is the diffusion coefficient of heptane in carbon tetrachloride, and t is time (*7*). For the parameters involved ($l \simeq 5$ cm, $D \simeq 10^{-5}$ cm²/sec) there can be only 0.06 percent heptane, even after 30 hours, in the carbon tetrachloride as a result of diffusion from the front.

A. TIMUR
I. FATT

College of Engineering,
University of California, Berkeley

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6. The uncertainty is from the standard deviation of the mean of the proportionality constant which in turn is based on six calibration runs.
7. The abbreviation erfc refers to a complementary error function.
8. Supported in part by grant 450A from the Petroleum Research Fund administered by the American Chemical Society.

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High-Pressure B-Type Polymorphs of Some Rare-Earth Sesquioxides

Abstract. *New high pressure forms of the sesquioxides of holmium, erbium, thulium, ytterbium, lutetium, and yttrium have been obtained by exposure of the C-type sesquioxides to pressures between 25 and 40 kilobars and temperatures between 900° and 1020°C. X-ray diffraction analysis shows that these new high-pressure phases are of the monoclinic B-type which is known for several of the lighter rare-earth sesquioxides (samarium through dysprosium).*

The crystal chemistry of the rare-earth sesquioxides was first studied in a systematic manner by Goldschmidt, Ulrich, and Barth (*1*). They found that these compounds could exist in three polymorphic forms, which were denoted as A, B, and C. This classification is still in use. The crystal structure of these polymorphs has been determined in a number of investigations (*2*). According to these, the A-modification is hexagonal (space group $P\bar{3}m1$), the B-modification is monoclinic (probably $C2/m$), and the C-modification is cubic ($Ia3$).

In their study of the stability relationships of the sesquioxide polymorphs (*1, 3*) Goldschmidt and his coworkers considered all phase transformations to be reversible. Subsequent studies (*4*) showed that for pure oxides the C → A and C → B transformations could be produced but not reversed, and no conclusive proof could be found for any transition between A and B modifications. Roth and Schneider (*5*) concluded that the C-modifications observed for some of the lighter rare earth oxides are metastable with respect to either the A- or B-form and that each rare earth sesquioxide is stable in only one of the three polymorphic forms.

Other recent investigations have modified this conclusion concerning the C → B transformation. Thus, the change has been shown to be reversible for pure Dy_2O_3 and Tb_2O_3 (*6, 7*), for Gd_2O_3, Eu_2O_3, and Sm_2O_3 in the presence of water as a catalyst (*8*), and is rendered reversible in Eu_2O_3 by stabilization of the C phase with ThO_2 (*8*). From these observations Warshaw and Roy (*6*) concluded that the sesquioxides of samarium through dysprosium exist in two stable enantiotropic forms with a transformation temperature that increases almost linearly with decreasing ionic radius. The apparent irreversibility of the B → C transformation in pure dry samarium, europium, and gadolinium sesquioxides is most likely due to unfavorable kinetics at the equilibrium temperatures.

At the present time the sesquioxides of yttrium, holmium, erbium, thulium, ytterbium, and lutetium have been found in only one crystalline form, the C type. Extrapolation of the temperature curve of the C → B transformation predicts conversion to the monoclinic phase above their melting points with the possible exception of yttrium sesquioxide.

In all previous investigations, the primary object has been the study of temperature effects on the crystal chemistry of the rare-earth (R) sesquioxides; the role of pressure has not been systematically investigated. From the fact that there is a decrease in volume per mole of R_2O_3 in going from C → B → A (Fig. 1) one expects that high pressures should favor the B- and A-forms over the C-form, and the A-form over the B-form. Since these transformations are of the reconstructive type, it can be expected that new high-pressure modifications could be retained by temperature and pressure quenching to ambient conditions.

In our investigation the influence of pressure on the C-type phases of the heavy rare-earth sesquioxides has been studied at elevated temperatures. Rare-earth sesquioxides of the C-type (99.9+ percent purity) which had been annealed in air at 1000°C for several hours to remove H_2O and CO_2 were used as starting material. Terbium sesquioxide was prepared by reduction of Tb_4O_7 with hydrogen.

For the high-pressure experiments a tetrahedral anvil apparatus (*9*) was used. In the pressure calibration a value of 25.3 kb was assumed for the Bi (I → II) transformation (*10*) and 40 kb for the Yb transformation (*11*).

Oxide samples (about 0.4 g) were placed in Pt envelopes (2 mil) and pressed to pellets at 0.4 kbar. Several pellets, separated by pyrophyllite spacers, were then placed in a pyrophyllite tube which fitted the graphite heater inside the pyrophyllite tetrahedron. Graphite disks were inserted at both ends of the heater to assure good contact with molybdenum tabs through which the power connections were made. The temperature was measured by a ceramic-coated thermocouple consisting of Pt and Pt containing 13 percent Rh encased in a stainless steel sheath (0.1 cm outside diameter). The thermocouple bead, coated with alundum cement, was located in the pyrophyllite tube containing the sample pellets. Temperatures could be read to ±1°C; fluctuations during a run were usually kept to within ±10°C, in some cases ±20°C. After the treatment at high pressure and high temperature,

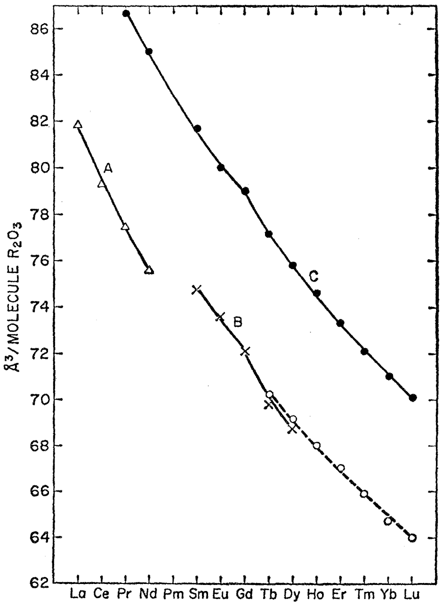

Fig. 1. Molecular volume of rare earth sesquioxide crystal modifications. Solid line, previous work; broken line, this work.

Table 1. Pressure-temperature conditions used in synthesis of B-type sesquioxides.

Sesquioxide	Pressure (kb)	Temp. (°C)
Yttrium	25	1000
Samarium	30	1020
Europium	25	905
Gadolinium	30	1020
Terbium	25	905
Dysprosium	30	1020
Holmium	25	1000
Erbium	30	1020
Thulium	40	1005
Ytterbium	40	1000
Lutetium	40	1005

* Heating time 30 minutes.

samples were quenched within a few seconds to approximately 50°C by turning the power off. Pressure was then released gradually over a 5- to 10-minute period. Samples were subsequently investigated at ambient conditions by x-ray diffractometer and film techniques.

We have prepared and retained at ambient conditions the B-modification of all previously unknown heavy rare-earth sesquioxides—Ho_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, and Lu_2O_3—and the B-form of Y_2O_3. Our experiments also indicate that the B-form of europium, gadolinium, terbium, and dysprosium sesquioxides can be prepared at substantially lower temperatures at high pressure than at atmospheric pressure. The conditions under which the new B-phases were synthesized are listed in Table 1.

Preliminary calculations for the lattice constants of the new phases (*12*) indicate that they agree with those predicted by extrapolation of previously known B-type sesquioxide parameters under consideration of the lanthanide contraction of the trivalent ions. The volume per R_2O_3 molecule obtained for these phases is included in Fig. 1.

Reversibility of the pressure-induced phase changes was checked for all B-type phases reported in Table 1 by heating them in air at 1000°C for several hours. Under these conditions all sesquioxides with the exception of those of europium and gadolinium reverted to the C-modification. This shows that the C → B pressure transformation is reversible for all new B-type phases and confirms the results of others on the pure dry samples of previously known B-type sesquioxides.

At present we are studying the temperature-pressure conditions under which the reversible C ↔ B transformation takes place for the various sesquioxides. Qualitative conclusions concerning the effect of pressure on the transformation temperature of a given oxide and the effect of the ionic radius can be derived from the experimental conditions listed in Table 1 and from the observation that, at 25 kb and 1000°C, C-type thulium sesquioxide did not transform into the B-modification and that, at 30 kb and 1000°C, only a small fraction of C-type ytterbium sesquioxide transformed into the B-modification. Thus, high pressure lowers the transformation temperature of a given sesquioxide whereas decreasing ionic radius of the metal component of the sesquioxide increases the transformation pressure.

We do not, at this time, have direct evidence for a B → A conversion in any of the samples investigated. Poor crystallinity of Sm_2O_3 samples heated at about 50 kb suggests that transformation to the hexagonal phase was imminent or that it had occurred but reverted to the monoclinic phase on release of pressure.

Our results reopen the problem of the polymorphy of the rare-earth sesquioxides by including pressure as a new variable. They prove that more rare-earth sesquioxides than had previously been expected can stably exist in more than one crystalline form. They confirm the enantiotropic nature of the C ↔ B transformation as advocated by Roy and co-workers (*6*, *7*), and show a wide occurrence of the monoclinic sesquioxide structure. It is likely that other C-type oxides, such as the thallium and indium sesquioxide, may form the B-modification at high pressures. Further work may also lead to reversible transitions between the A and B types and possibly the A- and C-modifications. The new B-type sesquioxides reported here appear to be true high-pressure phases which are metastable at atmospheric pressure at all temperatures. A possible exception is B-type yttrium sesquioxide, which may form between 2000°C and its melting point.

HENRY R. HOEKSTRA
KARL A. GINGERICH
Chemistry Division, Argonne National Laboratory, Argonne, Illinois

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Mayfly Distribution Indicates Water Quality on the Upper Mississippi River

Abstract. *Hordes of mayflies emerge during the summer months from most sections of the Upper Mississippi River, thus creating nuisance problems for shoreline residents and river traffic. The presence of these pollution-sensitive forms indicates, however, that the river is more river-like than sewer-like in a given area.*

People who live along most of the Upper Mississippi River are accustomed to periodic invasions by hordes of mayflies (Insecta: Ephemeroptera). Tree limbs droop under their weight, and drifts of the insects form under street lights where they decay and create objectionable odors. Shoppers desert downtown areas as the large, clumsy insects fly in their faces, cover windows, and blanket sidewalks. In extreme cases snowplows are called out to reopen highway bridges which have become impassable. Particles of cast mayfly cuticle cause allergic reactions in some people (*1*). Mayflies become a hazard to navigation when they are attracted by the powerful arc and mercury-vapor searchlights used by towboats to spot unlighted channel markers.

An analysis of data collected over a 7-year period indicates, however, that the systematic collection of pollution-sensitive species such as the mayfly can provide a reliable and economical method for determining the state of well-being of a river. It is ironi