Phase Relations in the System Ce$_2$O$_3$–Al$_2$O$_3$ in Inert and Reducing Atmospheres

A. Cuneyt Tas*
Department of Metallurgical Engineering, Middle East Technical University, Ankara 06531, Turkey

Mufit Akinc*
Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011

The 1:1 compound, CeAlO$_3$, in the system Ce$_2$O$_3$–Al$_2$O$_3$ has been synthesized from the oxides and shown to have a perovskite-like tetragonal unit cell with the lattice parameters $a = 3.736$ Å and $c = 3.792$ Å. A new XRD pattern is suggested for CeAlO$_3$. This compound is shown to be stable up to 1950°C. The 1:1 compound, CeAl$_2$O$_6$, has also been synthesized and shown to possess a magnetoplumbite-like hexagonal unit cell with the lattice parameters $a = 5.538$ Å and $c = 22.012$ Å. An XRD pattern is suggested for CeAl$_2$O$_6$ for the first time. The evolution of eutectic-like microstructures was observed and reported in the Ce$_2$O$_3$–Al$_2$O$_3$ rich side of this binary system.

I. Introduction

One of the two previously reported compounds of the Ce$_2$O$_3$–Al$_2$O$_3$ system, cerium monoaluminate (CeAlO$_3$), was first synthesized from the oxides by Zachariasen at 1600°C in a helium atmosphere. The crystal structure of the compound was reported to be perovskite-like, tetragonal pseudocubic with $a = 3.760 \pm 0.004$ Å and $c = 3.878 \pm 0.004$ Å. Keith and Roy later confirmed the presence of this compound at 1:1 molar ratio in this system. They used Ce$_2$(C$_2$O$_4$)$_3$·9H$_2$O and Al$_2$O$_3$ as the starting materials and observed the splitting in the (111) reflection that would indicate primitive hexagonal symmetry, contrary to Zachariasen. Roth observed the formation of CeAlO$_3$ in the perovskite structure at 1600°C in about 1 h in helium but with rhombohedral symmetry ($a = 3.766$ Å, $\alpha = 90.2^\circ$). Leongov reported the synthesis of bright green, cubic (3.77 Å) CeAlO$_3$ from 99.85% CeO$_2$ and hydrated aluminum oxide in inert or slightly reducing atmospheres at elevated temperatures. It was also noted that CeAlO$_3$ would completely decompose to CeO$_2$ and Al$_2$O$_3$ in air at 800°C at 1 h. The binary phase diagram given by Leonov and others for the Ce$_2$O$_3$–Al$_2$O$_3$ system showed two polymorphic transformations. The first occurs at 90°C (of unidentified nature) and the second was reported to be a rhombohedral-to-cubic transition at 980°C ± 20°C. Kim indexed this compound, synthesized from Ce(C$_2$O$_4$)$_3$·xH$_2$O and alumina under vacuum at 1600°C, on the basis of a hexagonal cell of rhombohedral symmetry (JCPDS PDF 21-0175) with the lattice constants of $a = 5.35$ Å and $c = 13.02$ Å. He reported the X-ray density as 6.62 g/cm$^3$, Geller and Raccab estimated the rhombohedral-to-cubic transition for CeAlO$_3$, if there is any, to occur at about 960°C by extrapolating the data they obtained for the transition temperatures of the La (522°C), Pr (1370°C), and Nd (1747°C) aluminates. Scott predicted, by Raman spectroscopy, the transition temperatures as 1047°C and 1367°C for Pr and Nd aluminates, respectively. Mizuno reported the cerium monoaluminate to be cubic at $T \geq 1500°C$ in inert atmosphere (JCPDS PDF 28-0260) with a lattice constant of 3.767 Å. They also claimed that the rhombohedral polymorph could be synthesized at temperatures less than 100°C. More recently, Kaufer reported CeAlO$_3$, in a flowing hydrogen atmosphere at 1000°C. The structure of the slowly cooled product was found to be pseudo cubic, tetragonal with the lattice parameters $a = 3.760 \pm 0.004$ Å and $c = 3.787 \pm 0.004$ Å. The XRD pattern of the tetragonal structure is not in the JCPDS files and to our knowledge has never been published.

The second compound, cerium hexaaluminate (Ce$_2$O$_3$–Al$_2$O$_3$), has also been included in the first phase diagram for this system suggested by Leonov et al., and it has been reported to melt incongruently in a reducing atmosphere at about 1950°C and to be stable down to room temperature upon cooling. In the more recent phase diagram suggested by Mizuno et al., the hexaaluminate field was indicated by dashed lines, due to the difficulty in preparing it as a single phase; it was shown to melt incongruently at 1890°C in a reducing atmosphere. It was reported to have a hexagonal structure with the lattice constants $a = 5.543$ Å and $c = 21.979$ Å that the sample contained CeAlO$_3$ and $\alpha$-Al$_2$O$_3$ as minor phases. This compound has been labeled as Ce$\beta$-Al$_2$O$_3$ in this phase diagram due mainly to the compositional similarity with Na$\beta$-Al$_2$O$_3$ (Na$_2$O-11Al$_2$O$_3$). The synthesis and characterization of cerium hexaaluminate, in its pure form, have been attempted, to our knowledge, only in the above two studies in literature. In both of these, this compound was assumed to have the $\beta$-alumina structure. A similar type of compound (La$_2$Al$_2$O$_7$) was reported to be present in the La$_2$O$_3$–Al$_2$O$_3$ system. It has been realized that the addition of one divalent cation, such as Mg$^{2+}$, Mn$^{2+}$, Co$^{2+}$, or Ni$^{2+}$, to the above formula unit would produce a series of new compounds, LaMAl$_3$O$_{10}$, with structures quite similar to that of the magnetoplumbite (PbFe$_2$O$_4$) phase shown to be present in PbO–Fe$_2$O$_3$ system. It so appeared that the divalent M ions selected to be used as dopants should be chosen from among the M oxides that were able to form spinel-type (MAlO$_4$) phases with $\alpha$-alumina. According to this scheme, Al$^{3+}$ substitutes for Fe$^{3+}$, La$^{3+}$ (or Ce$^{3+}$) substitutes for Pb$^{2+}$, and the divalent cation replaces one Fe$^{3+}$ to conserve the electrical neutrality. The magnetoplumbite and Na$\beta$-alumina structures are both composed of spinel blocks formed by the close packing of Al and O atoms. The only significant difference between the two structures is in the two mirror planes ($z = 0.25$ and 0.75). Each mirror plane in the $\beta$-alumina structure contains one large cation (Na$^+$) and one oxygen.$^{19,20}$ Figure 1 displays half of the unit cells of the two structures drawn according to the atomic coordinates reported by Gasperin et al., for LaMAl$_3$O$_{10}$, and those reported by Felsche for NaAl$_2$O$_4$. The non-close-packed mirror planes join the stable spinel blocks. Moreover, the sites...
of the large cation and one oxygen in these planes are not fully occupied, which leads to a disorder in the mirror planes caused by a possible indeterminacy in the position of the large ion. The mirror planes in the magnetoplumbite structure contain one large cation and one oxygen in these planes and four aluminums at the intersection of the c-cell edge with the mirror planes. The mirror planes in the magnetoplumbite-like structure were found, for \( \text{LaMAl}_3 \), Ö

III. Experimental Procedure

Compositions in the \( \text{CeO}_2-\text{Al}_2\text{O}_3 \) system were prepared by mixing and stirring the appropriate amounts of the starting oxides, \( \text{CeO}_2 \) (99.87\%, 0.7 \( \mu \)m, Cerac, Milwaukee, WI) and \( \text{Al}_2\text{O}_3 \) (99.96\%, 0.5 \( \mu \)m, Reynolds, Inc.) in ethanol in glass jars for about an hour followed by 15 min of ultrasonification. The contents of the jars were dried overnight at 70°C in air. The recovered cakes were then calcined in air at 950°C for 12 h to remove any remaining carbonaceous residues. The calcined mixtures were then lightly ground in an agate mortar for about 30 min. The details of the green pellet preparation, equilibration times (in reducing, inert and vacuum atmospheres), quench practices, and DTA analyses employed were reported elsewhere.

After equilibration and quenching, each sample was ground to a mean particle size of 7\( \mu \)m. Phase analysis was made by

<table>
<thead>
<tr>
<th>Composition</th>
<th>Temp (°C)</th>
<th>Time (h)</th>
<th>Atmosphere</th>
<th>Cooling</th>
<th>Phases observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeAlO₃</td>
<td>1450</td>
<td>30</td>
<td>Argon</td>
<td>Quench</td>
<td>Tetr. CeAlO₃</td>
</tr>
<tr>
<td>CeAlO₃</td>
<td>1550</td>
<td>40</td>
<td>Argon</td>
<td>Quench</td>
<td>Tetr. CeAlO₃</td>
</tr>
<tr>
<td>CeAlO₃</td>
<td>1450</td>
<td>50</td>
<td>Argon + 10%H₂</td>
<td>Quench</td>
<td>Tetr. CeAlO₃</td>
</tr>
<tr>
<td>CeAlO₃</td>
<td>1550</td>
<td>50</td>
<td>Argon + 10%H₂</td>
<td>Quench</td>
<td>Tetr. CeAlO₃</td>
</tr>
<tr>
<td>CeA1O₃</td>
<td>1650</td>
<td>20</td>
<td>Vacuum</td>
<td>Furnace quench</td>
<td>Tetr. CeAlO₃</td>
</tr>
<tr>
<td>CeO₂</td>
<td>1750</td>
<td>10</td>
<td>Vacuum</td>
<td>Furnace quench</td>
<td>Tetr. CeAlO₃</td>
</tr>
<tr>
<td>CeO₂</td>
<td>1850</td>
<td>3</td>
<td>Vacuum</td>
<td>Furnace quench</td>
<td>Tetr. CeAlO₃</td>
</tr>
<tr>
<td>CeO₂</td>
<td>1950</td>
<td>1</td>
<td>Vacuum</td>
<td>Furnace quench</td>
<td>Tetr. CeAlO₃</td>
</tr>
<tr>
<td>CeO₂</td>
<td>1550</td>
<td>50</td>
<td>Argon + 10%H₂</td>
<td>Quench</td>
<td>Tetr. CeAlO₃</td>
</tr>
<tr>
<td>CeAlO₃</td>
<td>1550</td>
<td>50</td>
<td>Argon</td>
<td>Quench</td>
<td>Tetr. CeAlO₃</td>
</tr>
<tr>
<td>CeA1O₃</td>
<td>1650</td>
<td>25</td>
<td>Vacuum</td>
<td>15°C/h to RT</td>
<td>Tetr. CeAlO₃</td>
</tr>
<tr>
<td>CeO₂-11AlO₃</td>
<td>1550</td>
<td>30</td>
<td>Argon</td>
<td>Quench</td>
<td>CeO₂-11AlO₃, Al₂O₃, + CeAlO₃, Ce₃AlO₄</td>
</tr>
<tr>
<td>CeO₂-11AlO₃</td>
<td>1550</td>
<td>30</td>
<td>Argon + 10%H₂</td>
<td>Quench</td>
<td>CeO₂-11AlO₃, Al₂O₃, + CeAlO₃, Ce₃AlO₄</td>
</tr>
<tr>
<td>CeO₂-11AlO₃</td>
<td>1775</td>
<td>12</td>
<td>Vacuum</td>
<td>Furnace quench</td>
<td>CeO₂-11AlO₃, Al₂O₃, + CeAlO₃, Ce₃AlO₄</td>
</tr>
<tr>
<td>CeO₂-11AlO₃</td>
<td>1880</td>
<td>2</td>
<td>Vacuum</td>
<td>Furnace quench</td>
<td>CeO₂-11AlO₃, Al₂O₃, + CeAlO₃, Ce₃AlO₄</td>
</tr>
<tr>
<td>CeO₂-11AlO₃</td>
<td>1880</td>
<td>2</td>
<td>Vacuum</td>
<td>10°C/m to RT</td>
<td>CeO₂-11AlO₃, Al₂O₃, + CeAlO₃, Ce₃AlO₄</td>
</tr>
<tr>
<td>CeO₂-11AlO₃</td>
<td>1915</td>
<td>0.1</td>
<td>Vacuum</td>
<td>Furnace quench</td>
<td>CeO₂-11AlO₃, Al₂O₃, + CeAlO₃, Ce₃AlO₄</td>
</tr>
<tr>
<td>CeO₂-11AlO₃</td>
<td>1915</td>
<td>0.1</td>
<td>Vacuum</td>
<td>10°C/m to RT</td>
<td>CeO₂-11AlO₃, Al₂O₃, + CeAlO₃, Ce₃AlO₄</td>
</tr>
<tr>
<td>12 mol% CeO₂-88 mol% Al₂O₃</td>
<td>1700</td>
<td>12</td>
<td>Vacuum</td>
<td>Furnace quench</td>
<td>CeO₂-11AlO₃, Al₂O₃, + CeAlO₃, Ce₃AlO₄</td>
</tr>
<tr>
<td>12 mol% CeO₂-88 mol% Al₂O₃</td>
<td>1820</td>
<td>8</td>
<td>Vacuum</td>
<td>Furnace quench</td>
<td>CeO₂-11AlO₃, Al₂O₃, + CeAlO₃, Ce₃AlO₄</td>
</tr>
<tr>
<td>74 mol% CeO₂-26 mol% Al₂O₃</td>
<td>1875</td>
<td>4</td>
<td>Vacuum</td>
<td>Furnace quench</td>
<td>CeO₂-11AlO₃, Al₂O₃, + CeAlO₃, Ce₃AlO₄</td>
</tr>
<tr>
<td>79 mol% CeO₂-21 mol% Al₂O₃</td>
<td>1940</td>
<td>3</td>
<td>Vacuum</td>
<td>Furnace quench</td>
<td>CeO₂-11AlO₃, Al₂O₃, + CeAlO₃, Ce₃AlO₄</td>
</tr>
<tr>
<td>83 mol% CeO₂-17 mol% Al₂O₃</td>
<td>1940</td>
<td>3</td>
<td>Vacuum</td>
<td>Furnace quench</td>
<td>CeO₂-11AlO₃, Al₂O₃, + CeAlO₃, Ce₃AlO₄</td>
</tr>
</tbody>
</table>
XRD in the 5°–160° 2θ range using a Cu-tube powder diffractometer (XDS 2000, Scintag, Santa Clara, CA) operated at 45 kV and 30 mA with a scanning rate range of 0.125°–0.6° 2θ/min. Least-squares cell refinement, indexing, and lattice constant determinations were performed using the Appleman and Evans[20] and TREOR[21] routines. Elemental silicon (NBS 640a) was used as an external standard.

Microstructural analyses were carried out by scanning electron microscopy (SEM, JSM-6100, JEOL, Peabody, MA) on polished or as-is surfaces (in order not to damage the samples) of the fired pellets. The chemical compositions of the microstructural features observed in SEM images of the polished samples were examined with energy-dispersive X-ray spectroscopy (EDXS, Model Delta-5, Kevex, Foster City, CA) using single-phase CeAlO₃ as a standard, and the information thus obtained was believed to be accurate to within ±3 at.%

III. Results and Discussion

Compositions of CeₓOᵧ-AlₓOₙ stoichiometry were heated either in flowing purified argon (O₂ + H₂O ≤ 50 ppm), argon + 10% H₂, or under vacuum (P₀₂ ≤ 6 × 10⁻⁵ atm) at maximum temperatures ranging from 1450°C to 1950°C for periods in the range of 1 to 50 h. The equilibration heat treatments carried out in this study are tabulated in Table I. All the thermal treatments of samples of this stoichiometry consistently produced a single-phase (without any free CeₓOᵧ and α-AlₓOₙ remaining) substance with a typical XRD pattern given in Table II. The pattern shown in this table was obtained from a sample heated at 1550°C for 50 h followed by slow cooling (15°C/h) to room temperature (21°–23°C) in the furnace under a flow of argon + 10% H₂ gas. The structure has been determined to be tetragonal, with lattice constants a = 3.763 Å and c = 3.792 Å. This phase therefore is not the one covered by either of the previously published JCPDS files (21-0175, hexagonal and 23-0260, cubic) for CeAlO₃. However, our lattice constants agree well with those published by Zachariasen[19] and by Kaufherr et al.[22] The splitting of the peaks and the proper observation of these were thought to be the most important factors in the correct resolution of such a structure. Figure 2 shows a portion of the peak analysis performed for the data of the above XRD pattern. For this structure to be regarded as cubic, the splitting of the peaks displayed in Figs. 2(A), (B), (D–F) should certainly be absent. Similarly, the peak splitting observed in Figs. 2(A) and (D) and the 004:400 splitting shown in the pattern given in Table II should be absent to index this structure on the basis of a hexagonal cell with rhombohedral symmetry. The rhombohedral symmetry also

![Figure 2](image-url)
requires the tetragonal 111 reflection, as we observed in Fig. 2(C), to split into 202 and 006 reflections of the hexagonal system.

Our repeated attempts to observe the polymorphic transformation that was previously reported to occur at 960° or 1000°C with differential thermal analysis have all failed. The DTA traces (4°C/min) all registered the undisturbed background from room temperature to 1950°C. Nevertheless, the enthalpy of such a transformation, if there really was one, might be too low to detect by DTA. We found that slow cooling (15°C/h) a CeAlO₃ sample following the equilibration at 1550°C (Ar + 10% H₂) or 1650°C (vacuum) to 500°C (holding there for 24 h) and then to room temperature followed in the furnace (21°C–23°C) also did not produce any changes at all in the suggested XRD pattern that would be indicative of a polymorphic transformation. One question that still remains is the possibility of the presence of an extremely sluggish transition that might occur below 100°C. On the other hand, it needs to be noted that the purity of the starting materials might play a much more important role, in the realm of high-temperature phase equilibria and structural chemistry, than it was once thought. For instance, it may well not be a coincidence for the two different groups of researchers (Keith and Roy and Kim) to use the same starting material, i.e., cerous oxalate; Ce(C₂O₄)₂·nH₂O, in the preparation of CeAlO₃, and to produce the rhombohedral "polymorph." Is the presence of carbon in the structure causing this rhombohedral symmetry? It might still be a possibility, which needs to be investigated, that the carbon would not "burn out" until the temperature reaches 960°–980°C. As another possibility, to our knowledge, LaAlO₃ does not have a reported "cubic" polymorph. In our laboratory we also were not able to produce a tetragonal or cubic form of LaAlO₃. Our quenched samples (from above 1550°C) of LaAlO₃ always showed the (202:2.190 Å)–(006:2.184 Å) splitting that was a prerequisite for the rhombohedral symmetry to set in and be identified. Therefore, considering the fact that the significant presence of La₂O₃ as an impurity in cerium oxides was not so uncommon one or two decades ago, the rhombohedral LaAlO₃, which might form at very small quantities might have acted as a seed which would then impose the CeAlO₃ structure to acquire the rhombohedral symmetry of LaAlO₃. Research is presently under way in our labs to test this hypothesis by investigating the chemical synthesis conditions of LaAlO₃ and CeAlO₃ via aqueous precipitation.

Small portions of equilibrated, single-phase CeAlO₃, samples were heated in Pt envelopes open on one surface in a flowing air atmosphere at 250°C (5 days) and 1000°C (12 h) to test the stability of the compound. The XRD analysis showed that CeAlO₃ was still perfectly intact at 250°C; however, in the 1000°C sample, only traces of CeAlO₃ could be detected among the major phases of CeO₂ and α-Al₂O₃. The same tetragonal XRD pattern as that given in Table II, observed in the sample heated in air at 250°C for 5 days, has excluded, again, for us the possibility of identifying the previously reported low-temperature, rhombohedral "polymorph."

If one considers the perovskite-like lattice of CeAlO₃, as composed of Al³⁺ ions being at the octahedral interstices (cell corners, CN = 6), O²⁻ ions at the edge centers, and finally the large Ce³⁺ being at the body center (CN = 12), then it would be noticed that the (111) planes of this structure will be the highest atomic density regions because of the close packing of ceriums and oxygens. The close-packed (111) faces of such a cell would
then be expected to display the hexagonal symmetry characterized by the presence of trigonal axes while being the most thermodynamically stable faces.\(^{25}\) especially during anomalous grain growth. As was very recently discussed by Drofenik\(^{25}\) for the BaTiO\(_3\) perovskite, predominant (111) faces displaying the trigonal axes might be the surface habit during the grain-growth stage of the densification process. We have observed such microstructures in studying CeAlO\(_3\). Figure 3(A) shows the SEM micrograph of the fracture surface of a CeAlO\(_3\) pellet equilibrated in argon at 1550°C for 35 h, followed by water quenching. The extensive grain growth and well-developed (111) faces are clearly visible, especially in the upper right-hand corner of this micrograph. This sample produced the typical "tetragonal" XRD pattern of Table II. The micrograph of Fig. 3(B) was taken from the fracture surface of a CeAlO\(_3\) sample equilibrated at 1650°C for 15 h under vacuum, followed by furnace quenching (by shutting off the main power, 600°C/min cooling from 1650° to 1000°C, more sluggish exponential decay-type cooling from 1000°C to room temperature) to retain the high-temperature phases and features. A (111) face is visible at the center that is surrounded by microfacets and steps. The sample still produces the characteristic tetragonal XRD pattern indicating one more time that the real symmetry of a crystal does not necessarily depend upon the symmetrical shape and size of its apparent faces. Figure 3(C) shows the as-is surface of a CeAlO\(_3\) pellet heated at 1950°C for 1 h under vacuum followed by furnace quenching to room temperature. In this sample, it was almost impossible to find a region of the fracture surface that shows the (111) faces. Apparently, recrystallization has occurred and the whole surface has been covered with cuboids and tetragonal rhombs. The XRD pattern of this sample still conforms to that given in Table II.

We synthesized the binary compound of Ce\(_2\)O\(_3\):11Al\(_2\)O\(_3\) from the starting oxides Ce\(_2\)O\(_3\) and Al\(_2\)O\(_3\) by heating the samples either in argon, argon + 10% H\(_2\), or under vacuum at temperatures above 1550°C. The resultant product was never pure; it always contained some \(\alpha\)-Al\(_2\)O\(_3\) as a minor phase whose quantity decreased significantly with increasing temperatures up to 1880°C. At lower temperatures, such as 1550°C, the samples also contained small amounts of tetragonal CeAlO\(_3\). Cerium hexaaluminate was found to be an incongruently melting compound as was predicted by Mizuno \textit{et al.}\(^{9}\) To determine the first liquid formation temperature, a small piece of a preequilibrated cerium hexaaluminate sample, with several sharp edges, was hung by a molybdenum wire in the vacuum furnace that was visible through a quartz viewing port. An IR pyrometer, calibrated just before this run against the melting point of Pt, was focused on the sample. The sample was heated at the rate of 3°C/min. The melting behavior of the chunk was continuously monitored through the pyrometer, and at 1915°±25°C the sharp edges of the sample became rounded. The chunk, at this point, began to flow and then fell as a drop onto a molybdenum foil placed just below the wire. Following a 5-min hold at this state, the sample was furnace-quenched to room temperature. We assumed this temperature (i.e., the peritectic temperature) as the incongruent melting temperature of this compound. This reading agrees well with the temperature reported for the same event by Mizuno \textit{et al.}\(^{9}\) The final sample of this experiment
showed, in its XRD analysis, \( \alpha-Al_2O_3 \) as the only crystalline phase present. Figures 4(A) and (B) depict the surface morphology of this sample, showing darker trigonal alumina crystals surrounded by a lighter, cerium-containing, once-liquid phase. Repeating the same experiment, but this time using a slow cooling from 1915°C to room temperature, yielded the most pure hexaaluminate sample we obtained in this study. Traces of \( \alpha-Al_2O_3 \) still found in that sample would be indicative of incomplete resorption.

We suggest an XRD pattern for cerium hexaaluminate, \( CeAl_{16}O_{46} \), in Table III. This pattern is obtained from a sample first heated at 1550°C for 30 h, water-quenched, ground, repelletized, and then heated at 1550°C for another 30 h in a flowing argon + 10% \( H_2 \) atmosphere, followed by quenching. The sample still contained some \( \alpha-Al_2O_3 \) that could easily be detected from the pattern and very small amounts of CeAlO, which could be detected in the pattern only after a Rietveld analysis of the diffraction data. The peaks of these minor phases are excluded from the pattern given in the above table. Figures 4(C) and (D) show the details of the fracture surfaces of this sample. Plate-like, large grains of CeAlO exhibited always been the characteristic microstructural features of our hexaaluminate samples in this study. The EDXS analyses carried out on the flat surfaces of the grains of this sample (by using pure, single-phase CeAlO as a standard) gave us the mean weight percentages of the three elements present as follows: Ce 19.0%, Al 40.8%, and O 40.2%. When compared with the theoretical percentages (Ce 19.33%, Al 40.94%, O 39.73%) that were calculated from CeAlO, within the limits of error of EDXS analysis, these may be considered as a good match.

The determination of the crystal structure among the two likely candidates, magnetoplumbite and Na-\( \beta' \)-alumina, while working with a powder sample rather than a single crystal of cerium hexaaluminate, had been a difficult question to answer in the scope of this study. The assessment of the degree of disorder and the extent of site splitting in the mirror planes of the CeAlO structure which might cause the possible, slight variations in the phase stoichiometry, as well as the exact determination of the structure type, need to await further powder neutron or single-crystal X-ray diffraction experiments.

We have confirmed that the eutectic between CeAlO and CeAlO occurred at 1785 ± 15°C as was predicted by Mizuno et al. The equilibrium heat treatments for a sample of composition 12-mol% CeO-88-mol% AlO at 1700° and 1820°C produced a solid-state phase mixture of CeAlO and CeAlO, and a mixture of CeAlO and liquid, respectively, upon furnace quenching, as predicted by the available phase diagram. The DTA runs for the same composition indicated a single endothermic event at 1785°C corresponding to the first liquid formation. The heating of one of these samples to 1820°C, soaking for 6 h at that temperature, and slowly cooling (5°C/min) to 1100°C caused the posteutectic liquid matrix surrounding the elongated CeAlO grains to crystallize. A sample micrograph of this structure is given in Fig. 5(A). The XRD pattern of this sample showed the presence of two crystalline phases, CeAlO and CeAlO.

We could not synthesize the R-compound that was reported to form at 79 mol% CeO, and decompose at temperatures below 1850°C by Mizuno et al. One probable reason for this might be the inadequate quenching rates we had in the vacuum.

Fig. 5. SEM micrographs of samples in the CeO-AlO system: (A) 12 mol% CeO, (Backscattered electron image) 1820°C, vacuum, 6 h, 5°C/min to 1100°C, furnace-quenched to RT. Eutectic matrix surrounding the elongated, dark \( \alpha \)-alumina crystals. CeAlO is also present in the sample. (B) 74 mol% CeO, (Backscattered electron image) 1875°C, vacuum, 4 h, furnace-quenched. Dark CeAlO grains, gray CeO matrix. (C) 79 mol% CeO, 1940°C, vacuum, 3 h, furnace-quenched. Eutectic-like matrix of CeAlO and CeO, with large gray grains of CeO (Bars = 10 \mu m).
furnace that would not be rapid enough to prevent the decomposition of this compound. We were only able to furnace-quench (i.e., the natural cooling of the furnace itself upon turning off the power) our samples, although Mizuno et al. reported that they were able to water-quench their samples from temperatures in excess of 1900°C. Heating a 74-mol% CeO₂-26-mol% Al₂O₃ sample (pre-equilibrated at 1550°C for 24 h, followed by water-quenching, grinding, and repelletizing) to 1875°C and furnace-quenching produced a solid-state phase mixture of CeAlO₃ and [CeO₂ + Ce₃O₅₋₆₋] as shown in Fig. 5(B). The darker phase is CeAlO₃ in this picture. The other two compositions we studied in the CeO₂-rich region of this system produced unique microstructures similar to that displayed in Fig. 5(C). Upon heating the 79-mol% and 83-mol% CeO₂ samples to 1940°C, followed by furnace-quenching, the liquid was formed, and during cooling the submicrometer-spaced, eutectic-like matrix evolved. At this point we choose to just report the microstructures observed, even though they may not represent the equilibrium conditions for this portion of the binary. The lighter phase in Fig. 5(C) was the crystalline mixture [CeO₂ + Ce₃O₅₋₆₋], whereas the darker phase was CeAlO₃.

Although our attempts to synthesize the orthorhombic R-compound have failed, we still detected the traces of an orthorhombic phase embedded in the backgrounds of the XRD patterns of the above three samples. The extremely low intensities (1 to 3 out of 10⁹) of that phase, with the tentative lattice constants \(a = 19.28 \text{ Å}, b = 12.35 \text{ Å}, \) and \(c = 6.37 \text{ Å}\), did not at this point warrant giving an accurate listing of the individual reflections. It needs to be noted that the R-compound in the CeO₂-Al₂O₃ system reported by Mizuno et al. had quite different lattice constants: \(a = 9.538 \text{ Å}, b = 5.850 \text{ Å}, \) and \(c = 15.205 \text{ Å}\).

### IV. Conclusions

The two binary compounds, CeAlO₃ and Ce₃Al₂O₇, of the system CeO₂-Al₂O₃ have been synthesized from the pure oxides CeO₂ and Al₂O₃. It has been found that the conditions of formation of these two compounds were not affected by the atmospheres used in this study, namely, argon, argon + 10% H₂, and vacuum. CeAlO₃ was shown to be stable in a perovskite-like tetragonal structure, with the lattice constants \(a = 3.763 \text{ Å}, b = 3.792 \text{ Å}, \) and \(c = 5.850 \text{ Å}\), in the atmospheres used in this study from room temperature to 1950°C. A new XRD pattern was suggested for CeAlO₃.

Ce₃Al₂O₇ was synthesized from the oxides and was shown to be an incongruently melting compound, confirming the findings of the previous researchers. It decomposed into \(\alpha\)-Al₂O₃ and a liquid phase at 1915°C ± 25°C upon heating. An XRD pattern was suggested, for the first time, for the hexagonal compound Ce₁₁Al₂O₁₅, with the lattice constants \(a = 5.558 \text{ Å}, b = 2.012 \text{ Å}\).

The eutectic reaction between CeAlO₁₈ and CeAlO₃ was confirmed to occur at 1785°C ± 15°C as reported by Mizuno et al. Although it was almost impossible for us to form the single-phase CeAlO₁₈ in the solid state, we were able to form the crystals of this compound, in the presence of a liquid phase, at a composition of 12-mol% CeO₂ (without any unreacted \(\alpha\)-Al₂O₃), within a eutectic matrix of CeAlO₁₁₈ and CeAlO₃.

### References