THERMAL EXPANSION AND PHASE INVERSION OF RARE-EARTH OXIDES

By Stephan Stecura and William J. Campbell

* * * * * report of investigations 5847

UNITED STATES DEPARTMENT OF THE INTERIOR
Stewart L. Udall, Secretary

BUREAU OF MINES
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This publication has been cataloged as follows:

Stecura, Stephan

Thermal expansion and phase inversion of rare-earth oxides,
by Stephan Stecura and William J. Campbell. [Washington]
U. S. Dept. of the Interior, Bureau of Mines [1961]

ii, 47 p. illus., tables. 27 cm. (U. S. Bureau of Mines. Report
of investigations, 5847)

Bibliography: p. 46-47

1. Rare-earth oxides--Thermal properties. I. Campbell, William
J. joint author. II. Title. III. Title: Phase inversion of rare-
earth oxides. (Series)

[TN23.U7 no. 5847] 622.06173

U. S. Dept. of the Int. Library

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THERMAL EXPANSION AND PHASE INVERSION OF RARE-EARTH OXIDES¹

by

Stephan Stecura² and William J. Campbell^{3 4}

SUMMARY

One of the principal objectives of the Bureau of Mines program for development of superrefractory ceramic materials is to obtain fundamental data on the physical properties of refractory oxides. Elements of particular interest to research workers in the Bureau include groups III and IV of the Periodic Table and the rare-earth group. This report contains thermal expansion and phase inversion measurements on oxides of scandium, yttrium, lanthanum and 12 lanthanide series elements (promethium and terbium omitted) up to 1,350° C. made by high-temperature X-ray diffractometer techniques.

Thermal expansion values were calculated from unit cell dimensions measured at selected temperatures; with anisotropic oxides expansion was determined parallel to each major crystallographic axis. The combined random and systematic errors in the thermal expansion values are considered to be less than 3 percent of the total expansion at 500° C. and approximately 2 percent at 1,000° C. No difference in expansion coefficients was observed between heating and cooling cycles for oxides that did not undergo phase inversion. Tabular data of linear expansion, in percent, linear expansion coefficients, and graphical presentation of linear expansion as a function of temperature are presented.

Phase inversions were determined by either the disappearance of the characteristic diffraction lines of the lower temperature phase, or by the appearance of the new high-temperature phase. All phase inversions of the rare-earth sesquioxides were time-temperature dependent.

¹Work on manuscript completed October 1960.

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Commercially available high-purity oxides were used throughout the study. Because of the common practice of the suppliers to report purity in terms of other rare earths, the suppliers' data were supplemented by optical spectrographic analyses.

INTRODUCTION

This investigation was undertaken as part of the Bureau of Mines program for the development and evaluation of high-temperature ceramic materials. One of the principal objectives of the program is to obtain fundamental data on the physical properties of refractory oxides; elements of particular interest include groups III and IV of the Periodic Table and the rare-earth group.

Many of the rare-earth oxides have high melting points, are stable at elevated temperatures in oxidizing atmospheres, and do not undergo phase inversion; therefore these oxides warrant consideration as refractory materials. Samarium and gadolinium oxides are of special interest in the nuclear field because of their very high thermal neutron absorption cross-sections.

The term "rare earths" is a misnomer because the elements are metals, not earths, and, secondly, as a group they are not particularly uncommon. Several of the lanthanide elements are more common than tin, silver, cadmium or tungsten, for example, cerium. Although most of the rare-earth oxides are still expensive (due primarily to the involved separation process) the prices have dropped rapidly during the past few years, for instance, ceric oxide is available for approximately \$5 a pound in lots of 100 pounds.

Thermal expansion is one of the more important physical properties to be determined on materials considered for application at elevated temperatures. Materials with high thermal expansion coefficients must be subjected to carefully controlled heating and cooling rates to avoid mechanical failure. Phase inversions must also be predetermined because a significant volume change normally accompanies inversion.

Thermal expansion measurements by X-ray diffractometry are obtained from unit cell dimensions of each crystallographic component at selected temperatures. Phase inversions are determined by disappearance of characteristic X-ray lines of the low-temperature phase, by appearance of new diffraction lines, or by marked changes in the slope of the expansion-temperature relationship.

X-ray diffractometer measurements of thermal expansion have the following advantages over dilatometer techniques:

1. Expansion in each crystallographic direction can be independently determined.
2. The expansion measurements are independent of particle size or shape or the way the crystallites fit together.
3. Samples of several grams are sufficient and binders are not required.

4. Measurements can be made on each crystalline phase in samples containing multiple components.

Thermal expansion data are presented on smoothed curves for rapid reference and in tabular form for critical review.

INSTRUMENTATION

The thermal expansion measurements were made with a high-temperature X-ray diffractometer furnace similar in design to the unit described by Mauer and Bolz (13).⁵ A general discussion of high-temperature X-ray diffractometry is given in a previous paper by Campbell, Stecura, and Grain (3); also, descriptions of several protective devices incorporated in the furnaces are included.

The Mauer and Bolz furnace, as modified for use by the authors, is shown in figure 1. In the original Mauer and Bolz design the sample was adjusted to the focusing circle of the X-ray diffractometer by a combined screw-lever movement. This combination resulted in a sensitive movement (0.009 inch per screw revolution) but had a very limited range of translation, approximately 0.025 inch. This limited range necessitated careful machining and matching of sample-support tubes and sample holders. In the modified furnace the sample is translated by a screw movement on a dove-tailed track; total translation is approximately 0.25 inch and the sensitivity is 0.046 inch per screw revolution. In addition to less critical demands on the machining of ceramic components there is no danger of tilting the sample, which might happen if the support straps of the Mauer and Bolz furnace bend unevenly. The movement is less sensitive than the original movement, but the sample height adjustment can be made to within ± 0.002 inch by an experienced operator. This error in the height adjustment corresponds to an error of $\pm 0.02^\circ 2\theta$ at $120^\circ 2\theta$ and decreasing with increasing 2θ .

The heating element consists of 20 gage platinum-20 percent rhodium wire wound on an alumina winding core of 1.25 inches outside diameter, 9 threads per inch. It was found experimentally that thermal gradients across the sample, parallel to the support tube axis, were minimized if six and five turns of the heating element were used before and after the sample respectively (see fig. 2). Insulation was provided by alumina K-28 brick cut to fit snugly in the furnace shell.

Sample support tubes of "Vycor,"⁶ mullite, and alumina were used in various phases of these investigations. "Vycor" has excellent thermal shock resistant properties but is limited in use to a maximum sample temperature of approximately $1,100^\circ\text{C}$. Although alumina can be used at higher temperatures

⁵Underlined numbers in parentheses refer to items in the bibliography at the end of this report. Page references refer to the pages in the items and not to those in this report.

⁶Reference to trade names is made to facilitate understanding and does not imply endorsement of such brands by the Bureau of Mines.

FIGURE 1. - High-Temperature X-Ray Diffractometer.

than mullite, the latter's superior thermal shock resistance makes mullite the choice because the thermal expansion measurements were limited to 1,350° C. The mullite tubes lasted 4 to 6 weeks as long as the heating and cooling rates did not exceed 100° C. per hour.

The mullite support tubes have the following dimensions:

Outside diameter.....	1.498 ± 0.001 inches
Length.....	4.81 ± 0.02 inches
Wall thickness.....	0.065 ± 0.003 inch.

For maximum tube life, stresses resulting from cutting and drilling for the sample holder and power leads should be relieved by annealing.

Sample holders were composed of 99.5⁺ alumina which was mixed with a volatile binder, pressed at 2,000 pounds per square inch, then heated to 1,700° C. The holders were machined to the proper dimensions and shape after being fired.

FIGURE 2. - Cutaway View of Furnace Showing Heater and Thermocouple Locations. A-1, Sample; 2, sample holder; 3, winding core; 4, platinum-20 percent rhodium winding; 5, sample holder support tube; 6, insulating brick. B-Numbers 1 to 7 indicate thermocouple locations.

TEMPERATURE MEASUREMENT

Sample temperatures were determined with uncalibrated⁷ 0.005-inch platinum and platinum-10 percent rhodium thermocouple wire embedded in the sample surface. The thermocouple junction was cut off and rewelded after each sample was studied. Thermal calibration of the X-ray diffractometer furnace (3) gives a probable error of $\pm 10^\circ$ to 20° C. in the region of $1,000^\circ$ C. Additional unpublished studies indicated that the thermocouple readings were systematically low by 8° , 5° , and 14° C., using inversion temperatures of 573° , 811° , and $1,194^\circ$ C. as references for alpha quartz, barium carbonate, and calcium sulfate respectively.

The sample area in direct contact with the thermocouple is cooler than the adjoining surface area due to heat loss along the thermocouple wire; therefore, the indicated temperatures are systematically low, the error being larger for samples of low thermal conductivity. The magnitude of this error was determined by comparing the expansion of platinum powder dispersed in magnesium oxide to that of platinum as a foil. The thermocouple embedded in the surface of the metal-oxide mixture read 10° C. lower at $1,000^\circ$ C. than that for the thermocouple welded to the platinum foil. This source of error was minimized by using fine (0.005-inch) wire and a large junction, and by running the wires through a hot zone of the furnace.

The following thermal gradient characteristics (see table 1 and fig. 2) were determined for the furnace used in these studies:

1. There is a thermal gradient of 30° to 40° C. per centimeter (at $1,000^\circ$ C.) from the center of the sample towards each end, along the Y axis. The length (along Y axis) of the sample in the X-ray beam varies with both the Bragg angle and the angular aperture of the divergence slits as expressed in the following equation.

$$L = \frac{l \cdot \gamma}{57.3 \times \sin \theta} \quad (1)$$

L = length of sample in X-ray beam, centimeters,

l = radius of goniometer, centimeters,

γ = divergence angle, normally 1° in front reflection, and 4° for back reflection.

At $30^\circ 2\theta$ with 1° divergence slits, L equals 1.15 centimeters. Therefore, if the temperature gradient is 30° C. per centimeter, the gradient along the portion of the sample in the X-ray beam is $\frac{1.15}{2} \times 30$, or 17° C. at $1,000^\circ$ C.

2. The magnitude and direction of the thermal gradient across the width of the sample along the Z axis, varies with the ratio of heater turns of either side of the holder and by the type and amount of insulation used to prevent heat loss down the ceramic sample support tube. On the side opposite the

²Supplier stated uncalibrated platinum and platinum-10 percent rhodium wire has a reliability of ± 0.2 percent up to $2,700^\circ$ F.

thermocouple leads the maximum number of turns possible is five (the number of turns is controlled by the length and pitch of the core) while it is possible to have as many as 15 turns on the thermocouple side.

TABLE 1. - Determination of thermal gradients in oxidizing atmosphere furnace¹

Thermocouple ²	Temperature, ° C.					
1.....	227	438	644	972	1,109	1,243
2.....	178	351	525	808	932	1,063
3.....	179	356	535	832	964	1,103
4.....	178	350	522	810	938	1,074
5.....	204	397	590	916	1,069	1,227

¹Data obtained with an alumina holder 4 centimeters thick.

²Thermocouple positioned as shown in figure 2.

In the initial studies using a winding ratio of 10 to 5 and a secondary insulator of potassium titanate inside the support tube, there was a positive thermal differential of 55° C. (at 1,100° C.) towards the thermocouple leads as determined by thermocouples 6 and 7. With a winding ratio of 6 to 5 and no insulation down the support tube, the differential was reduced to 10° C. and direction remained the same.

3. The thermal gradient through the 4-millimeter-thick alumina holder, X axis, was approximately 100° C. at 1,000° C. The depression for the powdered oxide sample is 0.5 millimeter deep, so there is a difference of approximately 15° C. through the total depth of sample. As the X-ray beam only penetrates about one-fifth of the sample depth, a gradient of 2 to 3° C. is expected in the depth of sample viewed by copper K α radiation.

A proportional control with reset and rate action permitted the use of a single thermocouple positioned on the sample for both temperature measurement and control because the rate action partly corrects for thermal lag. Temperature variations of $\pm 3^\circ$ C. at 1,000° C. were obtained with this type of control. A cam-driven programmer was also part of this temperature control unit.

SAMPLE PREPARATION

All samples used in these studies were high-purity, commercially available oxides. The suppliers of these oxides express purity in terms of other rare earths and do not take into account non-rare-earth impurities in their stated purity, for example, 99.9+ CeO₂ may have 0.2 percent CaO. Because of the possible effect of impurities on thermal expansion and phase inversion characteristics of each oxide, optical spectrographic analyses were obtained on all samples investigated (see table 2).

TABLE 2. - Optical spectrographic analyses of rare-earth oxides¹

Sample	Elements detected ^{2 3}													
	Al	B	Ca	Ce	Cr	Cu	Dy	Er	Eu	Fe	Gd	Ho	La	Lu
Sc ₂ O ₃	D	E	E+		F+	F+				E		E	D	
Y ₂ O ₃	F+		E			F		F+		F+				
La ₂ O ₃	F+		E			F+				F			A	
CeO ₂	E		E	A		E	E	E		F+	F+			F+
Pr ₆ O ₁₁			E+							F+				
Nd ₂ O ₃			D											
Sm ₂ O ₃			D						D					
Eu ₂ O ₃			E+							E			D+	
Gd ₂ O ₃			E+							F+	A			
Dy ₂ O ₃			D				A							
Ho ₂ O ₃	F		E+					D		F+		A		
Er ₂ O ₃			E+					A						
Tm ₂ O ₃			D											F
Yb ₂ O ₃			E+							F+				F
Lu ₂ O ₃	E	E	E+			F+			D					A

Sample	Elements detected ^{2 3}													
	Mg	Mn	Nd	Pb	Pr	Sc	Si	Sm	Th	Ti	Tm	Yb	Y	Zr
Sc ₂ O ₃	E	F+				A	D				D	D	E	E+
Y ₂ O ₃	F+	G+					E+						A	
La ₂ O ₃	E						E							
CeO ₂	F+				E		E		C		F+		F+	
Pr ₆ O ₁₁	F				A		F+							
Nd ₂ O ₃	E		A				F+	D+						
Sm ₂ O ₃	F+						E	A						
Eu ₂ O ₃	F+			E+			E+							
Gd ₂ O ₃	F+						E						E+	
Dy ₂ O ₃	E						F+						C+	
Ho ₂ O ₃	E						E					F+	F+	
Er ₂ O ₃	G+						F+							
Tm ₂ O ₃	F+			F+			E+				A	E	F+	
Yb ₂ O ₃	F+			E			E+			E	E+	A	E+	
Lu ₂ O ₃	F+	G+					F+	D+						

¹Analyses by M. J. Peterson and J. Zink (College Park).²Letters indicate estimates of concentration ranges in weight percent:

A over 10	D+	.03-.3	F+	.0003-.003
B 1.0-10	D	.01-.1	F	.0001-.001
C+ .3-3.0	E+	.003-.03	G+	.00003-.0003
C .1-1.0	E	.001-.01	G	.00001-.0001

³Elements sought but not detected: Ag, As, Ba, Be, Bi, Cd, Co, Cs, Ge, Hg, K, Li, Mo, Na, Nb, Ni, P, Rb, Sb, Sn, Sr, Ta, Tb, Tl, V, W, Zn.

All samples were presintered in platinum crucibles to the temperature specified using a muffle type furnace with silicon carbide heaters. Calibration of the furnace shows the temperatures to be accurate to $\pm 30^\circ \text{C}$. in the $1,000^\circ$ to $1,300^\circ \text{C}$. range. After preliminary sintering the oxides were packed into alumina sample holders and refired. The sample surfaces were leveled after firing by polishing them with a high density alumina disc.

CALCULATIONS

Linear expansion (percent) and linear expansion coefficients are determined from precision measurements of the Bragg reflection angle. Utilizing Bragg's equation the interplanar spacing can be calculated from the diffraction angle:

$$n\lambda = 2d \sin \theta \quad (2)$$

where

n = order of reflection
 λ = wavelength of X-radiation, A
 d = interplanar spacing, A
 θ = Bragg angle

The unit cell parameters are determined from the following equations relating d and a or c for cubic and hexagonal systems.

$$\text{Cubic} \quad a = d \sqrt{h^2 + k^2 + l^2} \quad (3)$$

where

a = unit cell parameter
 h, k, l = Miller indices

$$\text{Hexagonal} \quad \frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (4)$$

$$a = d \sqrt{\frac{4}{3} (h^2 + Hk + k^2) + \frac{l^2}{c^2/a^2}} \quad (5)$$

$$c = d \sqrt{\frac{4a^2}{3c^2} (h^2 + hk + k^2) + l^2} \quad (6)$$

For the cubic system, measurement of a single back reflection line is sufficient (after furnace alignment) whereas a minimum of two lines must be measured for the hexagonal systems in order to solve for a and c by simultaneous equations. Whenever it is possible to choose reflecting planes such as $hk0$ or $00l$ for the hexagonal systems then a and c respectively can be independently determined.

Thermal expansion was calculated by extrapolating the lattice parameter--temperature curve to 0°C . to get a value of a_0 . Using this value the linear expansion and the linear expansion coefficient are calculated from the following equations.

$$\text{linear expansion (percent)} = \frac{a_t - a_o}{a_o} \times 100 \quad (7)$$

where

a_o = lattice parameter at 0° C.

a_t = lattice parameter at $t^\circ \text{ C.}$

$$\text{Linear expansion coefficient} = \frac{a_t - a_o}{a_o} \times \frac{1}{t^\circ \text{ C.}} \quad (8)$$

ACCURACY OF EXPANSION MEASUREMENTS

To obtain accurate expansion measurements, the sample surface was adjusted to the focusing circle at each temperature to correct for shrinkage or expansion. At room temperature sample alignment is similar to ordinary diffractometry, but the height adjustment adds one additional parameter. A modified Soller slit arrangement was satisfactory for the initial alignment (3). At elevated temperatures a height adjustment technique originally suggested by Mauer and Bolz (13) was used. Mauer and Bolz observed that unit cell measurements are very sensitive to sample displacement in the front reflection ($\text{low } 2\theta$) region with rapidly decreasing sensitivity in the back reflection ($>90^\circ 2\theta$) region. The error in the parameter measurement due to sample displacement is minimized by adjusting the sample height until two diffraction lines, one in the front and one in the back reflection regions respectively, give the same unit cell parameter.

Previous studies by Mauer and Bolz (13) show that the height adjustment error has the same order of magnitude as the error in measuring the diffraction angle. Assuming the error in measuring the diffraction angle to be $\pm 0.01^\circ 2\theta$, the resultant error in the thermal expansion measurement can be calculated.

Isotropic expansion $\frac{\Delta d}{d}$ is equal to $\frac{\Delta a}{a}$ since

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

or $a = kd$ for a given reflection. At low temperatures Δd is small; therefore, small experimental errors in measuring 2θ results in large percentage errors in the thermal expansion measurements. At higher temperature Δd becomes large enough so that small experimental errors in 2θ measurements have little effect on the value of $\frac{\Delta d}{d}$; however, at this point temperature measurements become more

difficult. Table 3 lists calculated errors for alpha alumina using the 410 reflection and considering

$$\frac{\Delta d}{d} = \frac{\Delta a}{a};$$

experimental data obtained for alpha alumina are in agreement with the calculated deviations. The errors in the $\frac{\Delta d}{d}$ measurement are of a random nature, whereas the temperature errors are both random and systematic. The systematic errors are probably the most important. As mentioned earlier the thermocouple readings in the temperature range near 800° C. read 5° C. low; therefore the temperature error is -2 to -8° C. A critical evaluation of errors in the

expansion measurements is given by Mauer and Bolz (13); their conclusions are in general agreement with those of the authors.

TABLE 3. - Calculated errors for linear expansion measurements using diffractometer techniques¹

Temperature ° C.	Degrees, 2θ	d spacing, A	Δd, degrees 2θ	Calculated error, percent	
				Sample alinement ²	Temperature measurement ³
28.....	117.78	0.89964			
278.....	117.45	.90120	0.00156	6.0	1.5
527.....	117.08	.90298	.00334	2.8	1.0
807.....	116.61	.90526	.00562	1.7	1.0
1,066.....	116.08	.90786	.00822	1.1	2.0

¹For 410 reflection of alpha alumina assuming isotropic expansion.

²Error in linear expansion measurements due to alignment is equal to

$$\frac{9.4 \times 10^{-3}}{\Delta d} \text{ based on a } \pm \text{ error of } 0.01^\circ 2\theta; \pm 0.01^\circ 2\theta = \pm 4.7 \times 10^{-5} \text{ A at } 117^\circ 2\theta.$$

³Temperature error is a combination of systematic and random errors.

A study was made by the authors to determine the agreement of thermal expansion measurements obtained from each of two furnaces of very similar design operated by different personnel. The average deviation among duplicate runs by each worker was less than ± 1 percent, with a maximum deviation of ± 2 percent at 1,200° C. Comparison of the results from each furnace and measurements made by each worker indicates no systematic differences. No significant differences were observed between data taken on heating and cooling cycles or on successive runs (see fig. 3).

The authors' interest in lattice parameter measurements was in precision, not absolute accuracy. Thermal expansion is determined from the change in parameter with temperature; therefore, absolute values are not required. The parameters were determined from a single reflection; extrapolation methods to 180° 2θ were not used in any of these studies. For this reason some of the parameter values may disagree with published parameter values at room temperature in the second or third decimal place.

EXPERIMENT RESULTS AND DISCUSSION

Scandium Oxide (Sc₂O₃)

Sample: Scandium sesquioxide, supplied by Heavy Minerals Co., Chattanooga, Tenn., was stated to be 99.5 percent Sc₂O₃ in regard to rare-earth content. Optical spectrographic analyses (see table 2) indicated major non-rare-earth impurities were aluminum and silicon.

Sample Preparation: The sample was sintered at 1,150° C. for 24 hours, packed into an alumina sample holder, sintered at 1,200° C., cooled to 300° C. and placed in a vacuum desiccator for storage.

FIGURE 3. - Precision of Thermal Expansion Measurements.

Method: The 222 and 10.4.0 lines were used for furnace alinement. Thermal expansion was determined from the 10.3.1 and 10.4.0 lines; maximum deviation between values from both lines was less than ± 2 percent above 500°C .

Results: See table 4 and figure 4.

Discussion: Scandium sesquioxide is cubic with thallium oxide type structure (rare-earth oxide type C) and 16 Sc_2O_3 per unit cell, lattice parameter at 25°C . is $9.845\text{\AA}$ (19, vol. 3, 1954, p. 27). No phase inversion was observed in this study (25° - $1,320^{\circ}\text{C}$.).

FIGURE 4. - Thermal Expansion of Scandium Sesquioxide.

TABLE 4. - Thermal expansion of scandium oxide

Temperature, ° C.	Unit cell parameter, Å	Linear expansion, percent	Linear expansion coefficient ($\times 10^6$)
0.....	9.8428	0.00	
23.....	9.8440	.012	5.2
103.....	9.8483	.056	5.4
220.....	9.8571	.145	6.6
375.....	9.8690	.266	7.1
476.....	9.8777	.355	7.4
613.....	9.8894	.473	7.7
755.....	9.9017	.598	7.9
877.....	9.9147	.731	8.3
999.....	9.9267	.852	8.5
1,130.....	9.9426	1.014	8.9
1,250.....	9.9573	1.163	9.3
1,260.....	9.9606	1.179	9.3
1,300.....	9.9644	1.235	9.5
1,175.....	9.9483	1.072	9.1
953.....	9.9224	.809	8.4
405.....	9.8718	.295	7.2
266.....	9.8607	.182	6.8
157.....	9.8524	.098	6.2

Yttrium Oxide (Y_2O_3)

Sample: Yttrium sesquioxide, supplied by Heavy Minerals Co., Chattanooga, Tenn., was stated to be 99.9 percent Y_2O_3 in regard to rare-earth content. Optical spectrographic analyses (see table 2) indicated major non-rare-earth impurities were calcium and silicon.

Sample Preparation: The sample was sintered at 1,250° C. for 24 hours, packed into an alumina sample holder, sintered at 1,350° C. for 12 hours, cooled to 150° C. and placed in a vacuum desiccator for storage.

Method: The 222 and 12.4.2 lines were used for furnace alinement. Thermal expansion was determined from the 12.4.2 line.

Results: See table 5 and figure 5.

Discussion: Yttrium sesquioxide is cubic with thallium oxide type structure (rare-earth oxide type C) and 16 Y_2O_3 per unit cell; lattice constant at 27° C. is 10.604Å (19, vol. 3, 1954, pp. 28-29). No phase inversion was observed in this study (25°-1,300° C.). These results agree with those reported by Curtis (4) and Staritzky (17). Curtis (6) reported an overall linear expansion coefficient for 0° to 1,400° C. of

$$9.3 \times 10^{-6} \text{ in./in. per } ^\circ \text{C.};$$

however this value does not agree with his graph. This graphical data indicates 8.2×10^{-6} for 0° to 1,400° C. and 8.9 from 500° to 1,400° C.; these values are in agreement with those obtained by the authors.

TABLE 5. - Thermal expansion of yttrium oxide

Temperature, ° C.	Unit cell parameter, A	Linear expansion, percent	Linear expansion coefficient ($\times 10^6$)
0.....	10.6012	0.00	
28.....	10.6032	.019	6.7
80.....	10.6071	.056	7.0
106.....	10.6079	.073	6.8
226.....	10.6186	.164	7.2
336.....	10.6274	.247	7.3
439.....	10.6365	.333	7.5
541.....	10.6461	.424	7.8
657.....	10.6571	.527	8.0
759.....	10.6671	.622	8.1
887.....	10.6798	.741	8.3
993.....	10.6910	.847	8.5
1,100.....	10.7019	.950	8.6
1,156.....	10.7085	1.012	8.7
1,216.....	10.7150	1.074	8.8
1,264.....	10.7210	1.130	8.9
1,300.....	10.7250	1.168	8.9
1,136.....	10.7065	.993	8.7
993.....	10.6910	.847	8.5
900.....	10.6815	.758	8.4
696.....	10.6606	.560	8.0
556.....	10.6475	.437	7.8
412.....	10.6347	.316	7.6
260.....	10.6213	.190	7.2
148.....	10.6122	.104	7.0

Lanthanum Oxide (La_2O_3)

Sample: Lanthanum sesquioxide, supplied by Lindsay Chemical Co., West Chicago, Ill. (their code 528), was stated to be 99.9 percent La_2O_3 in regard to total rare-earth content. Optical spectrographic analyses (see table 2) indicated that the major non-rare-earth impurities were calcium, magnesium and silicon.

Sample Preparation: Because lanthanum oxide is very hygroscopic, special precautions were necessary. The sample was sintered at $1,000^\circ\text{C}$. for 24 hours, cooled rapidly to 500°C . and placed in a vacuum desiccator until room temperature was reached. The sample was packed into an alumina sample holder, sintered at $1,000^\circ\text{C}$. for 24 hours, cooled to 750°C . and placed in a vacuum desiccator for storage. Thermal expansion measurements were started immediately upon positioning the sample in the diffractometer furnace. Preliminary

FIGURE 5. - Thermal Expansion of Yttrium Sesquioxide.

studies indicated that no significant amount of moisture was absorbed by the calcined sample in the brief period of time, less than one hour, needed to bring the sample above 150° C.

Results: See table 6 and figure 6.

Discussion: Lanthanum sesquioxide is hexagonal (rare-earth oxide type A) with one La_2O_3 per unit cell; lattice parameters at 26° C. are 3.9373 and 6.1299A for a and c respectively (19, vol. 3, 1954, pp. 33-34). Quill (16) reported La_2O_3 to exist in both the A and C forms up to 500° C., above that temperature only the A form was stable. The authors found the sample, as received, to be a mixture of A type La_2O_3 plus $\text{La}(\text{OH})_3$. Samples fired to

1,200° to 1,300° C. and cooled to room temperature exhibited the A type only. High temperature X-ray diffraction studies showed an unreported high temperature phase which is not stable at room temperature (see table 7). If the calcined A type La_2O_3 is heated from room temperature (at a rate of 15° C. per minute) the new phase appears near 1,100° C. When the sample was cooled rapidly to 930° C. and then to 660° C. the same high temperature phase was present. Expansion data for the a-axis (see fig. 6) shows a marked change in expansion near 965° C., which may be the inversion point for the A type oxide. Since the phase inversions are time-temperature dependent, further studies will be required to obtain accurate inversion points.⁸

TABLE 6. - Thermal expansion of lanthanum oxide

Temperature, ° C.	Unit cell parameter, Å		Linear expansion, percent		Linear expansion coefficient ($\times 10^6$)	
	a	c	a	c	a	c
0.....	3.9365	6.1277	0.00	0.00		
23.....	3.9372	6.1295	.018	.029	7.8	12.6
162.....	3.9418	6.1420	.135	.233	8.3	14.3
288.....	3.9467	6.1546	.259	.439	8.9	15.2
423.....	3.9520	6.1674	.394	.648	9.3	15.3
527.....	3.9560	6.1784	.495	.827	9.3	15.6
646.....	3.9614	6.1912	.633	1.036	9.7	16.0
779.....	3.9677	6.2067	.793	1.289	10.1	16.5
924.....	3.9748	6.2251	.973	1.590	10.5	17.2
941.....	3.9754	6.2268	.988	1.617	10.4	17.1
852.....	3.9717	6.2156	.884	1.435	10.3	16.8
758.....	3.9666	6.2040	.765	1.245	10.0	16.4
558.....	3.9573	6.1812	.528	.873	9.4	15.6
338.....	3.9487	6.1595	.310	.519	9.1	15.3
214.....	3.9437	6.1474	.183	.322	8.5	15.0

TABLE 7. - Powder X-ray diffraction data for
lanthanum oxide at 1,100° C.

d-spacing, Å	$\frac{I}{I_{100}} \times 100$	d-spacing, Å	$\frac{I}{I_{100}} \times 100$
3.416	34	2.456	17
3.314	24	2.349	31
3.215	14	1.978	42
3.093	31	1.774	28
2.992	100	1.670	31
2.603	14	1.654	21

⁸After completion of this manuscript the authors became aware of a recent paper discussing phase inversion of rare-earth oxides; our work supplements the data reported in this paper. Roth, R. S., and Schneider, S. J., Phase Equilibria in Systems Involving the Rare-Earth Oxides. Part I. Polymorphism of the Oxides of the Trivalent Rare-Earth Ions: Jour. Research Nat. Bureau of Standards, vol. 64A, 1960, pp. 309-316.

FIGURE 6. - Thermal Expansion of Lanthanum Sesquioxide.

Cerium Dioxide (CeO_2)

Sample: Cerium dioxide, supplied by Lindsay Chemical Co., West Chicago, Ill. (their code 215), was stated to be 99.9 percent CeO_2 in regard to total rare-earth content. Optical spectrographic analyses (see table 2) indicated that the major non-rare-earth impurity was thorium.

Sample Preparation: The sample was sintered at 1,350° C. for 24 hours, packed into an alumina sample holder, sintered at 1,450° C. for 12 hours, cooled to 300° C. and placed in a vacuum desiccator for storage.

Method: The 111 and 621 lines were used for furnace alinement. Thermal expansion was determined from the 531 and 620 lines; maximum deviation between values from both lines was less than ± 2 percent above 500° C.

Results: See table 8 and figure 7.

Discussion: Cerium dioxide is cubic with fluorite type structure and 4 CeO_2 per unit cell; lattice parameter at 26° C. is 5.4110A (19, vol. 1, 1953, pp. 56-57). The crystal structure of nonstoichiometric CeO_x (where x is less than 2) is discussed by Honig (11). No phase inversion was observed in this study (25°-1,310° C.). Thermal expansion was obtained at increasing temperatures only because the furnace winding broke after the measurements at 1,310° C. were completed. Preliminary studies had shown that no hysteresis occurred in the expansion-temperature relationship.

TABLE 8. - Thermal expansion of cerium dioxide

Temperature, ° C.	Unit cell parameter, A	Linear expansion, percent	Linear expansion coefficient ($\times 10^6$)
0.....	5.4085	0.00	
26.....	5.4100	.028	10.7
118.....	5.4153	.126	10.6
140.....	5.4165	.148	10.5
220.....	5.4215	.240	10.9
268.....	5.4245	.296	11.0
346.....	5.4295	.388	11.2
415.....	5.4335	.462	11.1
503.....	5.4395	.573	11.3
570.....	5.4436	.649	11.3
616.....	5.4471	.712	11.5
720.....	5.4542	.845	11.7
845.....	5.4635	1.017	12.0
975.....	5.4736	1.204	12.3
1,131.....	5.4862	1.437	12.7
1,200.....	5.4919	1.541	12.8
1,261.....	5.4963	1.623	12.8
1,310.....	5.5003	1.697	12.9

FIGURE 7. - Thermal Expansion of Cerium Dioxide.

Praseodymium Oxide (Pr_6O_{11})

Sample: Praseodymium oxide, supplied by Lindsay Chemical Co., West Chicago, Ill. (their code 729.9), was stated to be 99.9 percent Pr_6O_{11} in regard to total rare-earth content. Optical spectrographic analyses (see table 2) indicated that the major non-rare-earth impurity was calcium.

Sample Preparation: The sample was sintered at 950° C. for 24 hours, packed into an alumina sample holder, sintered at 1,050° C. for 12 hours, cooled to 300° C. and placed in a vacuum desiccator for storage. Because praseodymium oxide is hygroscopic, precautions against prolonged exposure to moist air must be taken.

Method: The 222 and 622 lines were used for furnace alinement. Thermal expansion was determined from the 1022 line.

Results: See table 9 and figure 8.

Discussion: Praseodymium oxide ($\text{PrO}_{1.83}$) was reported in the ASTM X-ray diffraction card 6-0329 to be cubic with a lattice parameter of 5.4695Å at 25° C. Curtis (5) stated that Pr_2O_3 is a rare-earth oxide type C with a unit cell of $10.913 \pm 0.006\text{Å}$; the powder pattern is very similar to the ASTM data for $\text{PrO}_{1.83}$. The sample received from Lindsay, listed as Pr_6O_{11} ($\text{PrO}_{1.83}$), also agrees with the ASTM card. Honig (11) summarized, in his review on the PrO_x system, that under equilibrium conditions near 300° C., $x = 1.98$; for 350° to 450° C., $x = 1.83$; equilibrium conditions were obtained in several hours. In the region of 725° to 1,000° C., $x = 1.72$; equilibrium is achieved in several minutes. In the intermediate temperature ranges the sample composition is quite variable. Samples heated to elevated temperatures in air and cooled slowly will always have a composition close to $x = 1.83$.

TABLE 9. - Thermal expansion of praseodymium oxide

Temperature, ° C.	Unit cell parameter, Å	Linear expansion, percent	Linear expansion coefficient ($\times 10^6$)
0.....	10.9055	0.00	
25.....	10.9084	.027	10.8
101.....	10.9180	.115	11.3
206.....	10.9304	.228	11.0
208.....	10.9412	.327	11.6
426.....	10.9631	.528	12.3
520.....	10.9797	.680	13.0
625.....	11.0079	.939	15.0
726.....	11.0371	1.207	16.6
778.....	11.0556	1.376	17.6
830.....	11.0705	1.513	18.2
886.....	11.0891	1.683	18.9
950.....	11.1080	1.824	19.2
989.....	11.1133	1.906	19.2
1,020.....	11.1190	1.958	19.1

The sample, as received by the authors, was apparently a mixture of two cubic oxides, neither of which was well crystallized. All samples fired from 800° to 1,300° C. for times of 12 to 72 hours and cooled slowly to 200°-300° C. exhibited the same diffraction pattern (see table 10). Upon firing to 1,500° C. and cooling to room temperature, two distinct phases, cubic and hexagonal, were identified; the latter phase was similar to ASTM Card 6-0410. Using high temperature diffractometer techniques only one cubic phase was observed at 650° C. and 820° C., whereas two cubic phases exist (possibly one cubic and one rhombohedral) at 910° C. (see table 11). Further work is required to identify positively the transitions in the complex PrO_x system.

FIGURE 8. - Thermal Expansion of Praseodymium Oxide (Pr_6O_{11}).

TABLE 10. - Powder X-ray diffraction data for
praseodymium oxide at 25° C.¹

hkl	d-spacing, A	$\frac{I}{I_{100}} \times 100$	a, A	hkl	d-spacing, A	$\frac{I}{I_{100}} \times 100$	a, A
111	3.147	100	5.45	422	1.115	1	5.464
200	2.726	38	5.452	511	1.0516	5	5.465
220	1.929	40	5.456	440	.9634	1	5.467
311	1.646	31	5.458	531	.9244	2	5.468
222	1.576	1	5.460	600	.9113	1	5.468
400	1.365	1	5.460	620	.8641	1	5.466
331	1.253	1	5.462	533	.8334	1	5.467
420	1.222	1	5.463				

¹Fired at 1,000° C. for 12 hours.

TABLE 11. - Powder X-ray diffraction data for
praseodymium oxide at 910° C.

d-spacing, A	$\frac{I}{I_{100}} \times 100$	d-spacing, A	$\frac{I}{I_{100}} \times 100$
3.218	38	1.268	6
3.184	100	1.0853	3
2.758	48	1.0654	5
2.093	8	1.0493	4
1.963	30	1.0039	3
1.952	30	.9850	3
1.679	13	.9403	4
1.671	28	.9232	4
1.665	26	.9135	3
1.596	10	.8799	2
1.382	7	.8766	3

Neodymium Oxide (Nd₂O₃)

Sample: Neodymium sesquioxide, supplied by Lindsay Chemical Co., West Chicago, Ill. (their code 629.9), was stated to be 99.9 percent Nd₂O₃ in regard to total rare-earth content. Optical spectrographic analyses (see table 2) indicated that the major non-rare-earth impurities were calcium and magnesium.

Sample Preparation: The sample was sintered at 1,100° C. for 24 hours, packed into an alumina sample holder, sintered at 1,100° C for 12 hours, cooled to 750° C. and placed in a vacuum desiccator for storage.

Method: The 100, 300, and 215 lines were used for furnace alinement, the latter for final critical adjustment. Thermal expansion was determined from the 213, 311, and 215 lines using simultaneous equations for the a and c parameters.

Results: See table 12 and figure 9.

Discussion: Neodymium sesquioxide is polymorphic, existing in both the A and C forms. The thermal expansion measurements in this investigation was restricted to the hexagonal phase (rare-earth oxide type A) having a lanthanum oxide-type structure and 1 molecule of Nd_2O_3 per unit cell, lattice parameters at 26° C. of 3.831 and 5.999A for a and c axis respectively (19, vol. 4, 1955, p. 26).

TABLE 12. - Thermal expansion of neodymium oxide

Temperature, ° C.	Unit cell parameter, A		Linear expansion, percent		Linear expansion coefficient ($\times 10^6$)	
	a	c	a	c	a	c
0.....	3.8287	5.9950	0.00	0.00		
23.....	3.8293	5.9970	.016	.034	6.9	14.7
146.....	3.8332	6.0082	.118	.220	8.0	15.0
285.....	3.8386	6.0222	.259	.454	9.0	15.9
424.....	3.8438	6.0352	.394	.671	9.2	15.8
528.....	3.8479	6.0454	.502	.841	9.5	15.9
646.....	3.8525	6.0574	.622	1.041	9.6	16.1
783.....	3.8579	6.0715	.761	1.276	9.7	16.2
894.....	3.8621	6.0839	.872	1.483	9.7	16.5
1,027.....	3.8679	6.1005	1.024	1.760	9.9	17.1
1,122.....	3.8720	6.1116	1.131	1.945	10.0	17.3
1,158.....	3.8738	6.1165	1.178	2.027	10.1	17.5
1,063.....	3.8696	6.1043	1.068	1.823	10.0	17.1
656.....	3.8525	6.0580	.622	1.051	9.4	16.0
446.....	3.8444	6.0373	.409	.706	9.1	15.8
235.....	3.8369	6.0171	.214	.369	9.1	15.7

Quill (16) in a review article states that Nd_2O_3 exists in the C form below 775° C. and the A type at higher temperatures. Brauer and Gradinger (2) obtained A type Nd_2O_3 from ignition of oxalates and hydroxides to 750° C. while the C form was obtained from nitrates. Blum and Maguire (1) reported conversion of cubic to hexagonal Nd_2O_3 beginning at approximately 600° C.; at 800° C. only a trace of the cubic phase remained. Lohberg (12) found the cubic form by heating the oxide to 700° C. for 3 hours. It could be converted to the hexagonal form by heating it to 1,000° C. and then converted back to cubic form by heating it at 700° C.

FIGURE 9. - Thermal Expansion of Neodymium Sesquioxide.

The authors' starting sample was principally A-type oxide plus some hydroxide. Samples fired at 1,050° to 1,500° C. and cooled to room temperature were A type only. One sample of A type only was maintained at 700° C. for 20 hours then cooled quickly to room temperature. Only the A form was present; this finding, however, is not in agreement with the results reported by Lohberg (12). By high temperature diffractometer techniques two phases were found at 1,160° C., the A phase and an unknown major phase. After this temperature was maintained for 10 hours, only the new phase was present (see table 13). This unstable high temperature phase began to appear to approximately 1,070° C. When the diffractometer furnace was cooled rapidly to 930° C. and then 610° C., the unstable high temperature phase was still present.

TABLE 13. - Powder X-ray diffraction data for neodymium oxide at 1,160° C.

d-spacing, A	$\frac{I}{I_{100}} \times 100$	d-spacing, A	$\frac{I}{I_{100}} \times 100$
4.015	13	2.410	20
3.666	17	2.259	40
3.536	21	2.112	45
3.429	47	1.948	29
3.356	37	1.936	48
3.278	77	1.910	17
3.177	57	1.762	28
3.112	41	1.742	57
3.074	43	1.636	44
3.060	32	1.621	37
2.941	100	1.617	37
2.738	40	1.470	15
2.710	20	1.389	29
2.587	41	1.241	13
		1.200	13

Samarium Oxide (Sm_2O_3)

Sample: Samarium sesquioxide, supplied by Lindsay Chemical Co., West Chicago, Ill. (their code 823), was stated to be 99.9 percent Sm_2O_3 in regard to rare-earth content. Optical spectrographic data (see table 2) indicated that the major non-rare-earth impurities were calcium and silicon.

Sample Preparation: The sample was sintered at 850° C. for 24 hours, packed in an alumina sample holder, sintered at 900° C. for 24 hours, cooled to 300° C. and placed in a vacuum desiccator for storage.

Method: The 222 and 622 lines were used for furnace alinement. Thermal expansion was determined from the 622 lines.

Results: See table 14 and figure 10.

Discussion: Samarium sesquioxide is polymorphic; the cubic phase (rare-earth oxide type C) was used for the expansion measurements reported in this investigation (see table 15). Templeton and Dauben (20) reported a cubic Sm_2O_3 , a_0 of $10.932 \pm 0.009\text{A}$, with no mention of thermal history of the sample. The sample, as received was cubic; after 24 hours at 850° C., it was still cubic. However, after treatment at 950° C. for 12 hours, two phases, cubic and monoclinic (rare-earth oxide type B), were present. Samples fired at various temperatures on the range 1,000° C. to 1,500° C. for periods of from 3 to 72 hours and then cooled to room temperature were B type only. In the high temperature diffractometer the C phase was formed at 920° C.; at 975° C. for 14.5 hours the C phase was major with minor B phase. The C phase disappeared when the temperature was increased from 975° C. to 1,120° C. at 1/2° C. per minute (the pattern at this temperature is given in table 16).

FIGURE 10. - Thermal Expansion of Samarium Sesquioxide.

Curtis (6) reported that the cubic phase disappeared above 1,100° C.; Blum and Maguire (1) stated that X-ray analysis indicated a phase change about 900° C. The latter statement was in agreement with the authors' results.

Linear expansion coefficients of 9.9×10^{-6} for 100° to 1,000° C. (6) and 10.8×10^{-6} for 30° to 740° C. (15) were obtained on samples fired to 1,500° and 1,800° C. respectively. These temperatures give the B phase only and therefore they do not agree with the

results obtained in this investigation which was only concerned with the C type.

TABLE 14. - Thermal expansion of samarium oxide

Temperature, ° C.	Unit cell parameter, Å	Linear expansion, percent	Linear expansion coefficient ($\times 10^6$)
0.....	10.9085	0.00	
26.....	10.9109	.022	7.5
92.....	10.9170	.078	8.4
200.....	10.9271	.170	8.5
308.....	10.9369	.260	8.4
403.....	10.9459	.343	8.5
504.....	10.9558	.434	8.6
604.....	10.9660	.527	8.7
703.....	10.9759	.618	8.7
792.....	10.9850	.701	8.8
843.....	10.9896	.744	8.8
905.....	10.9953	.796	8.8
950.....	11.0006	.844	8.8

TABLE 15. - Powder X-ray diffraction data for C-type
samarium oxide at 25° C.¹

hkl	d-spacing, A	$\frac{I}{I_{100}} \times 100$	a, A	hkl	d-spacing, A	$\frac{I}{I_{100}} \times 100$	a, A
211	4.449	11	10.898	510	2.139	8	10.907
222	3.146	100	10.900	440	1.928	33	10.905
400	2.725	37	10.899	622	1.645	26	10.911
331	2.502	3	10.906	444	1.574	7	10.906
332	2.325	4	10.907				

¹Fired at 820° C. for 24 hours.

TABLE 16. - Powder X-ray diffraction data for
samarium oxide at 1,122° C.

d-spacing, A	$\frac{I}{I_{100}} \times 100$	d-spacing, A	$\frac{I}{I_{100}} \times 100$
3.455	27	2.185	37
3.238	76	1.951	37
3.078	73	1.851	25
3.029	95	1.751	27
2.930	51	1.678	29
2.888	68	1.659	15
2.868	100	1.573	15
2.244	22		

Europium Oxide (Eu₂O₃)

Sample: Europium sesquioxide, supplied by Lindsay Chemical Co., West Chicago, Ill. (their code 1011), was stated to be 99.9 percent Eu₂O₃ in regard to total rare-earth content. Optical spectrographic analyses (see table 2) indicated that the major non-rare-earth impurities were calcium, lead and silicon.

Sample Preparation: The sample was sintered at 1,000° C. for 16 hours, packed into an alumina sample holder, sintered at 1,060° C. for 12 hours, cooled to 300° C. and placed in a vacuum desiccator for storage.

Method: The 222 and 622 lines were used for furnace alinement. Thermal expansion was determined from the 622 line.

Results: See table 17 and figure 11.

Discussion: Europium sesquioxide is cubic at temperatures below 1,100° C. (rare-earth oxide type C); lattice parameter of $10.886 \pm 0.005A$, no temperature given (20). Curtis (7) found that the C phase from europium oxalate decomposed at 800° C. with a lattice parameter of $10.860 \pm 0.006A$. Samples fired to 1,050° C. for 60 hours were cubic only; at 1,100° C. for 24 hours

some transformation of C to B phase occurred. After 60 hours at 1,100° C. this transformation was complete and at temperatures above 1,100° C. only the B form was observed. A sample fired at 1,050° C. and indexed by the authors was found to contain only the cubic phase (see table 18).

Linear expansion coefficients of 10.3×10^{-6} for 0° to 1,200° C. (7) and 10.5×10^{-6} for 30° to 850° C. (15) were reported for samples fired to 1,500° and 1,800° C. respectively. At these temperatures only the monoclinic form (B type) would be present. The data obtained in this investigation is limited to the cubic phase; they are, therefore, not in agreement with the literature values. Ploetz and Krystyniak (14) reported bulk densities higher than theoretical densities on sintered compacts; their theoretical model was cubic, but their samples were sintered in the monoclinic region.

TABLE 17. - Thermal expansion of europium oxide

Temperature, ° C.	Unit cell parameter, A	Linear expansion, percent	Linear expansion coefficient ($\times 10^6$)
0.....	10.8245	0.00	
26.....	10.8261	.015	5.7
97.....	10.8314	.064	6.5
211.....	10.8392	.136	6.4
324.....	10.8474	.212	6.5
403.....	10.8537	.270	6.6
512.....	10.8623	.349	6.8
635.....	10.8726	.444	6.9
759.....	10.8848	.557	7.3
887.....	10.8976	.675	7.6
1,011.....	10.9106	.795	7.8
1,129.....	10.9241	.920	8.1
1,197.....	10.9325	.998	8.3
1,261.....	10.9412	1.078	8.5

TABLE 18. - Powder X-ray diffraction data for
europium oxide at 25° C.¹

hk1	d-spacing, A	$\frac{I}{I_{100}} \times 100$	a, A	hk1	d-spacing, A	$\frac{I}{I_{100}} \times 100$	a, A
211	4.408	12	10.797	631	1.593	3	10.806
222	3.115	100	10.791	444	1.560	4	10.807
400	2.699	32	10.797	800	1.351	3	10.806
411	2.546	5	10.802	811	1.330	3	10.807
331	2.479	6	10.807	831	1.256	3	10.807
332	2.304	5	10.805	662	1.240	6	10.806
510	2.119	9	10.805	840	1.208	4	10.807
440	1.910	39	10.806	844	1.103	3	10.807
622	1.629	26	10.805				

¹Fired at 980° C. for 12 hours.

FIGURE 11. - Thermal Expansion of Europium Sesquioxide.

Gadolinium Oxide (Gd_2O_3)

Sample: Gadolinium sesquioxide, supplied by Michigan Chemical Co., St. Louis, Mich., was stated to be 99.9 percent Gd_2O_3 in regard to total rare-earth content. Optical spectrographic analyses (see table 2) indicated that the major non-rare-earth impurities were calcium and silicon.

Sample Preparation: The sample was sintered at 1,150° C. for 24 hours, packed into an alumina sample holder, sintered at 1,150° C. for 12 hours, cooled to 350° C. and placed in a vacuum desiccator for storage.

Method: The 222 and 662 lines were used for furnace alinement. Thermal expansion was determined from the 622 and 662 lines; maximum deviation between values from both lines was less than ± 2 percent above 500° C.

Results: See table 19 and figure 12.

Discussion: Gadolinium sesquioxide is polymorphic; thermal expansion measurements are given for the cubic phase only in this report. Templeton and Dauben (20) reported a lattice parameter of $10.813 \pm 0.005\text{\AA}$. The temperature at which this parameter is valid was not stated. Guentert and Mozzi (10) used high temperature diffraction techniques and found only C type oxide at 900°C . in a 6-hour test, and in tests of $1,050^\circ$ and $1,200^\circ\text{C}$. for 1/2 hour each; at $1,400^\circ\text{C}$. in a 1-hour test, two phases, B and C, were found while at $1,600^\circ\text{C}$. only the B phase remained. The indexed B type (monoclinic) pattern is included in their report. Curtis (6) formed the B type from cubic Gd_2O_3 by firing it at $1,300^\circ\text{C}$. The sample used for expansion studies was sintered at $1,250^\circ\text{C}$. (maximum); only the cubic phase was observed. Although expansion measurements were obtained up to $1,310^\circ\text{C}$. the sample was only at the maximum temperature for approximately one-half hour. The indexed pattern for the cubic system is given in table 20.

FIGURE 12. - Thermal Expansion of Gadolinium Sesquioxide.

Linear expansion coefficients of 10.5×10^{-6} for 100° to $1,000^\circ$ C. (6) and 10.0×10^{-6} for 30° to 850° C. (15) were obtained on samples fired to $1,500^\circ$ and $1,800^\circ$ C. respectively. In both cases the B phase would be the only phase present; therefore, the results would not be in agreement with those of the authors for the cubic phase.

TABLE 19. - Thermal expansion of gadolinium oxide

Temperature, ° C.	Unit cell parameter, Å	Linear expansion, percent	Linear expansion coefficient ($\times 10^6$)
0.....	10.7970	0.00	
29.....	10.7992	.020	6.8
113.....	10.7964	.087	7.6
212.....	10.8146	.163	7.6
304.....	10.8223	.234	7.6
408.....	10.8306	.311	7.6
526.....	10.8408	.406	7.7
616.....	10.8497	.488	7.9
637.....	10.8517	.507	7.9
752.....	10.8619	.601	7.9
888.....	10.8761	.733	8.2
916.....	10.8792	.761	8.3
994.....	10.8870	.834	8.3
1,062.....	10.8959	.916	8.6
1,175.....	10.9081	1.029	8.7
1,207.....	10.9113	1.059	8.7
1,251.....	10.9164	1.106	8.8
1,295.....	10.9215	1.153	8.9
1,135.....	10.9029	.981	8.6
834.....	10.8715	.690	8.2
558.....	10.8447	.442	7.9
218.....	10.8153	.170	7.7

TABLE 20. - Powder X-ray diffraction data for
gadolinium oxide at 25° C.¹

hkl	d-spacing, Å	$\frac{I}{I_{100}} \times 100$	a, Å	hkl	d-spacing, Å	$\frac{I}{I_{100}} \times 100$	a, Å
211	4.394	12	10.76	811	1.329	4	10.799
222	3.108	100	10.768	831	1.256	8	10.802
400	2.695	35	10.778	662	1.239	8	10.803
411	2.541	7	10.781	840	1.208	7	10.801
331	2.476	3	10.794	851	1.139	2	10.804
332	2.299	4	10.783	844	1.103	5	10.805
431	2.115	10	10.785	10-2-0	1.0597	2	10.8069
440	1.907	43	10.790	10-2-2	1.0400	2	10.8080
611	1.751	5	10.793	10-3-1	1.0303	3	10.8069
622	1.623	31	10.795	871	1.0122	2	10.8073
631	1.592	7	10.794	10-4-0	1.0034	3	10.8059
444	1.559	7	10.799	10-4-2	0.9867	3	10.8084
721	1.470	4	10.799	11-2-1	0.9630	3	10.8096
800	1.350	4	10.799	10-6-2	0.9136	4	10.8094

¹Fired at $1,070^\circ$ C. for 24 hours.

Dysprosium Oxide (Dy_2O_3)

Sample: Dysprosium sesquioxide, supplied by Michigan Chemical Corp., St. Louis, Mich., was stated to be 99 percent Dy_2O_3 in regard to total rare-earth content. Optical spectrographic analyses (see table 2) indicated that the major non-rare-earth impurities were calcium and magnesium.

Sample Preparation: The sample was sintered at $1,150^\circ\text{C}$. for 24 hours, packed into an alumina sample holder, sintered at $1,150^\circ\text{C}$., cooled to 350°C . and placed in a vacuum desiccator for storage.

Method: The 222 and 840 lines were used for furnace alinement. Thermal expansion was determined from the 622 and 840 lines. Thermal expansion values from both lines agreed to within ± 2 percent above 500°C .

Results: See table 21 and figure 13.

TABLE 21. - Thermal expansion of dysprosium oxide

Temperature, $^\circ\text{C}$.	Unit cell parameter, A	Linear expansion, percent	Linear expansion coefficient ($\times 10^6$)
0.....	10.6530	0.00	
27.....	10.6542	.018	6.6
120.....	10.6625	.080	6.6
185.....	10.6678	.139	7.5
255.....	10.6732	.190	7.4
352.....	10.6817	.269	7.6
476.....	10.6924	.361	7.5
546.....	10.6987	.429	7.8
597.....	10.7027	.467	7.8
730.....	10.7152	.584	8.0
852.....	10.7269	.694	8.1
858.....	10.7277	.701	8.1
955.....	10.7376	.794	8.3
985.....	10.7396	.813	8.2
1,054.....	10.7472	.884	8.3
1,165.....	10.7595	1.000	8.5
1,207.....	10.7640	1.042	8.6
1,256.....	10.7702	1.100	8.7
1,285.....	10.7740	1.136	8.8
1,154.....	10.7581	.987	8.5
913.....	10.7331	.752	8.2
647.....	10.7076	.513	7.9
426.....	10.6879	.328	7.6
219.....	10.6707	.166	7.5
93.....	10.6600	.066	7.0

Discussion: Dysprosium sesquioxide is cubic with thallium oxide type structure (rare-earth oxide type C) and 12 Dy_2O_3 per unit cell; lattice constant at 25° C. is 10.665Å (19, vol. 9, 1960, pp. 30-31). No phase inversion was observed over the temperature range covered (25° to 1,300° C.). Staritzky (17) reported cubic Dy_2O_3 to be crystallized from the melt. When the authors' study on Dy_2O_3 was undertaken, the National Bureau of Standards data had not been published; indexing of the powder pattern by the authors is in good agreement with the recent NBS publication (19).

FIGURE 13. - Thermal Expansion of Dysprosium Sesquioxide.

Holmium Oxide (Ho_2O_3)

Sample: Holmium sesquioxide, supplied by Michigan Chemical Co., St. Louis, Mich., was stated to be 99.9 percent Ho_2O_3 in regard to total rare-earth content. Optical spectrographic analyses (see table 2) indicated that the major non-rare-earth impurities were calcium, magnesium, and silicon.

Sample Preparation: The sample was sintered at 1,300° C. for 24 hours, packed into an alumina sample holder, sintered at 1,300° C. for 24 hours, cooled to 200° C. and placed in a vacuum desiccator for storage.

Method: The 222 and 844 lines were used for furnace alinement. Thermal expansion was determined from the 844 and 12.4.2 lines; maximum deviation between values obtained from both lines was less than ± 2 percent above 500° C.

Results: See table 22 and figure 14.

Discussion: Holmium sesquioxide (Ho_2O_3) is cubic with the thallium oxide type structure (rare-earth oxide type C) with 16 H_2O_3 per unit cell; lattice parameter at 25° C. is 10.606A. (19, vol. 9, 1960, pp. 32-33). No phase inversion was observed over the temperature range covered (25° to 1,300° C.).

TABLE 22. - Thermal expansion of holmium oxide

Temperature, ° C.	Unit cell parameter, A	Linear expansion, percent	Linear expansion coefficient ($\times 10^6$)
0.....	10.6060	0.00	
26.....	10.6080	.019	7.2
108.....	10.6144	.079	7.3
152.....	10.6180	.113	7.4
255.....	10.6264	.192	7.5
333.....	10.6334	.258	7.7
438.....	10.6422	.342	7.8
500.....	10.6473	.389	7.7
616.....	10.6577	.488	7.9
675.....	10.6630	.541	8.0
712.....	10.6665	.570	8.0
860.....	10.6803	.701	8.1
969.....	10.6910	.802	8.2
1,070.....	10.7018	.903	8.4
1,147.....	10.7098	.979	8.5
1,207.....	10.7160	1.037	8.5
1,225.....	10.7178	1.054	8.6
1,295.....	10.7250	1.122	8.6
1,073.....	10.7018	.903	8.4
754.....	10.6704	.607	8.0
642.....	10.6606	.515	8.0
274.....	10.6283	.211	7.6

FIGURE 14. - Thermal Expansion of Holmium Sesquioxide.

Erbium Oxide (Er_2O_3)

Sample: Erbium sesquioxide, supplied by Lindsay Chemical Co., West Chicago, Ill. (their code 1305), was stated to be 99.9 percent Er_2O_3 in regard to total rare-earth content. Optical spectrographic analyses (see table 2) indicated that the major non-rare-earth impurity was calcium.

Sample Preparation: The sample was sintered at 1,300° C. for 24 hours, packed into an alumina holder, sintered at 1,350° C. for 12 hours, cooled to 300° C. and placed in a vacuum desiccator for storage.

Method: The 222 and 12.2,1 lines were used for furnace alinement. Thermal expansion was determined from the 10.6,2 and 12.2,1 lines. Thermal expansion values from both lines agreed to within ± 2 percent above 500° C.

Results: See table 23 and figure 15.

Discussion: Erbium sesquioxide is cubic with thallium oxide type structure (rare-earth oxide type C) and 16 Er_2O_3 per unit cell; lattice constant at 27° C. is 10.548Å (19, vol. 8, 1959, pp. 25-27). No phase inversion was observed over temperature range studied (25° to 1,300° C.). Staritzky (17) reported cubic Er_2O_3 to be crystallized from the melt.

FIGURE 15. - Thermal Expansion of Erbium Sesquioxide.

TABLE 23. - Thermal expansion of erbium oxide

Temperature, ° C.	Unit cell parameter, Å	Linear expansion, percent	Linear expansion coefficient ($\times 10^6$)
0.....	10.5450	0.00	
23.....	10.5465	.014	6.0
125.....	10.5538	.083	6.6
229.....	10.5613	.155	6.7
328.....	10.5690	.230	6.9
502.....	10.5829	.360	7.1
633.....	10.5938	.463	7.3
765.....	10.6054	.573	7.4
906.....	10.6194	.706	7.7
1,038.....	10.6322	.827	7.9
1,181.....	10.6472	.969	8.2
1,264.....	10.6569	1.061	8.3
1,312.....	10.6613	1.103	8.4
1,238.....	10.6542	1.036	8.3
1,110.....	10.6403	.905	8.1
913.....	10.6199	.710	7.7
720.....	10.6026	.546	7.5
582.....	10.5903	.430	7.3
467.....	10.5802	.334	7.1
248.....	10.5629	.170	6.8

Thulium Oxide (Tm_2O_3)

Sample: Thulium sesquioxide, supplied by Lindsay Chemical Co., West Chicago, Ill. (their code 1405), was stated to be 99.9 Tm_2O_3 in regard to total rare-earth content. Optical spectrographic analyses (see table 2) indicated that the major non-rare-earth impurities were calcium and silicon.

Sample Preparation: The sample was sintered at 1,200° C. for 24 hours, packed into an alumina sample holder, sintered at 1,300° C. for 12 hours, cooled to 400° C. and placed in a vacuum desiccator for storage.

Method: The 222 and 12.4.2 lines were used for furnace alinement. Thermal expansion was determined from the 10.6.2 and 12.4.2 lines; maximum deviation between values from both lines was less than ± 2 percent above 500° C.

Results: See table 24 and figure 16.

Discussion: Thulium sesquioxide is cubic with a thallium oxide type structure (rare-earth oxide type C) and 16 Tm_2O_3 per unit cell; lattice constant at 25° C. is 10.488Å (19, vol. 9, 1960, pp. 58-59). No phase inversion was observed over the temperature range covered (25° to 1,300° C.). At the time of this investigation the National Bureau of Standards data had not been published. The indexing of the powder diffraction data by the authors is in agreement with the recent publication (19).

FIGURE 16. - Thermal Expansion of Thulium Sesquioxide.

Ytterbium Oxide (Yb_2O_3)

Sample: Ytterbium oxide, supplied by Michigan Chemical Co., St. Louis, Mich., was stated to be 99.9 percent Yb_2O_3 in regard to rare-earth content. Optical spectrographic analyses (see table 2) indicated that the major non-rare earth impurities were calcium and silicon.

Sample Preparation: The sample was sintered at 1,300° C. for 24 hours, packed into an alumina sample holder, sintered at 1,400° C. for 12 hours, cooled to 250° C. and placed in a vacuum desiccator for storage.

TABLE 24. - Thermal expansion of thulium oxide

Temperature, ° C.	Unit cell parameter, A	Linear expansion, percent	Linear expansion coefficient ($\times 10^6$)
0.....	10.4843	0.00	
28.....	10.4863	.019	6.8
134.....	10.4937	.090	6.6
264.....	10.5041	.189	7.1
364.....	10.5128	.272	7.4
477.....	10.5220	.360	7.5
575.....	10.5308	.444	7.7
695.....	10.5415	.546	7.8
814.....	10.5527	.652	8.0
911.....	10.5622	.743	8.1
1,031.....	10.5733	.849	8.2
1,132.....	10.5832	.943	8.3
1,196.....	10.5897	1.005	8.4
1,271.....	10.5979	1.084	8.5
1,295.....	10.6000	1.104	8.5
1,206.....	10.5908	1.016	8.4
978.....	10.5685	.803	8.2
646.....	10.5368	.501	7.7
445.....	10.5195	.336	7.5
190.....	10.4978	.129	6.7

Method: The 222 and 12.4.2 lines were used for furnace alinement. Thermal expansion was determined from the 10.6.2 and 12.4.2 lines; maximum deviation between values from both lines was less than ± 2 percent above 500° C.

Results: See table 25 and figure 17.

TABLE 25. - Thermal expansion of ytterbium oxide

Temperature, ° C.	Unit cell parameter, A	Linear expansion, percent	Linear expansion coefficient ($\times 10^6$)
0.....	10.4325	0.00	
26.....	10.4343	.017	6.5
158.....	10.4438	.108	6.8
280.....	10.4534	.200	7.1
401.....	10.4632	.294	7.3
516.....	10.4730	.388	7.5
634.....	10.4837	.491	7.7
760.....	10.4948	.597	7.8
884.....	10.5065	.710	8.0
1,021.....	10.5194	.833	8.1
1,102.....	10.5263	.903	8.2
1,242.....	10.5415	1.044	8.4
1,293.....	10.5468	1.096	8.4
1,138.....	10.5305	.939	8.2
927.....	10.5106	.749	8.0
700.....	10.4897	.547	7.8

Discussion: Ytterbium sesquioxide is cubic (rare-earth oxide type C) with 16 Yb_2O_3 per unit cell, the lattice parameter is $10.435 \pm 0.001 \text{ \AA}$, at an unstated temperature (17). The indexed powder pattern (see table 26) is included in this report because these data are not available in the ASTM diffraction card system. No phase inversion was observed over the temperature range covered (25° to $1,350^\circ \text{ C.}$).

FIGURE 17. - Thermal Expansion of Ytterbium Sesquioxide.

TABLE 26. - Powder X-ray diffraction data for
ytterbium oxide at 25° C.¹

hkl	d-spacing, A	$\frac{I}{I_{100}} \times 100$	a, A	hkl	d-spacing, A	$\frac{I}{I_{100}} \times 100$	a, A
211	4.25	17	10.41	921	1.124	3	10.423
222	3.004	100	10.408	930	1.099	3	10.424
320	2.881	2	10.392	932	1.0757	4	10.4293
321	2.783	3	10.415	840	1.0640	7	10.4250
400	2.603	42	10.413	941	1.0535	4	10.4291
411	2.455	8	10.414	10·0·0	1.0429	2	10.4292
331	2.390	3	10.418	10·1·1	1.0326	1	10.4290
420	2.329	2	10.416	10·2·0	1.0227	5	10.4300
332	2.221	6	10.416	950	1.0130	7	10.4295
422	2.126	1	10.417	10·2·2	1.0036	4	10.4297
510	2.043	13	10.418	10·3·1	0.9945	4	10.4300
521	1.902	4	10.419	871	.9769	4	10.4300
440	1.840	47	10.411	10·4·0	.9684	2	10.4299
530	1.788	4	10.428	10·3·3	.9602	3	10.4302
600	1.738	2	10.426	10·4·2	.9521	3	10.4298
611	1.690	8	10.420	11·1·0	.9443	3	10.4305
620	1.648	2	10.424	11·2·1	.9292	2	10.4301
541	1.608	6	10.424	880	.9219	1	10.4304
622	1.570	37	10.412	10·4·4	.9077	3	10.4305
631	1.535	9	10.414	11·3·2	.9011	1	10.4308
444	1.503	10	10.412	10·6·0	.8944	2	10.4309
710	1.473	3	10.415	11·4·1	.8881	4	10.4329
640	1.444	2	10.414	10·6·2	.8816	1	10.4308
721	1.417	5	10.415	965	.8754	3	10.4311
642	1.392	2	10.416	12·0·0	.8693	4	10.4315
732	1.323	4	10.418	12·1·1	.8633	4	10.4315
800	1.302	5	10.418	12·2·0	.8575	4	10.4318
811	1.283	5	10.421	11·5·2	.8517	2	10.4314
820	1.263	3	10.419	12·2·2	.8461	3	10.4318
653	1.245	3	10.420	12·3·1	.8406	3	10.4319
822	1.228	2	10.422	11·6·1	.8299	3	10.4319
831	1.216	5	10.422	12·4·0	.8248	3	10.4324
662	1.196	10	10.422	12·3·3	.8196	2	10.4320
840	1.165	7	10.423	12·4·2	.8146	6	10.4324
910	1.151	1	10.422	11·6·3	.8097	2	10.4323
842	1.137	2	10.424	10·8·2	.8049	4	10.4326
				13·1·0	.8004	2	10.4353

¹Fired at 1,230° C. for 24 hours.

Lutetium Oxide (Lu₂O₃)

Sample: Lutetium sesquioxide, supplied by Lindsay Chemical Co., West Chicago, Ill. (their code 1505), was stated to be 99.9 percent Lu₂O₃ in total rare-earth content. Optical spectrographic analyses (see table 2) indicated that the major non-rare-earth impurities were calcium, magnesium, and silicon.

Sample Preparation: The sample was sintered at 1,200° C. for 24 hours, packed into an alumina sample holder, sintered at 1,250° C. for 12 hours, cooled to 300° C. and placed in a vacuum desiccator for storage.

Method: The 222 and 10.6.2 lines were used for furnace alignment. Thermal expansion was determined from the 844, 10.2.2 and 10.6.2 lines; maximum deviation between values from all three lines was less than ± 2 percent above 500° C.

Results: See table 27 and figure 18.

Discussion: Lutetium sesquioxide is cubic (rare-earth oxide type C), the lattice parameter is $10.391 \pm 0.005\text{\AA}$ at an unspecified temperature (20). Curtis (5) listed the stronger diffraction lines of Lu_2O_3 , and a more extensive tabulation by the authors is given in table 28. No phase inversion was observed over the temperature range covered (25° to 1,300° C.).

FIGURE 18. - Thermal Expansion of Lutetium Sesquioxide.

TABLE 27. - Thermal expansion of lutetium oxide

Temperature, ° C.	Unit cell parameter, Å	Linear expansion, percent	Linear expansion coefficient ($\times 10^6$)
0.....	10.3847	0.00	
27.....	10.3864	.016	5.9
148.....	10.3943	.092	6.2
175.....	10.3965	.107	6.1
352.....	10.4409	.235	6.6
385.....	10.4119	.262	6.8
472.....	10.4195	.335	7.0
555.....	10.4259	.397	7.1
599.....	10.4298	.434	7.2
695.....	10.4382	.515	7.4
750.....	10.4435	.566	7.5
860.....	10.4531	.659	7.6
880.....	10.4554	.681	7.7
984.....	10.4642	.766	7.7
1,045.....	10.4704	.825	7.8
1,100.....	10.4759	.878	7.9
1,152.....	10.4811	.928	8.0
1,235.....	10.4898	1.012	8.1
1,300.....	10.4957	1.068	8.2
1,095.....	10.4754	.873	7.9
954.....	10.4614	.739	7.7
860.....	10.4528	.656	7.6
640.....	10.4335	.470	7.3
305.....	10.4059	.204	6.6

TABLE 28. - Powder X-ray diffraction data for
lutetium oxide at 25° C.¹

hkl	d-spacing, A	$\frac{I}{I_{100}} \times 100$	a, A	hkl	d-spacing, A	$\frac{I}{I_{100}} \times 100$	a, A
211	4.21	9	10.31	842	1.133	2	10.382
222	2.984	100	10.335	921	1.120	4	10.383
321	2.764	3	10.342	851	1.095	4	10.385
400	2.595	40	10.378	932	1.0711	3	10.3846
411	2.440	5	10.352	844	1.0599	6	10.3853
331	2.376	2	10.356	941	1.0493	3	10.3865
332	2.208	7	10.355	10·0·0	1.0387	2	10.3875
431	2.032	11	10.359	10·2·0	1.0186	5	10.3893
440	1.832	30	10.363	943	1.0089	1	10.3918
433	1.778	4	10.365	10·2·2	0.9996	6	10.3884
611	1.681	5	10.360	10·3·1	.9905	4	10.3919
541	1.600	4	10.369	871	.9730	3	10.3919
622	1.563	22	10.369	10·4·0	.9647	4	10.3899
631	1.529	5	10.372	10·3·3	.9565	2	10.3876
444	1.497	6	10.372	10·4·2	.9485	4	10.3860
543	1.467	5	10.372	954	.9407	3	10.3944
640	1.439	2	10.373	11·2·1	.9257	3	10.3862
721	1.412	5	10.373	880	.9184	1	10.3876
642	1.386	3	10.373	10·4·4	.9045	2	10.3922
732	1.318	4	10.378	11·3·2	.8977	2	10.3954
800	1.298	5	10.384	10·6·0	.8911	1	10.3907
811	1.277	6	10.378	11·4·1	.8846	2	10.3944
820	1.259	3	10.379	10·6·2	.8783	5	10.3897
653	1.241	3	10.380	965	.8720	1	10.3944
822	1.223	3	10.378	12·0·0	.8661	2	10.3926
831	1.207	2	10.381	12·1·1	.8600	4	10.3895
662	1.191	10	10.380	12·2·0	.8543	3	10.3964
840	1.161	8	10.381	11·5·2	.8486	2	10.3955
833	1.147	2	10.383	12·2·2	.8429	3	10.3934

¹Fired at 1,330° C. for 24 hours.

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