The high-temperature phase relations in the system Ce₂O₃–Ce₅Si₂O₇ have been studied in the temperature range 1150° to 1970°C in inert and reducing atmospheres by conventional quenching and differential thermal analysis. Three eutectic reactions were found to occur at 1664°C and 27 mol% SiO₂ between Ce₂O₃ and Ce₅SiO₇, at 1870°C and 54 mol% SiO₂ between Ce₅SiO₇ and Ce₄Si₂O₇(OH)₂O, and at 1762°C and 65 mol% SiO₂ between Ce₄Si₂O₇(OH)₂O and Ce₅Si₂O₇.

Microstructural characteristics of the eutectic reactions (cerium pyrosilicate or disilicate) have been reported. Ce₅Si₂O₇ has been reported to have two polymorphs. The high-temperature phase transition was found to occur at 1274°C. The binary compounds of this system were all found to melt congruently. The enthalpy and entropy of melting of these binary compounds were calculated from the initial slopes of their experimentally determined liquidus lines.

I. Introduction

The present study is concerned with phase relations in the Ce₂O₃–Ce₅Si₂O₇ system that is the 0 to 66.67 mol% SiO₂ section of the Ce₂O₃–Ce₅Si₂O₇ binary. The presence of three binary compounds, i.e., Ce₅SiO₇ (cerium oxyorthosilicate), Ce₅Si₂O₇(OH)₂O (cerium oxyapatite), and Ce₅Si₂O₇ (cerium pyrosilicate or disilicate) have been reported. Ce₅Si₂O₇ has been reported to have two polymorphs. The high-temperature form has long been regarded to be the rare-earth G-type “pseudo-orthorhombic” (with a monoclinic angle of 90°). It has recently been shown by us that the high-temperature form is indeed monoclinic with a monoclinic angle of 90.13°. The low-temperature form has been reported to have a tetragonal unit cell. The extremely sluggish phase transition was found to occur at 1274°C.

Owing to the stable trivalent states of most of the rare-earth (RE) elements, many of their oxides are found to exist as sesquioxides (RE₂O₃). However, since cerium assumes the 4+ state in air, its stable oxide is CeO₂ with a cubic fluorite structure. Heating CeO₂ in a “reducing” atmosphere at a temperature not less than 1400°C will reduce it to Ce₂O₃. On the other hand, the complete conversion of Ce₂O₃ to CeO₂, in an “inert” atmosphere, such as vacuum or purified argon, requires temperatures in excess of 1700°C. At lower temperatures, the formation of a continuum of defect phases, usually designated as CeO₂, is observed in “inert” atmospheres. Hence, pure Ce₂O₃, obtained in an inert atmosphere by heating the cerium(IV) oxide, for instance, at 1850°C, can be brought down to room temperature only by careful and rapid quenching. Slow or even moderate cooling rates cause the conversion of Ce₂O₃ partially or totally to CeO₂, depending on the rate of cooling employed. To complicate matters further, Sata and Yoshimura have reported that pure Ce₂O₃ formed under vacuum begins to “sublime” upon heating to above 1900°C. On the other hand, the melting point for Ce₂O₃ in dry hydrogen was reported by the same authors to be 2210°C ± 10°C, without further mention of the problem of sublimation.

There have been no studies in the literature directly aimed at the experimental determination of the melting points of Ce₅Si₂O₇ and Ce₄.5(SiO₄)₃O. The melting point of Ce₅Si₂O₇ was previously determined by us to be 1788° ± 5°C, which is in relatively close agreement with the value of Toropov et al. (1770° ± 25°C).

There have been two versions of a phase diagram for the Ce₂O₃–SiO₂ system given in the literature. The early one given by Leonov and Koehler in 1970 did not even include the cerium oxygen apatite phase (Ce₄.5(SiO₄)₃O). It indicated the presence of a eutectic reaction occurring at 1700°C and at about 33 mol% SiO₂ between Ce₂O₃ (which was shown to melt at 2160°C) and Ce₅Si₂O₇ (which was shown to melt at 1870°C). The phase diagram also showed a polymorphic transformation for Ce₅Si₂O₇ at about 1200°C. The high-temperature polymorph was shown to melt incongruently at above 1700°C. The uncertain and wavy forms of the liquid drawn between Ce₂O₃ and SiO₂, and the total absence of the Ce₄.5(SiO₄)₃O phase in this diagram, suggested that further study of this system was needed. The second construction for this system was given by Kaufman et al. in 1982. This diagram was calculated from available thermodynamic data and from lattice stability parameters of the terminal members, Ce₂O₃ and SiO₂. This compilation indicated a eutectic between Ce₂O₃ and Ce₅Si₂O₇ at 1607°C; however, it also claimed that Ce₅Si₂O₇ decomposed above 1647°C. This diagram also showed the compounds Ce₅Si₂O₇ (SiO₄)O and Ce₅Si₂O₇ to melt congruently at 2172°C and 2242°C, respectively, but made no mention of a polymorphic transformation in Ce₅Si₂O₇.

In this work, compound formation, compound stability, and the phase relations at and above liquidus temperatures have been investigated to determine the phase diagram of the binary subsystem Ce₂O₃–Ce₅Si₂O₇ of the system Ce₂O₃–Ce₅Si₂O₇.

II. Experimental Procedure

(1) Materials and Sample Preparation

Compositions in the Ce₂O₃–Ce₅Si₂O₇ system were prepared by mixing Ce₂O₃ and SiO₂ in desired Ce:Sr ratios. Ce₂O₃ transforms into Ce₂O₃ at temperatures above 1400°C when heated either under vacuum (P₂O₅ ≤ 6 × 10⁻¹³ atm) or in an argon + 10% H₂ atmosphere. The starting oxides Ce₂O₃ (99.87%, 0.7μm) and fumed SiO₂ (99.98%, 0.607 μm), whose chemical analyses and surface areas were reported elsewhere, were...
heated in air at 975°C for 12 h prior to weighing, mainly to
ascertain the CeO2 stoichiometry and to remove any adsorbed
water on fumed SiO2. The stoichiometric amounts of the cal-
cined oxides were mixed in pure ethanol in glass jars for about
an hour with a mechanical stirrer. Following this, the jar con-
tents were dispersed by 15 min of ultrasonification prior to
overnight drying at 70°C. The recovered cakes were then cal-
cined in air at 950°C for 12 h as a precaution to remove hydro-
carbon residues that might be present. The calcined mixtures
were then lightly ground in an agate mortar for about 30 min.

Pellets, 1.0 cm diameter by 0.4 cm thick, were prepared by
uniaxial dry pressing of approximately 2.5 g of oxide mixtures
of each composition at 20 MPa in a tungsten carbide-lined steel
die, followed by cold isostatic pressing in latex bags at 200
MPa. The pressed samples were equilibrated at a predetermined
temperature in a MoSi2 quench furnace with a vertical sili-
nanite reaction tube 120 cm long by 5 cm diameter. The slightly
reducing atmosphere in the furnace tube was maintained by
constant flow of a prepurified mixture of argon + 10% H2 gas.
Sample pellets were placed in a molybdenum envelope (open
on one side) with wall thickness of 0.4 mm and suspended in the
hot zone of the furnace (Model 3320, ATS Inc., PA) by a
molybdenum wire hooked to the envelope. Three pellets
were put into each envelope; these were physically separated from
each other by small molybdenum strips. The temperature in the
furnace tube was controlled to within ±6°C in the temperature
range 1150°C–1560°C by a B-type control thermocouple that
feeds the programmable furnace temperature controller. The
temperature in the hot zone was monitored with a B-type
thermocouple placed next to the suspended sample
evapores. The sample thermocouple was calibrated after every
120 h of heating above 1400°C against the melting points of
Au (1064°C) and Pd (1554°C) under a moderate flow of argon.

At the end of the specified equilibration times, the samples were
quenched by dropping the envelope into a well-stirred deion-
ized water bath (which was brought to about 3°C by adding ice
cubes into the water bath at the quenching time), covered with a
thin layer of vacuum pump oil, which also served to seal the
bottom end of the furnace tube during the experiment.

(2) Phase and Microstructural Analyses

For phase analyses, every quenched sample was ground to a
mean particle size of about 7 μm and examined by XRD in the
5°–85° 2θ range using a Cu-tube powder diffractometer (XDS
2000, Scintag, Santa Clara, CA) with a scanning rate range of
0.2–0.4°/min. The X-ray data collected by the diffractometer
computer were later analyzed in 1° 2θ intervals by a separate
program (Peakfit 3.0, Jandel Scientific, Corte Madera, CA) used
for accurate measurement of peaks overlaps and for profile fitting
of weak reflections in every sample. Least-squares cell refinement
and lattice parameter determinations were performed by the
Appleman and Evans routine. To determine the resolution
power of the X-ray diffractometer that we used for the charac-
terization of the crystalline phases of this system, small quanti-
ties (1–3 mol%) of pure, prefired and equilibrated compounds
were added to each other (i.e., 1–3 mol% compound A + 99–
97 mol% compound B) at room temperature and thoroughly
mixed. We judged a minor phase to be present in the mixture if
the strongest reflection from that phase appeared in the XRD
trace of the mixture with a relative intensity of 1 or 2 on a scale
where the maximum is 100, and was accompanied by the next
two strongest reflections for that phase. The selected mixtures
were 1 mol% CeO2–99 mol% Ce5SiO7 (≈0.8 wt% CeO2),
3 mol% CeO2–97 mol% Ce5SiO7 (≈1.2 wt% CeO2), and 1 mol%
CeO2–99 mol% Ce5SiO7 (≈2.1 wt% CeO2). The XRD analyses of these
samples, at the maximum scanning rate of this study in the same
2θ range, the intensities of the strongest reflections of the three
minor phases in the above three mixtures were found to be 12,
4, and 9, respectively. This information was used as a guide for
the detection of minor phases by XRD in the samples of the rest
of this study. Elemental silicon (NBS640a) was used as an external
standard.

Microstructural analyses were carried out using scanning
electron microscopy (SEM, JSM-6100, JEOL, Peabody, MA) and
reflected light microscopy on polished or as-is surfaces (in
some cases, in order not to damage the surfaces) of the samples.
The chemical compositions of microstructural features observed in SEM images of polished samples were determined by
energy-dispersive X-ray spectrometry (EDXS, Model
Delta-5, Kevex, Foster City, CA) using pure CeO2, Ce4Si7-
(O3)6O and Ce4Si4O as standards, and the information obtained
was believed to be accurate to within ±4 at%. Analyses of
phase distribution and phase amounts were carried out on
polished surfaces with the X-ray mapping and automated image
analysis attachments to the SEM to give the elemental
distribution among the microstructural features and the areal
fractions of specific phases on polished surfaces, which were
used especially in ascertaining the positions of the liquid in the
binary phase diagram.

(3) Equilibration Experiments

The minimum times required for equilibration during prelim-
inary experiments were 100 h at 1150°C and 50 h at 1500°C in
argon + 10% H2. Equilibration at each temperature was judged
to have occurred when XRD traces showed no detectable
changes in phase assemblages. In all experiments, after 50 h
of heating, the samples were quenched, ground, examined
by XRD for phase identification, repelletized, and heated for
an additional 45–50 h, followed by quenching and phase
identification.

The equilibration runs above 1500°C were carried out in a
vacuum furnace (Centorr Associates, Suncook, NH) with
a tungsten mesh heater (maximum obtainable temperature
2050°C), which maintained a partial pressure of oxygen of
≤6 × 10−9 atm even at that temperature. The samples were
suspended in the hot zone in molybdenum crucibles that were
also visible through a fused quartz window during the runs. The
crucibles were tightly crimped to avoid or significantly reduce
evaporation from the liquid phases formed. The temperature of
the vacuum furnace was controlled by a C-type thermocouple.
Sample temperatures were monitored by an IR-pyrometer, cali-
brated frequently against the melting point of Pt (1772°C),
aimed directly at the samples. At the end of the equilibration
treatment, the samples were furnace-quenched to ambient by
shutting off the furnace power, typically providing cooling rates
in excess of 600°C/min in the temperature range 1950–
1150°C, and displaying an exponential decay-type cooling
behavior to room temperature with increasingly sluggish cool-
ing rates below about 1150°C.

(4) Differential Thermal Analyses

DTA experiments were carried out to monitor phase transi-
tions in this system. The DTA runs were performed in the vac-
uum furnace with a custom-built DTA module equipped with a
C-type differential thermocouple assembly and a capped
molybdenum sample block. The circular sample block con-
tained two 1-cm diameter by 1 cm deep cavities (one for the
sample and the other for the reference) drilled symmetrically
about the center of the block. The thermocouple tips reached
cavities from the top through the holes in the block cap.
Al2O3 (99.96%) was used as the reference material. Samples
(not less than 380 mg) were placed in molybdenum crucibles,
which fit snugly into the cavities in the sample block, made
from molybdenum foils by pressing and crimping them to the
shape of the cavities. The electrical outputs of the thermocou-
lcles were sent to two (one for the sample temperature and the
other for the temperature difference between the sample and the
reference cells) high-sensitivity millivoltimeters connected to a
personal computer (PC) to acquire the data in a time (s), tem-
perature (°C), and voltage difference (μV) string. The collected
temperature differences were then converted to temperature dif-
fences. The thermocouples of the DTA module were calibrated

after every 20 h of operation above 1675°C against the melting points of pure Au (1064°C), Li$_2$SiO$_3$ (1204°C), Pd (1554°C), and Pt (1772°C). For the determination of liquidus points in the binary system, samples were first equilibrated at 1550°C in argon + 10% H$_2$ for a prolonged time and then water-quenched to room temperature. These samples, after grinding to a fine powder, were used in DTA runs with a heating rate of 10° to 15°C/min in the low-temperature range (1150° to 1550°C), followed by slower heating rates, typically 4° to 5°C/min, to a final temperature of 1935°C. The DTA samples were furnace-quenched to room temperature to facilitate phase analysis of the recovered material by XRD and SEM, as described above. The thermal events indicated by DTA for specific temperature-composition points were then confirmed in equilibration experiments by heating portions of the same samples (equilibrated but not yet tested with DTA) to temperatures 10° above and 10° below the temperature read from the DTA traces followed by quenching and phase analysis.

III. Results and Discussion

(1) Stability and the Melting Points of the Compounds

The three previously reported binary compounds, i.e., Ce$_2$O$_3$, Ce$_{6.07}$SiO$_3$O$_2$, and Ce$_3$SiO$_5$, of this system have successfully been synthesized as single-phase substances in this work. It has been found that in the low-temperature range, it was almost impossible to form Ce$_2$O$_3$ even at 1550°C for a heating time of 180 h (followed by quenching). The other two were easily formed in an argon atmosphere at 1550°C in less than 7 h. The addition of 10% H$_2$ to argon allowed us to synthesize Ce$_2$O$_3$ at 1550°C in about 12 h. There has been no difference in the lattice parameters of samples of Ce$_{6.07}$SiO$_3$O$_2$, monoclinic Ce$_3$SiO$_5$, and tetragonal Ce$_3$SiO$_5$ prepared separately in pure argon and argon + 10% H$_2$. Pure Ce$_2$O$_3$, when heated in an argon + 10% H$_2$ atmosphere, was found to transform completely into Ce$_2$O$_3$ in 200 h at 1150°C, 185 h at 1250°C, 170 h at 1350°C, 100 h at 1450°C, and 70 h at 1550°C. It should be noted that these times were not the minimum required durations for this reduction to go to completion; they just represent the times selected by us for equilibration. In other words, the actual times could be significantly lower than these. We also encountered the same problem reported by Sata and Yoshinura, that Ce$_2$O$_3$ heated above 1875°C sublimed completely before melting in vacuum.

Ce$_3$SiO$_5$ was found to be stable in the temperature range of this study, i.e., 1150°–1970°C. A small piece of pure Ce$_3$SiO$_5$, with several sharp edges, was hung by a molybdenum wire in the vacuum furnace that was visible through the viewing port. The IR-pyrometer, calibrated just before this run, was focused on the sample. The sample was heated at a rate of 4°C/min. The melting behavior of the chunk was continuously observed through the pyrometer, and at 1970° ± 30°C the sharp edges of the samples began to be rounded. At this point, the sample was furnace-quenched. The recovered sample showed a tiny skin of black liquid formed around the sample, although the bulk of the sample was still showing the crystalline Ce$_3$SiO$_5$. This fact contradicts the calculated phase diagram of Kaufman et al. which predicts Ce$_3$SiO$_5$ to decompose into cerium oxygen apatite and liquid at temperatures above 1647°C, but agrees with that of Leonov and Koehler in being stable up to the melting point. We therefore assumed the above temperature, with the indicated degree of uncertainty, to be the melting point of Ce$_3$SiO$_5$.

The melting point of Ce$_{6.07}$SiO$_3$O$_2$ was determined in a similar way to be 1950° ± 30°C. The small chunk did again form a black, viscous liquid on the outside which did not crystallize upon quenching, as was the case with Ce$_3$SiO$_5$. This temperature was noted to be 220° lower than that reported by Kaufman et al. in their calculated phase diagram.

The melting point of the monoclinic, high-temperature form of Ce$_3$SiO$_5$, was previously found by us to be 1788° ± 5°C by repeated DTA experiments. Since our DTA module has had Al$_2$O$_3$ insulation tubes on its thermocouple wires, we did decide not to push it to the vicinity of 2000°C for the determination of the melting points of Ce$_3$SiO$_5$ and Ce$_3$Si(O$_2$)O$_2$. However, the DTA traces for these two compounds obtained between 1200° and 1930°C (4°C/min) did not show any thermal events. Table I shows the pertinent crystallographic and density data (the latter measured by using Archimedean’s principle) for the compounds of the Ce$_2$O$_3$–Ce$_3$SiO$_5$ system.

(2) Phase Relations between Ce$_2$O$_3$ and Ce$_3$SiO$_5$

The compositions investigated in the equilibration experiments in this portion of the system are denoted in Table II as Sili 9.5 (9.5 mol% SiO$_2$, balance Ce$_2$O$_3$) through Sili 50. The four different compositions (Sili 9.5, 18, 26, and 40), fired in a purified argon + 10% H$_2$ atmosphere at five different temperatures (1150°, 1250°, 1350°, 1450°, and 1550°C), all yielded solid-state phase mixtures of Ce$_2$O$_3$ and Ce$_3$SiO$_5$ after being quenched to room temperature. We found no solid solubility between the two phases and no reaction between the phases and the molybdenum crucibles used. From the XRD patterns of the final samples of this portion of the system, we were able to distinguish 15–16 reflections of Ce$_2$O$_3$, as well as more than 90 reflections of Ce$_3$SiO$_5$. The colors of the quenched samples in this composition range displayed a smooth variation from mustard (Ce$_2$O$_3$-rich) to dark-green (moderate Ce$_2$O$_3$) and finally to light-blue (Ce$_3$SiO$_5$-rich).

The DTA runs (5°C/min in the low-temperature range (11

For Table II, order ACSDD-217 from Data Depository Service, The American Ceramic Society, 735 Ceramic Place, Westerville, OH 43081-8720.
compositions SILI 27 and SILI 28 show only one endothermic peak, which corresponds to the eutectic temperature (Fig. 1). We were not able to detect a difference in the temperature of the beginning of the endothermic event in these two samples. Therefore, we assumed the eutectic composition to be 27 ± 1 mol% SiO$_2$. To observe the eutectic microstructure that would occur between Ce$_2$O$_3$ and Ce$_2$SiO$_5$, we heated a SILI 27 sample to 1700°C and held it at that temperature for 4 h, followed by cooling to 1600°C at 3°C/min. The sample was furnace-quenched in a vacuum to ambient temperature from 1600°C. Figures 2(D) and (E) show the eutectic microstructure consisting of submicrometer-sized lamellae with the bright fibriles of Ce$_2$O$_3$. It should be noted that the microstructure was found to be free of cracks, possibly due to the relatively slow cooling rate employed in this experiment. The information gathered from this portion of the system Ce$_2$O$_3$–Ce$_2$SiO$_5$ has been plotted into the phase diagram suggested in Fig. 3. We have put dashed rather than solid lines for the portions of the liquidus that extend beyond 1930°C in this diagram because our temperature control was outside the range ±30°C above that temperature. However, the extension of the Ce$_2$O$_3$ liquidus in Fig. 3 intersects the temperature axis at about 2260°C, which is in close agreement with the melting point of Ce$_2$O$_3$ reported by Sata and Yoshimura$^{15}$ as 2210° ± 10°C.

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### Table I. Crystallographic and Density Data of the Binary Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lattice parameters (Å)</th>
<th>Space Group*</th>
<th>Cell volume (Å$^3$)</th>
<th>Z</th>
<th>$D_{xpd}$ (g/cm$^3$)</th>
<th>$D_{tan}$ (g/cm$^3$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$_2$O$_3$ (hex)</td>
<td>$a = 3.891, c = 6.063$</td>
<td>$P321(150)$</td>
<td>79.51</td>
<td>1</td>
<td>6.85</td>
<td>6.80</td>
<td>TS, 17</td>
</tr>
<tr>
<td>Ce$_2$SiO$_5$ (mono)</td>
<td>$a = 9.278, b = 7.382, c = 6.956, \beta = 108°20'$</td>
<td>$P12_1/c1(14)$</td>
<td>452.26</td>
<td>4</td>
<td>5.70</td>
<td>5.74</td>
<td>TS, 7</td>
</tr>
<tr>
<td>Ce$_{10}(SiO$_4$)$_5$O (hex)</td>
<td>$a = 9.658, c = 7.119$</td>
<td>$P6_3/m(176)$</td>
<td>575.07</td>
<td>2</td>
<td>5.47</td>
<td>5.50</td>
<td>TS, 10</td>
</tr>
<tr>
<td>Ce$_2$Si$_2$O$_7$ (tetr)</td>
<td>$a = 6.792, c = 24.700$</td>
<td>$P4_2(76)$</td>
<td>1139.38</td>
<td>8</td>
<td>5.23</td>
<td>5.29</td>
<td>TS, 14</td>
</tr>
<tr>
<td>Ce$_2$Si$_2$O$_7$ (mono)</td>
<td>$a = 8.727, b = 13.080, c = 5.405, \beta = 90.13°$</td>
<td>$P21/n(14)$</td>
<td>617.11</td>
<td>4</td>
<td>4.83</td>
<td>4.78</td>
<td>TS, 14</td>
</tr>
</tbody>
</table>

*Hermann-Mauguin numbers are given in parentheses following the space group denoters. **TS is this study.
(3) Phase Relations between Ce$_2$SiO$_5$ and Ce$_{66+}$($\text{SiO}_4$)$_{30}$O

The compositions investigated to determine the phase relations between these two compounds have been labeled as SILI 50 through SILI 56.2 (corresponding to the composition of cerium oxygen apatite) in Table II. The heat treatments in an argon + 10% H$_2$ atmosphere in the temperature range 1150°–1550°C for the times listed in Table II followed by ice-water quenching have produced solid-state phase mixtures of Ce$_2$SiO$_5$ and Ce$_{66+}$(SiO$_4$)$_{30}$O, excluding the samples of compositions SILI 50 and SILI 56.2. Partial decomposition of Ce$_2$SiO$_5$ to Ce$_{66+}$(SiO$_4$)$_{30}$O, reported by Van Hal and Hintzen,' at 1200°C, could be resulting from “slow cooling” to room temperature after heating for 2 h in an H$_2$–N$_2$ atmosphere. The ice-water-quenched samples of this study did not show such a partial decomposition. Two separate samples having the composition SILI 53 were also equilibrated at 1790°C for 8 h and at 1850°C for 4.5 h under vacuum ($P_{\text{H}_2} \approx 6 \times 10^{-9}$ atm at all times during the heat treatments), followed by furnace quenching to room temperature. These two samples also did not form a liquid phase. In the XRD traces of the above samples, we were able to detect 52–53 separate reflections of Ce$_{66+}$(SiO$_4$)$_{30}$O in addition to more than 90 reflections of Ce$_2$SiO$_5$ in the 5°–85° 2θ range conforming to the lattice parameters given in Table I for these.
compounds. The typical scan rates employed to obtain this level of resolution in XRD traces were about 0.15°–0.20° 2θ/min. We did not see any signs of solid solution between these two compounds. The colors displayed by the quenched samples varied from pale mustard (Ce,SiO₂-rich samples) to dark mustard (Ce₄,SiO₇-rich samples), with the colors assuming darker tones with increasing temperatures.

The two DTA traces shown in Fig. 1 for the samples of SILI 52 and 55, recorded under conditions similar to those described in the previous section, both showed a significant endothermic event at 1870°C ± 25°C. Two minor endothermic peaks were observed at 1910°C ± 30°C and 1926°C ± 30°C, respectively. In order to investigate the nature of these events, we heated four samples with the compositions SILI 53, 53.5, 54, and 54.5 to a possible liquid formation temperature, i.e., 1920°C to 1930°C, under vacuum, followed by cooling to 1800°C at 3°C/min and then furnace-quenching to room temperature. The resulting phases were listed in Table II. Combining these results, we deduced that the first liquid forms at 1870°C between Ce,SiO₂ and Ce₄,SiO₇. The eutectic composition was found to be at 54 mol% SiO₂. The Ce,SiO₂ liquidus passes through the points [1970°C, 50%], [1910°C, 52%], and [1870°C, 54%]. On the other hand, the liquidus of Ce₄,SiO₇ could be defined by the points [1870°C, 54%], [1926°C, 55%], and [1950°C, 56.2%]. The equilibrated sample of SILI 54 produced the eutectic microstructure shown in Fig. 2(F). The XRD trace of this sample had the reflections of both oxyorthosilicate and apatite phases. The microstructure of the sample of composition SILI 53.5 heated to 1920°C contained relatively thick strands of Ce,SiO₂ crossing the eutectic mixture of Ce,SiO₂ and Ce₄,SiO₇(O) that is given in Fig. 4(A). The rather scarce but well-defined hexagonal crystals of Ce₄,SiO₇(O) in a eutectic mixture were the major characteristics of the microstructure of the SILI 54.5 sample heated to 1920°C that is depicted in Eq. 2(B). The black, glassy looking samples of the above compositions were extremely brittle, and our repeated attempts to polish them all failed, resulting in shattered samples. Hence, in order not to destroy the observed microstructures, micrographs were taken from the “as is” surfaces of these samples.

(4) Phase Relations between Ce₄,SiO₇(O) and Ce₄SiO₇

Some of the compositions studied in this portion of the system Ce₂SiO₅–Ce₄SiO₇ are listed in Table II and denoted with SILI 56.2 through SILI 66.7. It is known²⁴ that Ce₄SiO₇ exhibits a polymorphic transformation at 1274°C. The high-temperature form has been shown to have a monoclinic unit cell (see Table I), which has long been misrepresented as a pseudo-orthorhombic crystal structure having a monoclinic space group. The low-temperature polymorph is known²⁵,²⁶ to have a tetragonal unit cell. The equilibration heatings of samples, in argon + 10% H₂, followed by quenching, in this composition range have all confirmed again the presence of these two polymorphs of Ce₄SiO₇. Although the monoclinic Ce₄SiO₇ was formed and identified easily in the samples heated to above 1300°C, the tetragonal low-temperature form required, for the completion of this sluggish transformation, slower cooling rates (typically on the order of 3°C to 4°C/h) from above 1300°C to below the transformation temperature. The samples used in the equilibration heatings in the temperature range 1150°C–1550°C produced XRD patterns of two crystalline phase mixtures of either Ce₄,SiO₇(O) and M-Ce₄,SiO₇(O) (at and above 1350°C) or Ce₄,SiO₇(O) and T-Ce₄,SiO₇(O) (at and below 1250°C). The colors of the equilibrated samples have varied from mustard to ivory with the increasing amounts of Ce₄,SiO₇(O). The liquid phases formed between these two compositions were again black like the rest of the liquid phases of this system.

The sample DTA traces (obtained under conditions similar to those described above), given in Fig. 1 for the compositions 59, 62, and 65 mol% SiO₂, all show a major endothermic event at 1762°C ± 10°C, whereas the samples of 59 and 62 mol% showed two minor endothermic peaks at 1895°C and 1806°C, respectively. Further DTA traces of samples of 60.5 and 63.5 mol%
Fig. 4. (A) 53.5 mol% SiO$_2$ sample showing the strands of Ce$_2$SiO$_5$ over a eutectic matrix which was quenched from 1800°C after heating at 1920°C. (B) 54.5% SiO$_2$. Large hexagonal crystals of Ce$_{12}$SiO$_{22}$O distributed in a eutectic matrix having the same thermal history as the sample of (A). (C) 59 mol% SiO$_2$. Hexagonal crystals of Ce$_{12}$SiO$_{22}$O formed above the eutectic temperature. Quenched from 1730°C after being heated at 1840°C. (D) and (E) 65 mol% SiO$_2$. Microstructure of the eutectic reaction occurring between the binary compounds Ce$_{12}$SiO$_{22}$O and Ce$_2$SiO$_5$. Quenched from 1730°C after the equilibration heating at 1770°C. (F) 66 mol% SiO$_2$. Long streaks of the high-temperature monoclinic form of Ce$_2$SiO$_5$ crossing the eutectic matrix. Quenched from 1730°C following the equilibration soaking at 1770°C. (All bars = 10 µm.)

SiO$_2$ show small secondary endothermic peaks at 1850°C and 1782°C, respectively, besides the primary event also occurring at 1762°C. The suggested Ce$_{12}$SiO$_{22}$O liquidus (Fig. 3) passes through the points {1950°C, 56.25%}, {1895°C, 59%}, {1850°C, 60.5%}, {1806°C, 62%}, {1782°C, 63.5%}, and {1762°C, 65%}. On the other hand, the Ce$_2$SiO$_5$ liquidus lies on the points {1788°C, 66.7%} and {1762°C, 65%}. The eutectic reaction was found to occur between Ce$_{12}$SiO$_{22}$O and Ce$_2$SiO$_5$ at 1762°C and 65 ± 0.5 mol% SiO$_2$.

The microstructure of a SILI 59 sample, heated to about 1840°C (4°C/min) under vacuum, and then cooled to 1730°C after being held at high temperature for 2 h, showed hexagonal crystals of Ce$_{12}$SiO$_{22}$O dispersed in a eutectic matrix, as shown in Fig. 4(C). The micrographs of Figs. 4(D) and (E) display the characteristic eutectic microstructure between these two compounds, which were taken from a sample of composition SILI 65 heated to 1770°C under vacuum and cooled to 1730°C (followed by furnace quenching) after a soaking time of 2 h. A sample of composition SILI 66 heated to 1770°C under vacuum and cooled to 1730°C after a soaking time of 4 h displayed rather long and darker streaks of Ce$_2$SiO$_5$ over a eutectic matrix in its microstructure, which is reproduced in Fig. 4(F). The XRD traces of this sample showed more than 50 reflections of Ce$_{12}$SiO$_{22}$O and about 125 reflections of monoclinic Ce$_2$SiO$_5$ in the 5°-85° 2θ range collected with a scanning rate of 0.1° 2θ/min.
(5) Enthalpy of Melting Calculations

Assuming ideal mixing in the liquid phase and complete immiscibility of CeO₂ in solid Ce₂SiO₅, the enthalpy of melting of Ce₂SiO₅ can be calculated from the experimentally determined liquidus line, using the freezing point depression of Ce₂SiO₅ by the addition of CeO₂, according to

$$\log X_A = -\frac{\Delta H_{m,a}}{2.303R}\left[\frac{\left(T_{m,A} - T_L\right)}{T_{m,A}T_L}\right]$$  \hspace{1cm} (1)

where \( A = \text{Ce}_2\text{SiO}_5 \). Therefore, a plot of \( \log X_{\text{Ce}_2\text{SiO}_5} \) (liquids) is drawn against the term \( \left[\left(T_{m,\text{Ce}_2\text{SiO}_5} - T_L\right)/T_{m,\text{Ce}_2\text{SiO}_5}T_L\right] \) should be a straight line with a slope equal to \(-\Delta H_{m,\text{Ce}_2\text{SiO}_5}/2.303R\). This translates to a value for \( \Delta H_{m,\text{Ce}_2\text{SiO}_5} \) of \( 102.3 \pm 6 \text{ kJ/mol} \) at the melting point of \( 1950^\circ\text{C} \). Repeating the calculations for \( \text{Ce}_2\text{SiO}_5 \) liquidus (56.2 to 65 mol% \( \text{SiO}_2 \)) and \( \text{Ce}_2\text{SiO}_5 \) liquidus, we estimated the \( \Delta H_{m,\text{Ce}_2\text{SiO}_5} \) to be \( 222.5 \pm 13 \text{ kJ/mol} \) and the \( \Delta H_{m,\text{Ce}_2\text{SiO}_5} \) to be \( 39.0 \pm 3 \text{ kJ/mol} \). The straight lines produced from Eq. (1) for the liquid of these two phases were also plotted in Fig. 5. The corresponding entropies for these two phases were found to be \( \Sigma S_{\text{Ce}_2\text{SiO}_5} \) liquidus \( = 100.1 \pm 6 \text{ J/mol-K} \) at the melting point of \( 1950^\circ\text{C} \) and \( \Sigma S_{\text{Ce}_2\text{SiO}_5} \) liquidus \( = 19.0 \pm 2 \text{ J/mol-K} \) at the melting point of \( 1788^\circ\text{C} \). Although no values were found in the literature for the enthalpy and entropy of melting of \( \text{Ce}_2\text{SiO}_5 \) and \( \text{Ce}_2\text{SiO}_5 \) liquidus, the enthalpy of melting calculated in this system for \( \text{Ce}_2\text{SiO}_5 \) as \( 39 \pm 3 \text{ kJ/mol} \) agrees well with the enthalpy of melting reported \( (36.8 \text{ kJ/mol}) \) for the same phase in a study of the phase diagram of the \( \text{Al}_2\text{O}_3-\text{Ce}_2\text{SiO}_5 \) system.

IV. Conclusions

The high-temperature phase relations have been investigated in the \( \text{CeO}_2-\text{Ce}_2\text{SiO}_5 \) section of the \( \text{CeO}_2-\text{SiO}_2 \) binary between \( 1150^\circ\text{C} \) and \( 1970^\circ\text{C} \). Three eutectics have been found in this system. The first eutectic reaction occurs at \( 1664^\circ\text{C} \pm 5^\circ\text{C} \) and \( 27 \text{ mol}\% \text{SiO}_2 \) between \( \text{CeO}_2 \) and \( \text{Ce}_2\text{SiO}_5 \). The binary compound \( \text{Ce}_2\text{SiO}_5 \) melts congruently at \( 1970^\circ\text{C} \pm 5^\circ\text{C} \). The second eutectic occurs at \( 1870^\circ\text{C} \pm 25^\circ\text{C} \) and \( 54 \text{ mol}\% \text{SiO}_2 \) between \( \text{Ce}_2\text{SiO}_5 \) and \( \text{Ce}_2\text{SiO}_5 \). The binary compound \( \text{Ce}_2\text{SiO}_5 \) melts congruently at \( 1950^\circ\text{C} \pm 30^\circ\text{C} \). The third eutectic is at \( 1762^\circ\text{C} \pm 10^\circ\text{C} \) and \( 65 \text{ mol}\% \text{SiO}_2 \) among \( \text{Ce}_2\text{SiO}_5 \), \( \text{Ce}_2\text{SiO}_5 \), and \( \text{Ce}_2\text{SiO}_5 \). \( \text{Ce}_2\text{SiO}_5 \) exhibits a polymorphic transformation at \( 1724^\circ\text{C} \) between a tetragonal low-temperature form and a monoclinic high-temperature form before melting congruently at \( 1788^\circ\text{C} \pm 5^\circ\text{C} \). Microstructural characteristics of these eutectic assemblages are documented and found to be extremely sensitive to the conditions of thermal history. No solid solubility has been detected between the phases of this system. The enthalpies and entropies of melting of the three binary compounds are calculated from the initial slopes of the corresponding liquidus lines. Finally, a binary phase diagram is suggested, for the first time, for the \( \text{CeO}_2-\text{Ce}_2\text{SiO}_5 \) system, which accounts for the three binary compounds \( \text{Ce}_2\text{SiO}_5 \), \( \text{Ce}_2\text{SiO}_5 \), and \( \text{Ce}_2\text{SiO}_5 \).