Thermal expansion of the sesquioxides of yttrium, scandium, and gadolinium

Denzil Wayne Stacy

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THERMAL EXPANSION OF THE SESQUIOXIDES OF YTTRIUM, SCANDIUM, AND GADOLINIUM

by

Denzil Wayne Stacy

A Thesis Submitted to the Graduate Faculty in Partial Fulfillment of The Requirements for the Degree of MASTER OF SCIENCE

Major Subject: Ceramic Engineering

Iowa State University Of Science and Technology Ames, Iowa

1967
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INTRODUCTION

The rare earth oxides are promising high-temperature refractory materials. This is shown by their high melting temperatures and chemical stability at elevated temperatures in oxidizing atmospheres. The variation in nuclear properties of these oxides suggests wide application as reactor materials.

Thermal expansion is an important design property of refractory materials. This property is a measure of the change in physical size of a material as it is heated. The magnitude of the thermal expansion partially determines the ability of solid bodies to withstand thermal shock. In applications where one body is constrained by another at high temperatures, it is necessary that their thermal expansion characteristics be similar. Thus, measuring thermal expansion of materials which are to be used as refractories is essential.

The purpose of this study was to measure the thermal expansion of the rare earth oxides -- yttrium sesquioxide, scandium sesquioxide, and gadolinium sesquioxide.

Yttrium sesquioxide (yttria) was chosen for investigation because of its high melting temperature of 2410°C (1) and its very low thermal neutron cross section of 1.38 barns (1). An anomaly in the heat content (2) and internal friction (3) at 1057°C was also of interest.

Scandium sesquioxide (scandia) was chosen for investigation because it is the least dense of the rare earth oxides. It has
a high melting temperature of 2300°C (4) and intermediate thermal neutron cross section of about 23 barns (5).

Gadolinium sesquioxide (gadolinia) was selected for investigation because it has a very high thermal neutron cross section of 40,000 barns (6) and high melting temperature of 2350°C (6). Gadolinia exists in two crystallographic forms; the cubic-to-monoclinic transformation occurs between 1250°C and 1400°C and is irreversible (7). Thermal expansion was measured on both crystallographic forms of gadolinia.
Techniques of Measuring Thermal Expansion

The most common techniques used to measure thermal expansion of ceramic materials are interferometer, micrometer telescopes, high-temperature X-ray diffraction, and dilatometer. These techniques for measuring thermal expansion are among those summarized by Hidnert and Sønder (8).

**Interferometer Technique**

Merritt (9) presented a detailed description of the interferometer technique and Wilfong et al. (10) gave a concise summary of this technique as used in measuring the thermal expansion of rare earth oxides. Wilfong's apparatus employed two sapphire plates which were ground so the faces of each plate were inclined at a small angle. Three pyramidal specimens were placed between the plates and the assembly was supported inside a vertical tubular resistance furnace. Collimated monochromatic light illuminated the sapphire plates and the light reflected from the surfaces touching the specimens was observed with a telescope. The light from the faces of the plates which did not touch the specimens was reflected out of the field of vision. If twice the distance between the surfaces which touched the specimens (the path difference for reflected beams) was an integral number of wavelengths, the reflected light from these planes was in phase and a bright band was observed in the telescope. If the optical path difference was
an odd number of half wavelengths, the reflected light was out of phase and a dark band was observed.

Bands of constructive and destructive interference traversed the field of view of the telescope as the furnace was heated and the specimens expanded. One bright band was observed for each half wavelength increase in specimen height. Thus by knowing the initial length of the specimens and by measuring their temperature with thermocouples, thermal expansion could be calculated by counting the number of bands.

The interferometer technique has the advantage that it may be used with continuous or stepwise heating of the specimens. Small specimens may be used, but there may be difficulty in getting them the same length and obtaining proper alignment of the interferometer plates. Both of these conditions are necessary in obtaining good interference patterns.

**Micrometer telescope technique**

The micrometer telescope technique of measuring the thermal expansion of materials has been described by Hidnert and Souder (8). A 10 to 50 cm. specimen was positioned horizontally in a furnace such that thin refractory metal wires attached to its ends would hang through slots in the bottom of the furnace. Weights were attached to the wires and suspended in a liquid bath to dampen vibrations. Two "micrometer microscopes" were mounted on a horizontal comparator and positioned so that one wire could be observed in each microscope. The
expansion of the specimen at each temperature was determined by the increase in distance between the wires as shown on the micrometers.

A variation of this technique was used by Nielsen and Leipold (11) to measure the thermal expansion of yttria above 1000°C. A 3 inch specimen stood vertically in an induction furnace. The displacement of the specimen was observed with two "telemicroscopes" fitted with filar micrometer eyepieces which were calibrated to an accuracy of ± 5 × 10⁻⁵ in. Optical pyrometers were used to measure the temperature.

High-temperature X-ray diffraction technique

The high-temperature X-ray diffraction technique was used by Stecura and Campbell (12) to measure the thermal expansion of rare earth oxides. Their diffractometer furnace was similar to one used by Mauer and Bolz (13). The heating element consisted of platinum-20 percent rhodium wire wound on an alumina core. The core was inserted in a mullite support tube which was surrounded by alumina insulating brick. The brick was cut so it fit snugly inside the furnace shell. A slot was cut through the brick, sample support tube, and winding core so that incident and diffracted beams were not obstructed. The specimen was held by an alumina sample holder positioned so that the specimen surface was on the axis of the furnace. This allowed the incident beam to focus on the specimen as the furnace was rotated. Linear expansion was calculated from the
increase in lattice parameter at elevated temperatures.

Klein (14) used an adaptation of the diffractometer furnace designed by Chiotti (15). The vacuum furnace element was a tantalum cylinder which was surrounded by three molybdenum heat shields. A longitudinal slot in the element and heat shields and a beryllium foil window in the furnace shell allowed the beam to enter and leave the furnace. A platinum-platinum rhodium thermocouple was used to measure temperatures over the appropriate range while an optical pyrometer was used at higher temperatures.

Several advantages of the X-ray diffraction technique of measuring thermal expansion have been given by Mauer and Bolz (13) and Stecura and Campbell (12). Expansion can be measured independently for each crystallographic direction of anisotropic materials. Only a small amount of material is needed and sample fabrication is not difficult. The data depend upon the crystal lattice and not on how the crystallites fit together. Measurements may be made on each phase of a multiple component system.

Klein (14) listed three disadvantages of the X-ray diffraction technique. Furnace design is difficult because of the beam and temperature gradients are caused by the necessity of openings in the heating element and heat shields. Reduction of data is more time-consuming than with other methods.
Dilatometer technique

A dilatometer was described by Hidnert and Souder (8) in their summary of thermal expansion techniques. The dilatometer employed a fused-quartz tube which was closed at the bottom. A cylindrical specimen was inserted into the tube and a fused-quartz rod rested on the specimen. A dial indicator was attached to the tube so that the plunger of the indicator touched the top of the fused-quartz rod. The dilatometer assembly was placed in an electrical tube furnace with the indicator protruding from the top. The indicator registered the difference between the expansion of the specimen and an equal length of fused-quartz. Thus the expansion of fused-quartz was added to the dial reading to give the thermal expansion of the specimen.

Beals and Lauchner (16) used the difference in e.m.f. generated by two photocells to indicate the expansion of a dilatometer specimen. One photocell was exposed directly to a light source. The other photocell was separated from the light source by a shield whose movement was effected by the expansion of the specimen. The dilation curve was plotted automatically as a function of the specimen temperature.

Fulkerson's dilatometer (17) utilized three synthetic sapphire rods to support the specimen and another as a push rod to actuate either a dial indicator or a linear variable differential transformer (LVDT). A porcelain tube surrounded the rod assembly to allow for controlled atmospheres or vacuum.
Many other modifications of the dilatometer technique can be found in the literature (18).

Thermal Expansion of Yttrium Sesquioxide

Curtis (1) measured the thermal expansion of yttria with a sapphire rod dilatometer and dial indicator. A heating rate of \(3^\circ \pm 0.5^\circ\) C per minute was used to 1400°C. The apparent density of the 99% pure specimen which had been fired to 1800°C was reported as 3.86 gm./cm\(^3\). The density would be 76.7% based on 5.03 gm./cm\(^3\). Curtis reported the over-all coefficient from 0\(^\circ\) to 1400°C as 9.3 \(\times 10^{-6}\) in./in./\(^\circ\)C. However, as pointed out by Stecura and Campbell (12), the curve presented in Curtis' report indicated an over-all coefficient of 8.2 \(\times 10^{-6}\) in./in./\(^\circ\)C. The coefficients given in Table 1 were taken from the curve.

Fitzsimmons (19) used the micrometer telescope technique to measure the thermal expansion of yttria to 1550°C. A portion of the curve is shown in Figure 1. The 4 in. long specimen had been sintered to 1620°C and had 96.3% theoretical density. The coefficients given in Table 1 were calculated from expansion data.

High temperature X-ray diffraction was used by Stecura and Campbell (12) to measure the thermal expansion of yttria. The specimen was 99.9% pure with regard to rare earth content and had been fired 24 hours at 1250°C then refired at 1350°C for 12 hours. The coefficient from 0\(^\circ\) to 1300°C was reported as 8.9 \(\times 10^{-6}\) in./in./\(^\circ\)C. The coefficients given in Table 1
were calculated from expansion data taken from the expansion curve. The curve on Figure 1 was plotted from thermal expansion data presented in a table.

To measure the thermal expansion of yttria below 1000°C, Nielsen and Leipold (20) used a fused-quartz dilatometer described by Duwez and Martens (21). The transducer consisted of a series of levers which moved an electrical contact along a slide wire. The location of the contact was transmitted electrically to a recorder. From 1000°C to above 2000°C, Nielsen and Leipold (20) used the micrometer telescope technique in both oxygen and argon-hydrogen atmospheres without significant differences in results. Specimens of 99.5 to 99.8% pure yttria were pressed and sintered in air at 1700°C. The curve presented in Figure 1 was calculated from mean coefficients (the slope of the expansion curve at the center of a temperature interval) which were used as over-all coefficients. Thus the curve will be slightly low. The mean coefficients were used in Table 1.

Wilfong et al. (10) measured the thermal expansion of yttria with a sapphire interferometer. The curve of Figure 1 was plotted from expansion data of the first two runs reported. The coefficient of expansion from 25° to 1000°C was 8.10 X 10⁻⁶ in./in.°C. Yttria specimens were dry pressed at 25,000 psi with 2 percent Varsol and 2 percent paraffin dissolved in benzene as binders. The compacts were sintered at 1800°C for one hour. After the interferometer specimens were ground, the
10 specimens were reheated to 1500°C for 1 hour. See Table 1.

Thermal expansion measurements by General Electric Co. were made on a Leitz UBD dilatometer. Yttria specimens were prefired at 1000°C for 2 hours, machined into bars, and fired at 1750°C for four hours in hydrogen. The bars had a density of 4.67 gm./cm³ (92.8% theoretical based on 5.03 gm./cm³).

The curve of Figure 1 is plotted from the curve of thermal expansion. The coefficients given in Table 1 were calculated from data from a thermal expansion curve.

Table 1. Thermal expansion coefficients of yttria X 10⁶ (in./in.⁰C)

<table>
<thead>
<tr>
<th>Temperature (⁰C)</th>
<th>Author</th>
<th>600</th>
<th>800</th>
<th>1000</th>
<th>1100</th>
<th>Type of coefficient</th>
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<tr>
<td></td>
<td>Curtis</td>
<td>7.33</td>
<td>7.81</td>
<td>8.00</td>
<td>8.00</td>
<td>Over-all from 25⁰C</td>
</tr>
<tr>
<td></td>
<td>Fitzsimmons</td>
<td>8.00</td>
<td>8.13</td>
<td>8.21</td>
<td>8.28</td>
<td>Over-all from 25⁰C</td>
</tr>
<tr>
<td></td>
<td>Stecura &amp;</td>
<td>7.9</td>
<td>8.2</td>
<td>8.5</td>
<td>8.6</td>
<td>Over-all from 0⁰C</td>
</tr>
<tr>
<td></td>
<td>Campbell</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nielsen &amp;</td>
<td>7.70</td>
<td>8.00</td>
<td>8.30</td>
<td>8.50</td>
<td>Mean from 25⁰C</td>
</tr>
<tr>
<td></td>
<td>Leipold</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wilfong et al.</td>
<td>7.64</td>
<td>7.89</td>
<td>8.10</td>
<td>--</td>
<td>Over-all from 25⁰C</td>
</tr>
<tr>
<td></td>
<td>General Electric</td>
<td>7.30</td>
<td>7.61</td>
<td>7.95</td>
<td>8.10</td>
<td>Over-all from 25⁰C</td>
</tr>
</tbody>
</table>
Figure 1. Linear thermal expansion of yttria

Wilkinson - Interneter
Nielson - Leipold - Dilatometer
Coooling
Leipold - Microscope Above 1000°C
Fielding - Microscope
Fitzsimmons - Microscope
This Study - Dilatometer, Graphical
This Study - Dilatometer, Analytical
Thermal Expansion of Scandium Sesquioxide

Stecura and Campbell (12) determined the thermal expansion of scandia by high-temperature X-ray diffraction. The sample was 99.5% pure with regard to rare earth content. The specimen had been sintered at 1150°C for 24 hours, then resintered at 1200°C. The coefficient of thermal expansion from 0°C to 1130°C was $8.9 \times 10^{-6}$ in./in./°C and $9.5 \times 10^{-6}$ in./in./°C from 0°C to 1300°C. The curve in Figure 2 was plotted from the thermal expansion data.

The study of thermal expansion of scandia by Brown and Kirchner (23) was also by X-ray diffraction. The curve in Figure 2 was calculated from lattice constant versus temperature data for scandia which was greater than 99% pure. Brown and Kirchner estimated the maximum error in thermal expansion coefficient measurement to be $0.17 \times 10^{-6}$ for the interval 25 to 1000°C and $0.14 \times 10^{-6}$ from 25 to 1200°C.

A summary of coefficients of expansion of scandia at selected temperatures as determined by these two authors is given in Table 2.

Table 2. Thermal expansion coefficients of scandia X $10^6$
(in./in./°C)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Author</th>
<th>600</th>
<th>800</th>
<th>1000</th>
<th>1100</th>
<th>Type of coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Stecura &amp; Campbell</td>
<td>7.7</td>
<td>8.0</td>
<td>8.5</td>
<td>8.9</td>
<td>Over-all from 0°C</td>
</tr>
<tr>
<td></td>
<td>Brown &amp; Kirchner</td>
<td>8.50</td>
<td>8.76</td>
<td>8.84</td>
<td>9.23</td>
<td>Over-all from 25°C</td>
</tr>
</tbody>
</table>
Figure 2. Linear thermal expansion of scandia
Thermal Expansion of Gadolinium Sesquioxide

The thermal expansion of monoclinic gadolinia has been measured by Curtis and Johnson (6) and by Ploetz et al. (24).

Curtis and Johnson gave the thermal expansion coefficient of gadolinia as 10.5 X 10^{-6} in./in.°C from 25° to 1000°C as indicated in Figure 3. The gadolinia which contained 2% terbium and smaller amounts of other rare earth oxides had a density of 7.64 gm./cm^3. No technique was given for the thermal expansion measurements.

Ploetz et al. used the interferometer technique to measure the thermal expansion of monoclinic gadolinia. The density of the specimens was 7.06 gm./cm^3 or 84.8% theoretical based on 8.33 gm./cm^3. The heating rate was 3° to 5°C per minute. The coefficient from 30° to 840°C was reported as 10.0 X 10^{-6} in./in.°C. The curve of Figure 3 was drawn from a thermal expansion curve given by Ploetz et al. They neglected to give the units on the expansion axis, but units were assumed on the basis of the thermal expansion coefficients given. Thermal expansion coefficients for monoclinic gadolinia are given in Table 3.

The thermal expansion of cubic gadolinia has been measured by Stecura and Campbell (12) by high-temperature X-ray diffraction. The sample was 99.9% pure with respect to rare earth content. It was sintered at 1150°C for 24 hours, then resintered at the same temperature for 12 hours. The specimen was held at 1310°C, the maximum temperature of expansion measurements, for
approximately one-half hour, but remained cubic. The curve in Figure 3 was plotted from thermal expansion data. The coefficients of thermal expansion are given in Table 4.

Table 3. Thermal expansion coefficients of monoclinic gadolinia $\times 10^6$ (in./in.$^\circ$C)

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>Author</th>
<th>600</th>
<th>800</th>
<th>1000</th>
<th>1100</th>
<th>Type of coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Curtis &amp; Johnson</td>
<td>--</td>
<td>--</td>
<td>10.5</td>
<td>--</td>
<td>Over-all from 25$^\circ$C</td>
</tr>
<tr>
<td></td>
<td>Ploetz et al.</td>
<td>9.55</td>
<td>9.97</td>
<td>--</td>
<td>--</td>
<td>Over-all from 30$^\circ$C</td>
</tr>
</tbody>
</table>

Table 4. Thermal expansion coefficients of cubic gadolinia $\times 10^6$ (in./in.$^\circ$C)

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>Author</th>
<th>600</th>
<th>800</th>
<th>1000</th>
<th>1100</th>
<th>Type of coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Stecura &amp; Campbell</td>
<td>7.9</td>
<td>8.1</td>
<td>8.4</td>
<td>8.6</td>
<td>Over-all from 0$^\circ$C</td>
</tr>
</tbody>
</table>
Figure 3. Linear thermal expansion of gadolinia
Description of Apparatus

The dilatometer built for this study was similar to that designed by Fulkerson (17). It employed four synthetic sapphire rods which were obtained from Linde Division of Union Carbide Corporation. The manufacturer stated that the axis of the rods was approximately 60° from the crystallographic c direction. Three 1/8 in. diameter sapphire support rods 12 3/4 in. long were fastened with refractory cement into holes in a high density alumina base plate. The top ends of the support rods were fitted into holes in a brass support block. See Figure 4. Set screws tipped with Tygon plugs were used to secure the rods in the holes. A fourth sapphire push rod 1 1/8 in. shorter than the support rods acted as a link between the specimen and the transducer. The top end of the push rod was hollow ground to make a firm contact with the rounded end of the transducer plunger. The push rod was held in place by the spring tension of the transducer plunger.

The support block was fastened firmly to a 1 in. brass plate. The plate was supported by a table which also supported the Kanthal A-1 wound tube furnace. The furnace was mounted so that it could be lowered away from the dilatometer to facilitate changing specimens. The furnace resistance was 10 ohms. The tube was 7/8 in. inside diameter and closed at the bottom with a refractory plug.
Figure 4. Dilatometer
A fused-quartz tube was attached to the under side of the 1 in. brass plate to protect the sapphire rods from air currents. During an expansion run, the furnace was raised so that the top of the furnace touched the bottom of the fused-quartz tube. A small notch in the lower edge of the fused quartz tube provided an exit for the thermocouple wires.

The transducer was a model 103C-200 linear variable differential transformer manufactured by Daytronic Corporation. This transformer had two secondary coils wound symmetrically about a primary coil on a ceramic cylinder. A magnetic iron core was supported inside the cylinder by the non-magnetic plunger of the transducer. The secondaries were electrically connected so the voltage induced in one was opposed by the other. When the magnetic core was in the null position, the net voltage induced in the two secondaries was zero. As the core was displaced from the null position, the voltage induced in one secondary was greater than that induced in the other, giving a net output which varied linearly with the displacement of the core. The model 103C-200 had a linear range of ± 0.1 inch from the null position and was linear to 0.1% of that range. The transducer was magnetically shielded to prevent 60 cycle pickup.

Daytronic model 300CF transducer amplifier-indicator with a type 61 plug-in unit provided the 3000 cycle, 3 volt excitation voltage for the transducer. This device supplied a ± 50 m.v. DC output to a potentiometric type recorder for all of
eight sensitivity ranges corresponding to ± 0.100 to ± 0.0001 inch displacement of the transducer plunger. A meter on the amplifier-indicator showed the output to the recorder. According to the manufacturer, the error of the recorder output was 1% of full scale.

The transducer and amplifier-indicator were calibrated to assure proper recorder output for a given displacement of the transducer core. The transducer was mounted on a jig opposite to a micrometer. A known linear displacement was applied to the transducer plunger by the micrometer. Adjustments were made on the amplifier-indicator to make the meter indicate the same displacement as that of the core. A separate adjustment was made so the recorder output corresponded to the displacement shown on the meter.

The transducer was screwed into the top of the support block and locked into position with the lock nut. Large adjustments were made by turning the transducer, while small adjustments were effected with an electrical zeroing device on the amplifier-indicator.

The output of the amplifier-indicator was recorded with a Varian model G-10 graphic recorder. This potentiometric recorder had 100 mV DC span and the limit of error was 1% of the span. Temperature was recorded with a platinum-platinum-10 percent rhodium thermocouple and a Brown strip-chart recorder calibrated for this type thermocouple. The thermocouple protection tube was attached to one of the sapphire support rods.
with platinum wire. The thermocouple bead was positioned at the vertical center of the specimen. The bead was about 1/8 in. from the specimen to ensure that the movement of the thermocouple protection tube did not misalign the specimen during the expansion run. Comparison of the thermocouple output with that of a thermocouple which had been calibrated by the National Bureau of Standards showed that the temperature readings from 25°C to 1300°C were high with a maximum error of $+3^\circ$C. The temperature could be read from the recorder trace to an accuracy of about $\pm 2^\circ$C.

The heating rate of less than $5^\circ$C per minute was obtained by using a powerstat driven by an electric motor.

Calibration of Dilatometer

The dilatometer used in this study did not measure the absolute thermal expansion of the specimen, but instead, a difference between the expansion of the specimen and that of the sapphire rods. Ideally, if a specimen of sapphire of the same orientation as the support rods was used as a specimen, no extension would be detected by the transducer. However, there were conditions in the dilatometer which caused the transducer to register a displacement. The most obvious cause of the displacement was a difference in thermal gradients of the support rods and the push rod. The support rods made firm contact with the thick brass plate, while the push rod touched only the end of the transducer plunger. Therefore, it was necessary to calibrate the dilatometer before accurate thermal expansion measurements could be made.
A 1.000 in. specimen of Linde synthetic sapphire rod 1/8 in. in diameter was used for the calibration of the dilatometer. According to the manufacturer, the orientation of the rod was about 60° from the c crystallographic axis. This orientation was confirmed by the back-reflection Laue method of X-ray diffraction. Geller and Yavorsky (25) measured the orientation of four rods from Linde and found the orientation of all rods to be 57.34° from the crystallographic c axis. Wachtman et al. (26) presented the thermal expansion of 57.6° sapphire and stated that this was the orientation frequently used in sapphire rod dilatometers. Since the exact orientation of the rod was not known, and since the relative difference in expansion of 57.6° and 60° sapphire is only 0.4%, the thermal expansion data of Wachtman et al. were used as the expansion of the calibration specimen.

Wachtman et al. measured the expansion of the sapphire to 827°C by the interferometer technique and extrapolated the curve by using an equation based on the theory of thermal expansion. The expansion curve presented by Wachtman et al. agreed well with the work of Wilfong et al. (10) who measured the thermal expansion of "approximately 60° orientation" sapphire to 1000°C by the interferometer technique. Geller and Yavorsky's data (25) on 57.6° sapphire agreed with the results of the other two authors. Wachtman's curve is plotted on Figure 5.
The calibration of the dilatometer is shown in Figure 5. The data curve for the single crystal sapphire rod represents a visual average of the data from two runs. The magnitude of this curve is the correction which is caused by the thermal gradients in the support and push rods. This curve was graphically subtracted from the known thermal expansion of sapphire to give the calibration curve for the dilatometer. The calibration curve is shown in Figure 5.

The calibration was also done analytically by fitting the thermal expansion of sapphire and the sapphire rod data with polynomial equations of the form \( \Delta L/L = A + Bt + Ct^2 \). \( \Delta L/L \) represents linear thermal expansion in percent, \( t \) represents temperature in \( ^\circ C \), and \( A, B, \) and \( C \) are constants. The curves were fitted by the method of least squares using an IBM 360/50 computer. The difference of the two equations is the equation of the calibration curve.
Figure 5. Calibration of the dilatometer
PROCEDURE

Specimen Preparation

Yttria was provided by the Ames Laboratory as clinker from calcination of the oxalate. The clinker was reduced to a fine powder by hand grinding with a porcelain mortar and pestle. Scandia of 99.9% purity was received as a fine powder from Research Chemicals. Cubic gadolinia was obtained from the Oak Ridge Operations Office as clinker and was reduced to powder by tumbling for six hours in a glass jar with rubber stoppers. Spectrographic analyses of the three oxides are given in Table 5. A semi-quantitative analysis was made for those elements for which the Ames Laboratory Spectrographic Group had standards. Other elements are reported only on a qualitative basis. The major impurities were tantalum and calcium in yttria, tantalum in scandia, and europium in gadolinia.

Prismatic bars were made by pressing the powders in a steel die to 1000 psi. The bars were inverted and repressed to 1200 psi. The inversion of specimens was to prevent warpage when the specimens were pressed to 50,000 psi in an isostatic press.

With the exception of two bars, the bars were fired at the desired temperature in an electrical resistance furnace in air or in a graphite induction furnace under reducing conditions. One specimen was fired in a vacuum resistance furnace and one was hot pressed in a graphite die at 3300 psi. Specimens which were fired in the graphite induction furnace and hot press were
refired at 1300° to 1400°C for several hours to remove carbon which collected on the specimens during firing and to reoxidize the specimens if any reduction had occurred.

The bars were ground to 1.000 ± 0.001 in. on a grinding wheel using 180 mesh silicon carbide paper. During the grinding, the length of each specimen was measured frequently with micrometer calipers to assure that its ends were flat and parallel. Specimens were about 1/8 in. by 1/4 in. in cross section.

Table 5. Spectrographic analysis of impurities (ppm)

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Y$_2$O$_3$</th>
<th>Sc$_2$O$_3$</th>
<th>Gd$_2$O$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>faint trace</td>
<td>80</td>
<td>≤ 10</td>
</tr>
<tr>
<td>Ca</td>
<td>400</td>
<td>40</td>
<td>30</td>
</tr>
<tr>
<td>Cr</td>
<td>≤ 40</td>
<td>≤ 20</td>
<td>≤ 10</td>
</tr>
<tr>
<td>Cu</td>
<td>≤ 70</td>
<td>≤ 20</td>
<td>10</td>
</tr>
<tr>
<td>Dy</td>
<td>≤ 100</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Er</td>
<td>≤ 50</td>
<td>≤ 50</td>
<td>--</td>
</tr>
<tr>
<td>Eu</td>
<td>--</td>
<td>--</td>
<td>800</td>
</tr>
<tr>
<td>Fe</td>
<td>≤120</td>
<td>≤ 30</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>Gd</td>
<td>≤ 30</td>
<td>--</td>
<td>constituent</td>
</tr>
<tr>
<td>Ho</td>
<td>≤ 60</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Lu</td>
<td>--</td>
<td>20</td>
<td>--</td>
</tr>
<tr>
<td>Mg</td>
<td>20</td>
<td>&lt; 10</td>
<td>10</td>
</tr>
<tr>
<td>Nd</td>
<td>≤200</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Ni</td>
<td>--</td>
<td>≤ 20</td>
<td>≤ 10</td>
</tr>
<tr>
<td>Sc</td>
<td>--</td>
<td>constituent</td>
<td>--</td>
</tr>
<tr>
<td>Si</td>
<td>60</td>
<td>160</td>
<td>≤ 10</td>
</tr>
<tr>
<td>Sm</td>
<td>≤200</td>
<td>--</td>
<td>≤200</td>
</tr>
<tr>
<td>Ta</td>
<td>≤400</td>
<td>350</td>
<td>≤200</td>
</tr>
<tr>
<td>Ti</td>
<td>≤ 30</td>
<td>≤ 20</td>
<td>--</td>
</tr>
<tr>
<td>Tb</td>
<td>≤200</td>
<td>--</td>
<td>≤100</td>
</tr>
<tr>
<td>Tm</td>
<td>faint trace</td>
<td>≤ 20</td>
<td>--</td>
</tr>
<tr>
<td>Y</td>
<td>constituent</td>
<td>&lt; 10</td>
<td>100</td>
</tr>
<tr>
<td>Yb</td>
<td>&lt;100</td>
<td>≤ 5</td>
<td>--</td>
</tr>
<tr>
<td>Zr</td>
<td>faint trace</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>
X-ray diffraction analysis was made on each gadolinia specimen before and after thermal expansion measurements to assure that the crystallographic form had not been altered.

Density measurements were made by water displacement after thermal expansion runs were completed. Only expansion runs which had less than $1 \times 10^{-4}$ in. final displacement of the transducer plunger after the furnace had cooled were used. Larger displacements could have been caused by misalignment or sintering of the specimen.

Specimen firing conditions and percent theoretical densities are given in Table 6. Theoretical densities of yttria, scandia, and cubic gadolinia were calculated as 5.03, 3.84, and 7.62 gm./cm$^3$ respectively, from X-ray data given by Stecura and Campbell (12). From their X-ray data, Guentert and Mozzi (27) calculated the theoretical density of monoclinic gadolinia to be 8.33 gm./cm$^3$.

Measurement of Thermal Expansion

In preparation for making a thermal expansion run, the specimen was placed in a dryer at 110°C overnight. The specimen was removed from the drier and allowed to cool for about 15 minutes while the electrical equipment was warming up. The furnace was lowered away from the dilatometer assembly and the bottom end of the sapphire push rod was grasped with tweezers and lifted against the spring load in the transducer plunger. The old specimen was removed and the new one was centered on
Table 6. Firing conditions and density of specimens

<table>
<thead>
<tr>
<th>Specimen number</th>
<th>Temperature (°C)</th>
<th>Atmosphere</th>
<th>Density (% theoretical)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y₂O₃-1</td>
<td>--</td>
<td>--</td>
<td>75.2</td>
</tr>
<tr>
<td>-2</td>
<td>2150</td>
<td>reducing</td>
<td>77.6</td>
</tr>
<tr>
<td>-3</td>
<td>1500</td>
<td>hot press</td>
<td>96.7</td>
</tr>
<tr>
<td>-4</td>
<td>2000</td>
<td>reducing</td>
<td>94.5</td>
</tr>
<tr>
<td>-5</td>
<td>2000</td>
<td>reducing</td>
<td>94.3</td>
</tr>
<tr>
<td>Sc₂O₃-1</td>
<td>1950</td>
<td>reducing</td>
<td>89.9</td>
</tr>
<tr>
<td>-2</td>
<td>1950</td>
<td>reducing</td>
<td>89.3</td>
</tr>
<tr>
<td>-3</td>
<td>1900</td>
<td>reducing</td>
<td>89.7</td>
</tr>
<tr>
<td>Monoclinic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gd₂O₃-1</td>
<td>1700</td>
<td>vacuum</td>
<td>81.3</td>
</tr>
<tr>
<td>-2</td>
<td>1500 18½ hr. air</td>
<td>reducing</td>
<td>85.1</td>
</tr>
<tr>
<td>-3</td>
<td>2000</td>
<td>reducing</td>
<td>85.1</td>
</tr>
<tr>
<td>-4</td>
<td>1300 45 min. air</td>
<td>reducing</td>
<td>87.3</td>
</tr>
<tr>
<td>-5</td>
<td>1300 45 min. air</td>
<td>reducing</td>
<td>87.3</td>
</tr>
<tr>
<td>-6</td>
<td>1900</td>
<td>reducing</td>
<td>87.3</td>
</tr>
<tr>
<td>Cubic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gd₂O₃-7</td>
<td>1200 18 hr.</td>
<td>air</td>
<td>67.2</td>
</tr>
<tr>
<td>-8</td>
<td>1200 18 hr.</td>
<td>air</td>
<td>67.4</td>
</tr>
</tbody>
</table>

The base plate. The push rod was lowered to make firm contact with the top of the specimen. The furnace was then lifted to surround the dilatometer assembly. Visual inspection of the furnace from the bottom assured that the furnace tube did not touch the dilatometer assembly.

The electrical zeroing device of the amplifier-indicator was adjusted so the pen of the displacement recorder was at the desired starting point. The furnace power and the chart drives of the displacement and temperature recorders were started simultaneously. All measurements were then made automatically.
When the desired temperature was reached, the furnace was shut off and allowed to cool overnight.

The next day, after warming up the equipment, the final displacement of the specimen was recorded. Only runs with final displacement of less than 0.0001 in. were used. The displacement was corrected with the electrical zeroing device on the amplifier-indicator and the second run made in the same way as the first.

The temperature and displacement recorder traces were combined by plotting displacement versus temperature at half hour intervals. All data curves so obtained for one specimen were plotted on a graph and a visual average was taken. The average data curve was then added graphically to the calibration curve to give the expansion of the specimen as is shown in Figure 5 for specimen Gd$_2$O$_3$-4.

A second-degree polynomial equation was also fitted to the expansion data of each specimen. This equation was then added to the equation of the calibration curve to give an equation for the thermal expansion of the specimen.

Data curves were made on the sapphire standard periodically throughout the course of measurements. A new calibration curve was determined after each run on the sapphire standard.
RESULTS

Linear thermal expansion values for each specimen of yttria, scandia, monoclinic and cubic gadolinia are given in Tables 7, 8, 9, and 10 respectively. These values were obtained from the graphical addition of data and calibration curves. Values of the linear thermal expansion of Sc$_2$O$_3$-1 which were computed from the equation of thermal expansion for that specimen are also included in Table 8. The agreement of expansion values from the two methods of data treatment was similar for the other specimens.

The values in Table 11 represent the average of expansion values for all specimens of each material. Curves of the average expansion for yttria, scandia, and the two crystallographic forms of gadolinia are compared with the results of other authors in Figures 1, 2, and 3.

Table 7. Percent linear thermal expansion of yttria specimens

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>$Y_2O_3$-1</th>
<th>$Y_2O_3$-2</th>
<th>$Y_2O_3$-3</th>
<th>$Y_2O_3$-4</th>
<th>$Y_2O_3$-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>100</td>
<td>0.048</td>
<td>0.045</td>
<td>0.049</td>
<td>0.045</td>
<td>0.046</td>
</tr>
<tr>
<td>200</td>
<td>0.122</td>
<td>0.116</td>
<td>0.122</td>
<td>0.110</td>
<td>0.118</td>
</tr>
<tr>
<td>300</td>
<td>0.204</td>
<td>0.198</td>
<td>0.206</td>
<td>0.186</td>
<td>0.193</td>
</tr>
<tr>
<td>400</td>
<td>0.288</td>
<td>0.284</td>
<td>0.293</td>
<td>0.266</td>
<td>0.274</td>
</tr>
<tr>
<td>500</td>
<td>0.362</td>
<td>0.363</td>
<td>0.372</td>
<td>0.346</td>
<td>0.360</td>
</tr>
<tr>
<td>600</td>
<td>0.438</td>
<td>0.441</td>
<td>0.447</td>
<td>0.430</td>
<td>0.453</td>
</tr>
<tr>
<td>700</td>
<td>0.527</td>
<td>0.520</td>
<td>0.525</td>
<td>0.516</td>
<td>0.517</td>
</tr>
<tr>
<td>800</td>
<td>0.608</td>
<td>0.606</td>
<td>0.610</td>
<td>0.606</td>
<td>0.603</td>
</tr>
<tr>
<td>900</td>
<td>0.693</td>
<td>0.693</td>
<td>0.692</td>
<td>0.692</td>
<td>0.688</td>
</tr>
<tr>
<td>1000</td>
<td>0.765</td>
<td>0.775</td>
<td>0.769</td>
<td>0.770</td>
<td>0.774</td>
</tr>
<tr>
<td>1100</td>
<td>0.856</td>
<td>0.850</td>
<td>0.846</td>
<td>0.842</td>
<td>0.861</td>
</tr>
<tr>
<td>1120</td>
<td>0.885</td>
<td>0.865</td>
<td>0.860</td>
<td>0.855</td>
<td>0.877</td>
</tr>
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</table>
Table 8. Percent linear thermal expansion of scandia specimens

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Sc$_2$O$_3$-1 (analytical)</th>
<th>Sc$_2$O$_3$-2</th>
<th>Sc$_2$O$_3$-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.000 (-0.012)</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>100</td>
<td>0.046 (0.043)</td>
<td>0.048</td>
<td>0.049</td>
</tr>
<tr>
<td>200</td>
<td>0.114 (0.120)</td>
<td>0.118</td>
<td>0.120</td>
</tr>
<tr>
<td>300</td>
<td>0.190 (0.198)</td>
<td>0.198</td>
<td>0.195</td>
</tr>
<tr>
<td>400</td>
<td>0.272 (0.280)</td>
<td>0.282</td>
<td>0.275</td>
</tr>
<tr>
<td>500</td>
<td>0.359 (0.362)</td>
<td>0.368</td>
<td>0.356</td>
</tr>
<tr>
<td>600</td>
<td>0.453 (0.448)</td>
<td>0.459</td>
<td>0.440</td>
</tr>
<tr>
<td>700</td>
<td>0.543 (0.536)</td>
<td>0.551</td>
<td>0.529</td>
</tr>
<tr>
<td>800</td>
<td>0.634 (0.626)</td>
<td>0.646</td>
<td>0.621</td>
</tr>
<tr>
<td>900</td>
<td>0.727 (0.718)</td>
<td>0.740</td>
<td>0.717</td>
</tr>
<tr>
<td>1000</td>
<td>0.817 (0.813)</td>
<td>0.831</td>
<td>0.810</td>
</tr>
<tr>
<td>1100</td>
<td>0.915 (0.910)</td>
<td>0.927</td>
<td>0.912</td>
</tr>
<tr>
<td>1130</td>
<td>0.944 (0.940)</td>
<td>0.958</td>
<td>0.944</td>
</tr>
</tbody>
</table>

Table 9. Percent linear thermal expansion of monoclinic gadolinia specimens

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Gd$_2$O$_3$-1</th>
<th>Gd$_2$O$_3$-2</th>
<th>Gd$_2$O$_3$-3</th>
<th>Gd$_2$O$_3$-4</th>
<th>Gd$_2$O$_3$-5</th>
<th>Gd$_2$O$_3$-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>100</td>
<td>0.059</td>
<td>0.056</td>
<td>0.060</td>
<td>0.060</td>
<td>0.057</td>
<td>0.061</td>
</tr>
<tr>
<td>200</td>
<td>0.137</td>
<td>0.140</td>
<td>0.145</td>
<td>0.140</td>
<td>0.138</td>
<td>0.150</td>
</tr>
<tr>
<td>300</td>
<td>0.228</td>
<td>0.215</td>
<td>0.238</td>
<td>0.221</td>
<td>0.225</td>
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<tr>
<td>400</td>
<td>0.318</td>
<td>0.299</td>
<td>0.332</td>
<td>0.312</td>
<td>0.317</td>
<td>0.346</td>
</tr>
<tr>
<td>500</td>
<td>0.405</td>
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<td>0.436</td>
<td>0.406</td>
<td>0.412</td>
<td>0.434</td>
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<td>600</td>
<td>0.489</td>
<td>0.478</td>
<td>0.543</td>
<td>0.500</td>
<td>0.507</td>
<td>0.522</td>
</tr>
<tr>
<td>700</td>
<td>0.566</td>
<td>0.579</td>
<td>0.650</td>
<td>0.603</td>
<td>0.603</td>
<td>0.617</td>
</tr>
<tr>
<td>800</td>
<td>0.695</td>
<td>0.684</td>
<td>0.756</td>
<td>0.702</td>
<td>0.701</td>
<td>0.713</td>
</tr>
<tr>
<td>900</td>
<td>0.808</td>
<td>0.787</td>
<td>0.859</td>
<td>0.804</td>
<td>0.803</td>
<td>0.813</td>
</tr>
<tr>
<td>1000</td>
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<td>0.885</td>
<td>0.958</td>
<td>0.904</td>
<td>0.896</td>
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<td>1.056</td>
<td>0.996</td>
<td>1.056</td>
<td>1.005</td>
<td>0.995</td>
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<tr>
<td>1135</td>
<td>1.081</td>
<td>1.035</td>
<td>1.089</td>
<td>1.039</td>
<td>1.028</td>
<td>1.073</td>
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</table>
Table 10. Percent linear thermal expansion of cubic gadolinia specimens

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Gd$_2$O$_3$-7</th>
<th>Gd$_2$O$_3$-8</th>
</tr>
</thead>
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<tr>
<td>25</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>100</td>
<td>0.052</td>
<td>0.048</td>
</tr>
<tr>
<td>200</td>
<td>0.125</td>
<td>0.117</td>
</tr>
<tr>
<td>300</td>
<td>0.201</td>
<td>0.193</td>
</tr>
<tr>
<td>400</td>
<td>0.270</td>
<td>0.266</td>
</tr>
<tr>
<td>500</td>
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<tr>
<td>600</td>
<td>0.400</td>
<td>0.403</td>
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<tr>
<td>700</td>
<td>0.475</td>
<td>0.481</td>
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<td>0.554</td>
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<td>900</td>
<td>0.638</td>
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<td>1000</td>
<td>0.723</td>
<td>0.728</td>
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<tr>
<td>1100</td>
<td>0.817</td>
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</tr>
<tr>
<td>1125</td>
<td>0.889</td>
<td>0.842</td>
</tr>
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</table>

Table 11. Percent linear thermal expansion of yttria, scandia, monoclinic and cubic gadolinia

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Y$_2$O$_3$</th>
<th>Sc$_2$O$_3$</th>
<th>Monoclinic Gd$_2$O$_3$</th>
<th>Cubic Gd$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
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<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>100</td>
<td>0.047</td>
<td>0.048</td>
<td>0.059</td>
<td>0.050</td>
</tr>
<tr>
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<td>0.118</td>
<td>0.117</td>
<td>0.142</td>
<td>0.121</td>
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<td>0.197</td>
<td>0.194</td>
<td>0.229</td>
<td>0.197</td>
</tr>
<tr>
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<td>0.276</td>
<td>0.321</td>
<td>0.268</td>
</tr>
<tr>
<td>500</td>
<td>0.361</td>
<td>0.361</td>
<td>0.413</td>
<td>0.333</td>
</tr>
<tr>
<td>600</td>
<td>0.438</td>
<td>0.451</td>
<td>0.507</td>
<td>0.402</td>
</tr>
<tr>
<td>700</td>
<td>0.523</td>
<td>0.541</td>
<td>0.606</td>
<td>0.478</td>
</tr>
<tr>
<td>800</td>
<td>0.607</td>
<td>0.634</td>
<td>0.709</td>
<td>0.559</td>
</tr>
<tr>
<td>900</td>
<td>0.693</td>
<td>0.728</td>
<td>0.812</td>
<td>0.643</td>
</tr>
<tr>
<td>1000</td>
<td>0.775</td>
<td>0.819</td>
<td>0.913</td>
<td>0.726</td>
</tr>
<tr>
<td>1100</td>
<td>0.853</td>
<td>0.918</td>
<td>1.020</td>
<td>0.818</td>
</tr>
<tr>
<td>1120</td>
<td>0.868</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1125</td>
<td></td>
<td>0.949</td>
<td></td>
<td>0.841</td>
</tr>
<tr>
<td>1130</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1135</td>
<td></td>
<td></td>
<td></td>
<td>1.058</td>
</tr>
</tbody>
</table>
Over-all coefficients of linear thermal expansion from 25°C to selected temperatures are given in Table 12. These values were obtained by dividing the average expansion at each temperature, t, by t - 25.

Table 12. Over-all coefficients of linear thermal expansion $10^3$ (in./in.$^\circ\text{C}$) for yttria, scandia, monoclinic and cubic gadolinia

| Temp. Interval (°C to °C) | $Y_2O_3$ | $Sc_2O_3$ | Monoclinic $Gd_2O_3$ | Cubic $Gd_2O_3$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>25 to 600</td>
<td>7.62</td>
<td>7.84</td>
<td>8.82</td>
<td>6.99</td>
</tr>
<tr>
<td>25 to 800</td>
<td>7.83</td>
<td>8.18</td>
<td>9.15</td>
<td>7.21</td>
</tr>
<tr>
<td>25 to 1000</td>
<td>7.95</td>
<td>8.40</td>
<td>9.36</td>
<td>7.45</td>
</tr>
<tr>
<td>25 to 1100</td>
<td>7.93</td>
<td>8.54</td>
<td>9.49</td>
<td>7.61</td>
</tr>
<tr>
<td>25 to 1120</td>
<td>7.93</td>
<td></td>
<td></td>
<td>7.65</td>
</tr>
<tr>
<td>25 to 1125</td>
<td></td>
<td>8.59</td>
<td></td>
<td>9.53</td>
</tr>
<tr>
<td>25 to 1130</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25 to 1135</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Equations for the thermal expansion of each material were obtained by computing the thermal expansion of each specimen of that material at 50°C intervals from its expansion equation. The computed expansion values of all the specimens of each material were then fitted by a second degree polynomial equation by the method of least squares. The constants for the equations, standard errors of estimate, and temperature range for each equation are given in Table 13.

Instantaneous coefficients of thermal expansion may be obtained from the derivatives of the thermal expansion equations with respect to temperature by evaluating the resulting
expressions at the desired temperature.

When sufficient data were presented, thermal expansion equations of the results of other authors were determined by least squares fitting. Constants of the second degree polynomial equations, standard errors of estimate, and temperature range for each equation are given in Table 14.

Table 13. Linear thermal expansion equations

\[ \frac{\Delta L}{L} = A + Bt + Ct^2 \]

where \( \frac{\Delta L}{L} \) = linear thermal expansion in percent, \( t \) = temperature in °C, and \( A, B, \) and \( C \) are constants.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>A X 10</th>
<th>B X 10^3</th>
<th>C X 10^6</th>
<th>Standard Error of Estimate (%) Expansion</th>
<th>Temp. range (°C to °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Y}_2\text{O}_3 )</td>
<td>-0.31051</td>
<td>0.76517</td>
<td>0.03544</td>
<td>0.47652</td>
<td>25 to 1120</td>
</tr>
<tr>
<td>( \text{Sc}_2\text{O}_3 )</td>
<td>-0.29156</td>
<td>0.71693</td>
<td>0.12915</td>
<td>0.71436</td>
<td>25 to 1130</td>
</tr>
<tr>
<td>Monoclinic ( \text{Gd}_2\text{O}_3 )</td>
<td>-0.29570</td>
<td>0.83134</td>
<td>0.10804</td>
<td>1.7157</td>
<td>25 to 1135</td>
</tr>
<tr>
<td>Cubic ( \text{Gd}_2\text{O}_3 )</td>
<td>-0.19845</td>
<td>0.65499</td>
<td>0.09273</td>
<td>0.11945</td>
<td>25 to 1125</td>
</tr>
</tbody>
</table>
Table 14. Linear thermal expansion equations
\[ \Delta L/L = A + Bt + Ct^2 \] where \( \Delta L/L \) = linear thermal expansion in percent, \( t \) = temperature in °C, and \( A, B, \) and \( C \) are constants

<table>
<thead>
<tr>
<th>Oxide and Author</th>
<th>A x 10</th>
<th>B x 10^3</th>
<th>C x 10^6</th>
<th>Standard Error of Estimate</th>
<th>Temp. range</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Y}_2\text{O}_3 ) Wilfong et al.</td>
<td>-0.20270</td>
<td>0.69109</td>
<td>0.12109</td>
<td>0.17609</td>
<td>25 to 1000</td>
</tr>
<tr>
<td>( \text{Y}_2\text{O}_3 ) Stecura &amp; Campbell</td>
<td>-0.02428</td>
<td>0.70599</td>
<td>0.14922</td>
<td>0.23082</td>
<td>0 to 1300</td>
</tr>
<tr>
<td>( \text{Y}_2\text{O}_3 ) Fitzsimmons</td>
<td>-0.18453</td>
<td>0.74140</td>
<td>0.08033</td>
<td>0.54971</td>
<td>25 to 1550</td>
</tr>
<tr>
<td>( \text{Sc}_2\text{O}_3 ) Stecura &amp; Campbell</td>
<td>-0.00853</td>
<td>0.60603</td>
<td>0.26045</td>
<td>0.58660</td>
<td>0 to 1300</td>
</tr>
<tr>
<td>( \text{Sc}_2\text{O}_3 ) Brown &amp; Kirchner</td>
<td>-0.24113</td>
<td>0.76064</td>
<td>0.13456</td>
<td>0.88816</td>
<td>25 to 1200</td>
</tr>
<tr>
<td>Cubic ( \text{Gd}_2\text{O}_3 ) Stecura &amp; Campbell</td>
<td>0.05350</td>
<td>0.68972</td>
<td>0.15151</td>
<td>0.48042</td>
<td>0 to 1300</td>
</tr>
</tbody>
</table>
DISCUSSION

This dilatometer technique gave reproducible values of linear thermal expansion which compare favorably with values obtained by others using the dilatometer technique.

The linear thermal expansion values of specimens of scandia and cubic gadolinia were reproducible as should be expected of specimens with similar heat treatment and density. However, good agreement was also found for the thermal expansion values of the specimens of yttria which had different heat treatments and densities varying from 75 to 97% of the theoretical density.

The greatest spread in linear thermal expansion values was found for specimens of monoclinic gadolinia. Specimens fired at higher temperatures, thus having higher densities, had higher expansion values. Diffractometer traces of the low density monoclinic gadolinia showed no peaks to indicate incomplete transformation from the cubic phase.

Throughout the comparison of expansion values with those of other authors, it was observed that thermal expansion values obtained by X-ray diffraction were higher than those obtained from other techniques. The expansion values observed with X-ray diffraction are those of a single crystal of theoretical density, while the expansion values observed by other techniques are the expansion of a bulk specimen of material. If the bulk specimen is polycrystalline and somewhat porous, there is a reduction in thermal expansion caused by grain boundaries and
pores. Thus the expansion values obtained for polycrystalline cubic gadolinia of 67% of theoretical density are lower than those reported by Stecura and Campbell (12) who used the X-ray technique. Also the expansion values reported by Ploetz et al. on monoclinic gadolinia of 85% theoretical density were higher than those observed in this study on monoclinic gadolinia of average density 74% of theoretical. Expansion values of 90% theoretical density scandia were only slightly lower than the values measured by X-ray techniques.

The decrease in over-all thermal expansion coefficient of yttria at 1100°C may be an indication of a thermal expansion anomaly near 1050°C. However, no abrupt change in the thermal expansion values was observed from 1000°C to 1100°C.

95% of expansion values obtained by this dilatometer technique may be expected to lie within ± twice the standard error of estimate for the curves determined by least squares fitting. Estimated experimental error in expansion values was much smaller than twice the standard error of estimate indicating all sources of error had not been identified.

It was found that the transformation from cubic to monoclinic gadolinia was completed in 45 minutes at 1300°C. Partial transformation was observed in cubic gadolinia heated at 1240°C for 19 hours, but the cubic form was stable when heated for 18 hours at 1200°C. Monoclinic gadolinia was stable when heated at 1100°C for 18 hours. The temperature range and irreversibility of the transformation agree with the results of Stecura (7).
SUMMARY

Linear thermal expansion measurements of the sesquioxides of yttrium, scandium, and gadolinium were made from room temperature to above 1100°C with a sapphire-rod dilatometer. Expansion measurements were made on both the monoclinic and cubic crystallographic forms of gadolinia. The over-all coefficients of linear thermal expansion from 25°C to 1100°C were found to be $7.93 \times 10^{-6}$ in./in.°C for yttria, $8.54 \times 10^{-6}$ in./in.°C for scandia, $9.49 \times 10^{-6}$ in./in.°C for monoclinic gadolinia, and $7.61 \times 10^{-6}$ in./in.°C for cubic gadolinia. Expansion measurements compared favorably with those of other authors.
LITERATURE CITED


ACKNOWLEDGMENTS

The author wishes to express his appreciation to Dr. D. R. Wilder for his guidance and encouragement during this research, to the National Science Foundation for support in the form of a Graduate Traineeship, and to his wife, Karen, for her understanding and patience in typing this thesis.