except Sm_2O_3 . The indicated equilibrium temperature for Sm_2O_3 , 875°, is so low that equilibration should be extremely sluggish. However, all indications are that the $B \rightarrow C$ transformation is possible and that a reversible system exists for all members of the series.

The high-pressure data, qualitative as they are, do permit an estimation of the entropy and enthalpy change in the cubic-to-monoclinic phase transformation. One observes an approximate 5-kbar decrease in transition pressure for a 450° increase in temperature. Application of the Clapeyron equation indicates that the $C \rightarrow B$ phase change results in an entropy increase of 1.5 eu and an enthalpy change of some 2 kcal/mole.

Acknowledgment.—The author is indebted to Frank Gallagher and Roger Cramer, who assisted with some of the high-pressure experiments and the crystal structure calculations.

