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Phase Relations in the System Ce₂O₃–Al₂O₃ in Inert and Reducing Atmospheres

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The 1:1 compound, $CeAlO_3$, in the system Ce_2O_3–Al_2O_3 has been synthesized from the oxides and shown to have a perovskite-like tetragonal unit cell with the lattice parameters $a = 3.763$ 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 1:11 compound, $CeAl_{11}O_{18}$, has also been synthesized and shown to possess a magnetoplumbite-like hexagonal unit cell with the lattice parameters $a = 5.558$ and $c = 22.012$ Å. An XRD pattern is suggested for $CeAl_{11}O_{18}$ for the first time. The evolution of eutectic-like microstructures was observed and reported in the Ce_2O_3-rich side of this binary system.

I. Introduction

ONE of the two previously reported compounds of the Ce_2O_3–Al_2O_3 system, cerium monoaluminate ($CeAlO_3$), was first synthesized from the oxides by Zachariasen[1] 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 $c = 3.787 \pm 0.004$ Å. Keith and Roy[2] later confirmed the presence of this compound at 1:1 molar ratio in this system. They used $Ce_2(C_2O_4)_3 \cdot 9H_2O$ and Al_2O_3 as the starting materials and observed the splitting in the (111) reflection that would indicate primitive hexagonal symmetry, contrary to Zachariasen.[1] Roth[3] 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, $\alpha = 90.2°$). Leonov[4] reported the synthesis of bright green, cubic ($a = 3.77$ 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_2O_3 in air at 800°C at 1 h. The binary phase diagram given by Leonov *et al.*[5] for the Ce_2O_3–Al_2O_3 system showed two polymorphic transformations. The first occurs at 90°C (of unidentified nature) and the second was reported to be a rhombic-to-cubic transition at 980° ± 20°C. Kim[6] indexed this compound, synthesized from $Ce(C_2O_4)_3 \cdot xH_2O$ 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/cm³. Geller and Raccah[7] 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[8] predicted, by Raman spectroscopy, the transition temperatures as 1047° and 1367°C for Pr and Nd aluminates, respectively. Mizuno *et al.*[9] reported the cerium monoaluminate to be cubic at $T \geq 150°C$ 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, Kaufherr *et al.*[10] prepared $CeAlO_3$ 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 ($Ce_2O_3 \cdot 11Al_2O_3$), has been included in the first phase diagram for this system suggested by Leonov *et al.*,[5] 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.*,[9] 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 and that the sample contained $CeAlO_3$ and α-Al_2O_3 as minor phases. This compound has been labeled as Ce-β-Al_2O_3 in this phase diagram due mainly to the compositional similarity with Na-β'-Al_2O_3 ($Na_2O \cdot 11Al_2O_3$). 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 β-alumina structure. A similar type of compound ($LaAl_{11}O_{18}$) was reported[11,12] to be present in the La_2O_3–Al_2O_3 system. It has been realized[13–18] 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, $LaMAl_{11}O_{19}$, with structures quite similar to that of the magnetoplumbite ($PbFe_{12}O_{19}$) phase shown to be present in PbO–Fe_2O_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 (MAl_2O_4) phases with α-alumina.[18] According to this scheme,[15] 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-β'-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 β-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.*[17] for $LaMnAl_{11}O_{19}$ and those reported by Felsche[20] for $NaAl_{11}O_{17}$. The non-close-packed mirror planes join the stable spinel blocks. Moreover, the sites
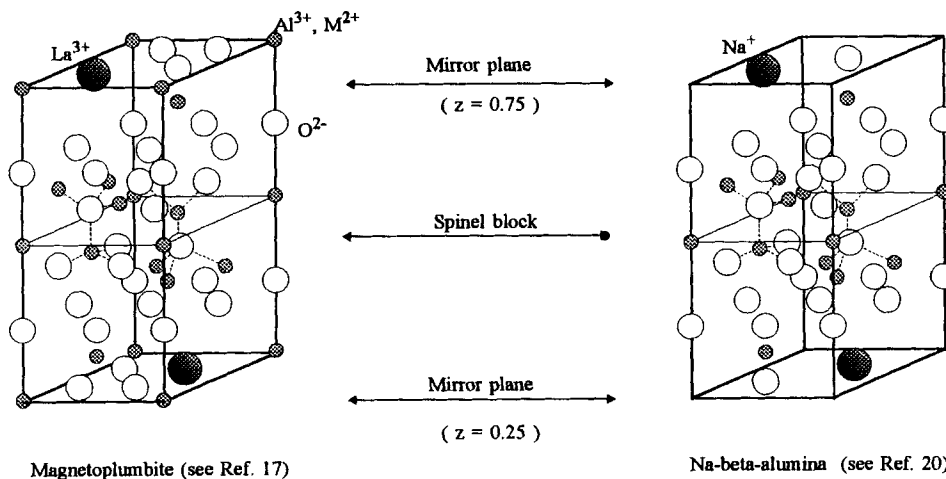
Fig. 1. Half unit cells of magnetoplumbite and sodium β-alumina structures.

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 (La^{3+} or Ce^{3+}) and three oxygens lying within the plane and four aluminums at the intersection of the c-cell edge with the mirror planes.[18] The mirror planes in the magnetoplumbite-like structure were found,[17] for $LaMAl_{11}O_{19}$-type compounds, to be disordered; the single, fully occupied, ideal site (2/3, 1/3, 1/4) for the large cation is split into two partially occupied, close sites in the plane. This gave the large cation of such structures a rather large volume in which it could move in a diffuse manner. The packings of the spinel blocks are virtually the same in both structures. The added divalent ions (M^{2+}), for $LaMAl_{11}O_{19}$-type compounds, were commonly found to localize themselves among the tetrahedrally coordinated Al sites within the spinel blocks[17] of the structure rather than achieving a statistical distribution over all the available Al sites. Hence, prior to this study, the previous literature has shown that the lanthanide-hexaaluminates, excluding that of cerium, exhibited structures similar to that of magnetoplumbite rather than that of Na-β'-alumina. Moreover, there have been no attempts to suggest an XRD pattern for the pure compound $Ce_2O_3 \cdot 11Al_2O_3$, although the JCPDS files did contain an entry for the divalent

cation-doped version, $CeMgAl_{11}O_{19}$, of the magnetoplumbite type (JCPDS PDF 26-0872).[21]

The present study focuses on the structural characterization of $CeAlO_3$ and $CeAl_{11}O_{18}$, using powder X-ray diffraction, and the high-temperature phase equilibria in Ce_2O_3–Al_2O_3 system in reducing (Ar + 10% H_2), inert (Ar), and vacuum atmospheres.

II. Experimental Procedure

Compositions in the Ce_2O_3–Al_2O_3 system were prepared by mixing and stirring the appropriate amounts of the starting oxides, CeO_2 (99.87%, 0.7 μm, Cerac, Milwaukee, WI) and Al_2O_3 (99.96%, 0.5 μm, 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 heatings (in reducing, inert and vacuum atmospheres), quench practices, and DTA analyses employed were reported elsewhere.[22]

After equilibration and quenching, each sample was ground to a mean particle size of 7 μm. Phase analysis was made by

Table I. Results of Equilibration Runs in the System Ce_2O_3–Al_2O_3

Composition	Temp (°C)	Time (h)	Atmosphere	Cooling	Phases observed
$CeAlO_3$	1450	50	Argon	Quench	Tetr. $CeAlO_3$
$CeAlO_3$	1550	40	Argon	Quench	Tetr. $CeAlO_3$
$CeAlO_3$	1450	50	Argon + 10%H_2	Quench	Tetr. $CeAlO_3$
$CeAlO_3$	1550	40	Argon + 10%H_2	Quench	Tetr. $CeAlO_3$
$CeAlO_3$	1650	20	Vacuum	Furnace quench	Tetr. $CeAlO_3$
$CeAlO_3$	1750	10	Vacuum	Furnace quench	Tetr. $CeAlO_3$
$CeAlO_3$	1850	3	Vacuum	Furnace quench	Tetr. $CeAlO_3$
$CeAlO_3$	1950	1	Vacuum	Furnace quench	Tetr. $CeAlO_3$
$CeAlO_3$	1550	50	Argon + 10%H_2	15°C/h to RT	Tetr. $CeAlO_3$
$CeAlO_3$	1550	50	Argon	15°C/h to RT	Tetr. $CeAlO_3$
$CeAlO_3$	1650	25	Vacuum	15°C/h to RT	Tetr. $CeAlO_3$
$Ce_2O_3 \cdot 11Al_2O_3$	1550	30	Argon	Quench	$Ce_2O_3 \cdot 11Al_2O_3$ + Al_2O_3 + $CeAlO_3$
$Ce_2O_3 \cdot 11Al_2O_3$	1550	30	Argon + 10%H_2	Quench	$Ce_2O_3 \cdot 11Al_2O_3$ + Al_2O_3 + $CeAlO_3$
$Ce_2O_3 \cdot 11Al_2O_3$	1775	12	Vacuum	Furnace quench	$Ce_2O_3 \cdot 11Al_2O_3$ + Al_2O_3 + $CeAlO_3$
$Ce_2O_3 \cdot 11Al_2O_3$	1880	2	Vacuum	Furnace quench	$Ce_2O_3 \cdot 11Al_2O_3$ + Al_2O_3
$Ce_2O_3 \cdot 11Al_2O_3$	1880	2	Vacuum	10°C/m to RT	$Ce_2O_3 \cdot 11Al_2O_3$ + Al_2O_3
$Ce_2O_3 \cdot 11Al_2O_3$	1915	0.1	Vacuum	Furnace quench	Liquid + Al_2O_3
$Ce_2O_3 \cdot 11Al_2O_3$	1915	0.1	Vacuum	10°C/m to RT	$Ce_2O_3 \cdot 11Al_2O_3$ + trace Al_2O_3
12 mol% Ce_2O_3–88 mol% Al_2O_3	1700	12	Vacuum	Furnace quench	$Ce_2O_3 \cdot 11Al_2O_3$ + $CeAlO_3$
12 mol% Ce_2O_3–88 mol% Al_2O_3	1820	8	Vacuum	Furnace quench	Liquid + $Ce_2O_3 \cdot 11Al_2O_3$
74 mol% Ce_2O_3–26 mol% Al_2O_3	1875	4	Vacuum	Furnace quench	$CeAlO_3$ + Ce_2O_3 + CeO_{2-x}
79 mol% Ce_2O_3–21 mol% Al_2O_3	1940	3	Vacuum	Furnace quench	$CeAlO_3$ + Ce_2O_3 + CeO_{2-x}
83 mol% Ce_2O_3–17 mol% Al_2O_3	1940	3	Vacuum	Furnace quench	$CeAlO_3$ + Ce_2O_3 + CeO_{2-x}

XRD in the 5°–160° 2 range using a Cu-tube powder diffracto-meter (XDS 2000, Scintag, Santa Clara, CA) operated at 45 kV and 30 mA with a scanning rate range of 0.125°–0.6° 2 /min. Least-squares cell refinement, indexing, and lattice constant determinations were performed using the Appleman and Evans[23] and TREOR[24] routines. Elemental silicon (NBS 640a) was used as an external standard.

Microstructural analyses were carried out by scanning elec-tron 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 micro-structural features observed in SEM images of the polished samples were examined with energy-dispersive X-ray spectros-copy (EDXS, Model Delta-5, Kevex, Foster City, CA) using single-phase $CeAlO_3$ as a standard, and the information thus obtained was believed to be accurate to within ±3 at.%.

III. Results and Discussion

Compositions of $Ce_2O_3 \cdot Al_2O_3$ stoichiometry were heated either in flowing purified argon (O + H₂O ≤ 50 ppm), argon + 10% H₂, or under vacuum (P_{O_2} ≤ 6 × 10^{-9} atm) at maximum temperatures ranging from 1450° 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 Ce_2O_3 and α-Al_2O_3 remaining) sub-stance with a typical XRD pattern given in Table II.† The pat-tern 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 pub-lished JCPDS files (21-0175, hexagonal and 23-0260, cubic) for $CeAlO_3$. However, our lattice constants agree well with those published by Zachariasen[1] and by Kaufherr et al.[10] The splitting of the peaks and the proper observation of those 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 per-formed 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

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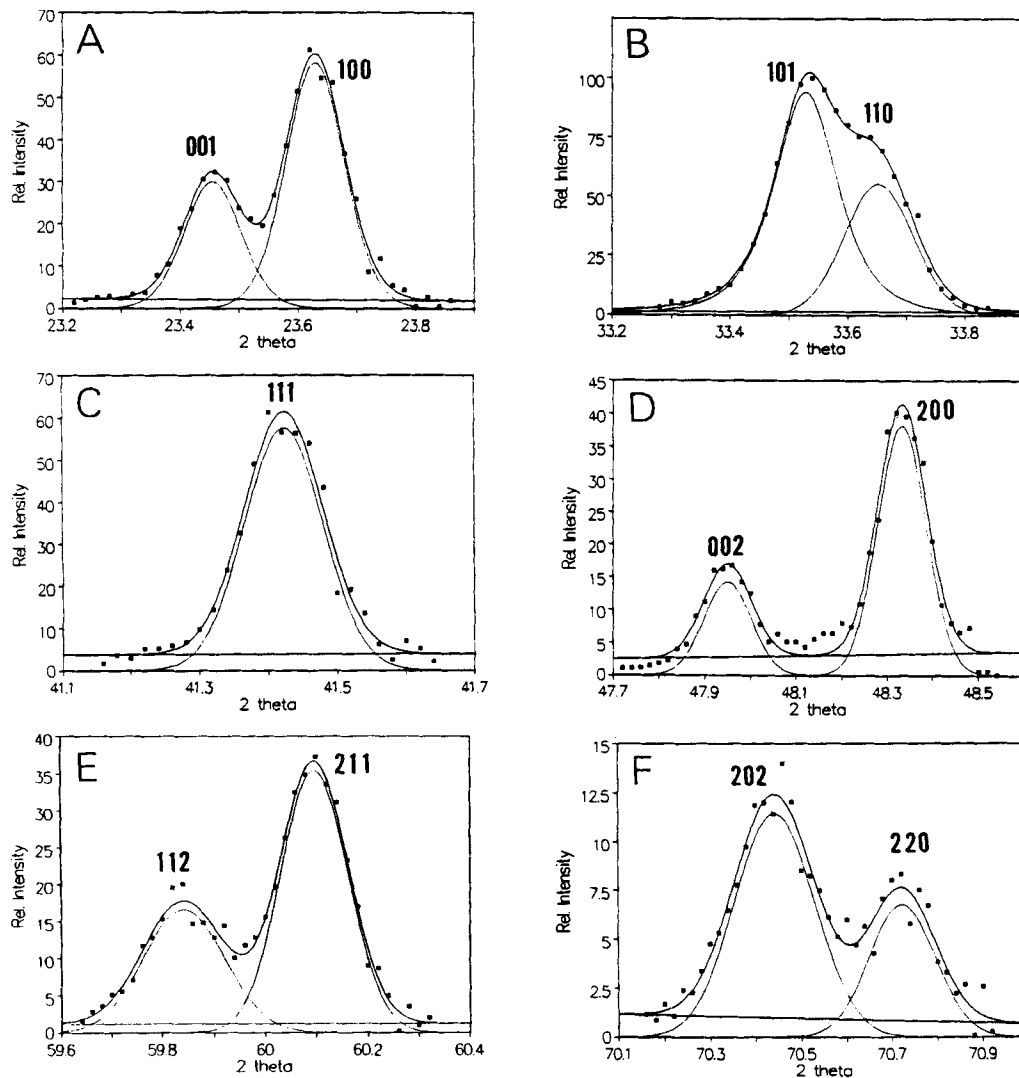**Fig. 2.** Splitting of the XRD peaks in tetragonal $CeAlO_3$ (a = 3.763 Å, c = 3.792 Å).

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[7-9] to occur at 960° or 100°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 by 1- to 2-h holding in the furnace (21°–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[2] and Kim[6]) to use the same starting material, i.e., cerous oxalate; Ce(C₂O₄)₃·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,[6] 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
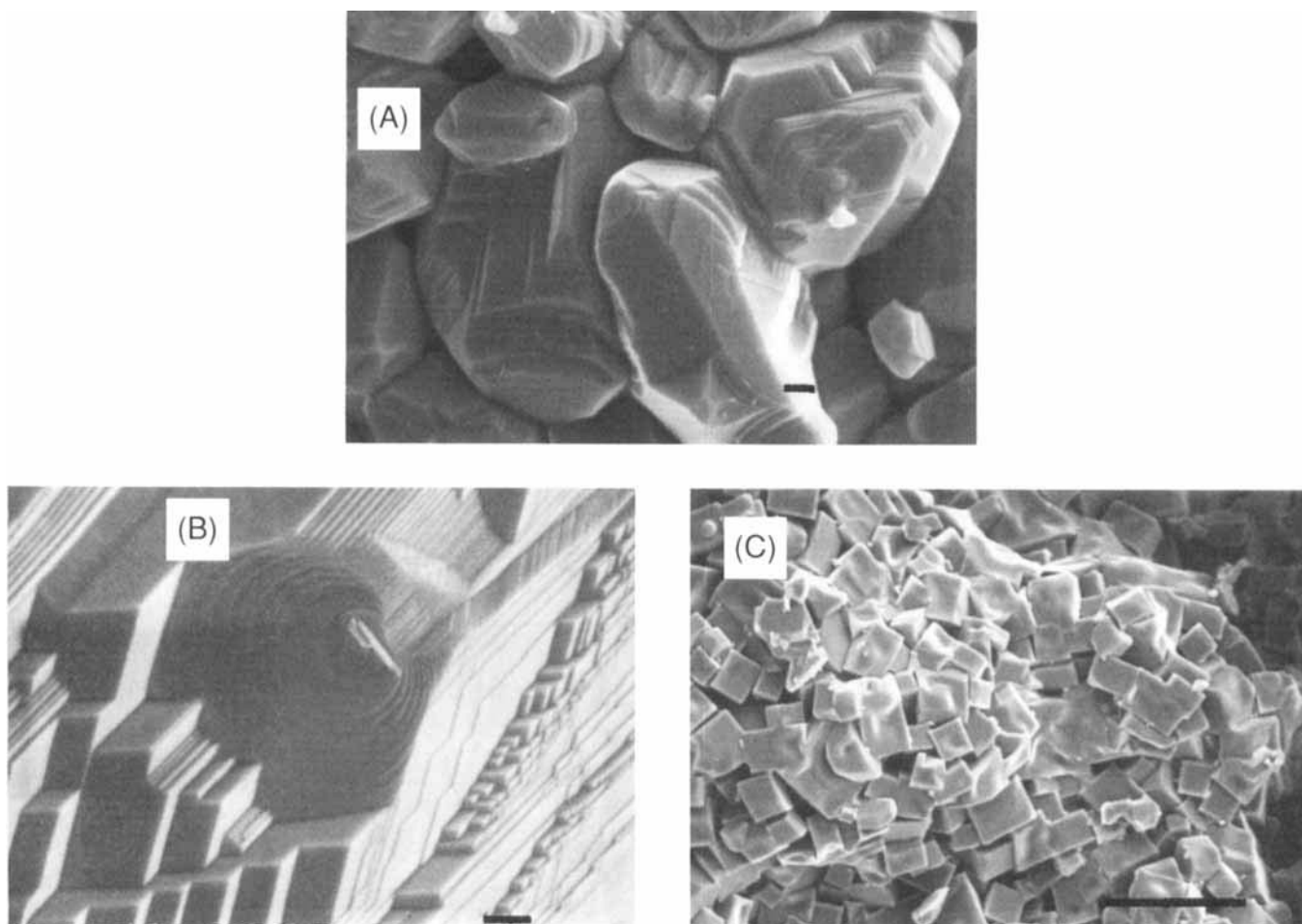

Fig. 3. SEM micrographs of CeAlO₃ samples: (A) 1550°C, argon, 35 h, quenched (bar = 1 μm); (B) 1650°C, vacuum, 15 h, furnace-quenched (bar = 1 μm); (C) 1950°C, vacuum, 1 h, furnace-quenched (bar = 10 μm).

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 $Ce_2O_3 \cdot 11Al_2O_3$ from the starting oxides CeO_2 and Al_2O_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 α-Al_2O_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 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 et al.[9] The final sample of this experiment
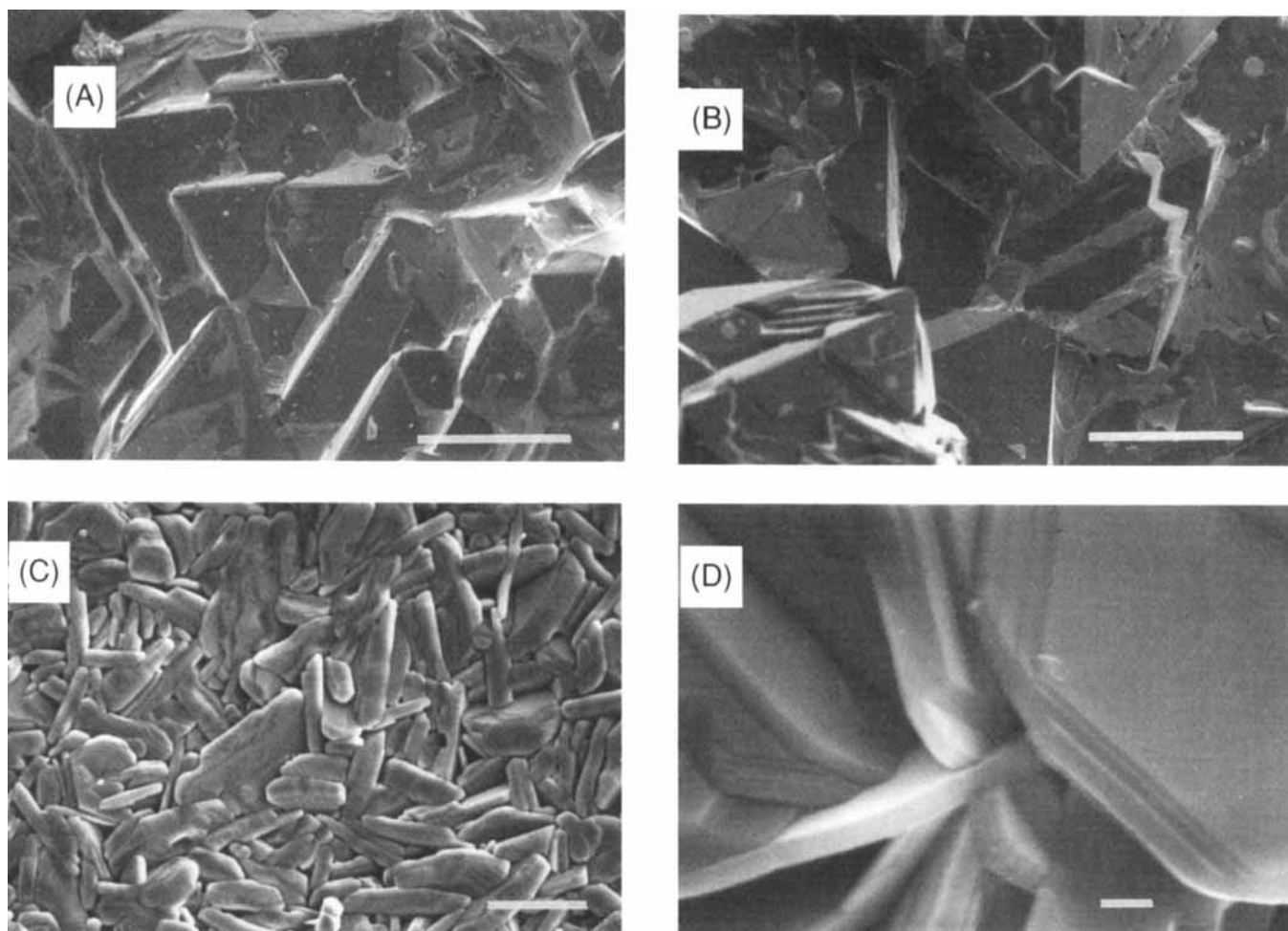
Fig. 4. SEM micrographs of samples of $CeAl_{11}O_{18}$ composition: (A) and (B) backscattered electron images. 3°C/min to 1915°C, 5 min, furnace-quenched to RT. Darker trigonal α-alumina crystals surrounded by lighter, cerium-containing, once-liquid phase. (Bars = 100 μm.) (C) 1550°C, 30 h, quenched, ground, repelletized, 1550°C, 30 h, quenched (bar = 10 μm). (D) Same sample as in (C) (bar = 1 μm).

showed, in its XRD analysis, α-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 α-Al_2O_3 still found in that sample would be indicative of incomplete resorption.

We suggest an XRD pattern for cerium hexaaluminate, $CeAl_{11}O_{18}$, 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 α-Al_2O_3 that could easily be detected from the pattern and very small amounts of $CeAlO_3$ 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. Platelike, large grains of $CeAl_{11}O_{18}$ had 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 $CeAlO_3$ 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 $CeAl_{11}O_{18}$, 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-β'-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 $CeAl_{11}O_{18}$ 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 $CeAl_{11}O_{18}$ and $CeAlO_3$ occurred at 1785 ± 15°C as was predicted by Mizuno *et al.*[9] The equilibrium heat treatments for a sample of composition 12-mol% Ce_2O_3–88-mol% Al_2O_3 at 1700° and 1820°C produced a solid-state phase mixture of $CeAl_{11}O_{18}$ and $CeAlO_3$, and a mixture of $CeAl_{11}O_{18}$ and liquid, respectively, upon furnace quenching, as predicted by the available phase diagram.[9] 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 $CeAl_{11}O_{18}$ 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, $CeAlO_3$ and $CeAl_{11}O_{18}$.

We could not synthesize the R-compound that was reported to form at 79 mol% Ce_2O_3 and decompose at temperatures below 1850°C by Mizuno *et al.*[9] One probable reason for this might be the inadequate quenching rates we had in the vacuum
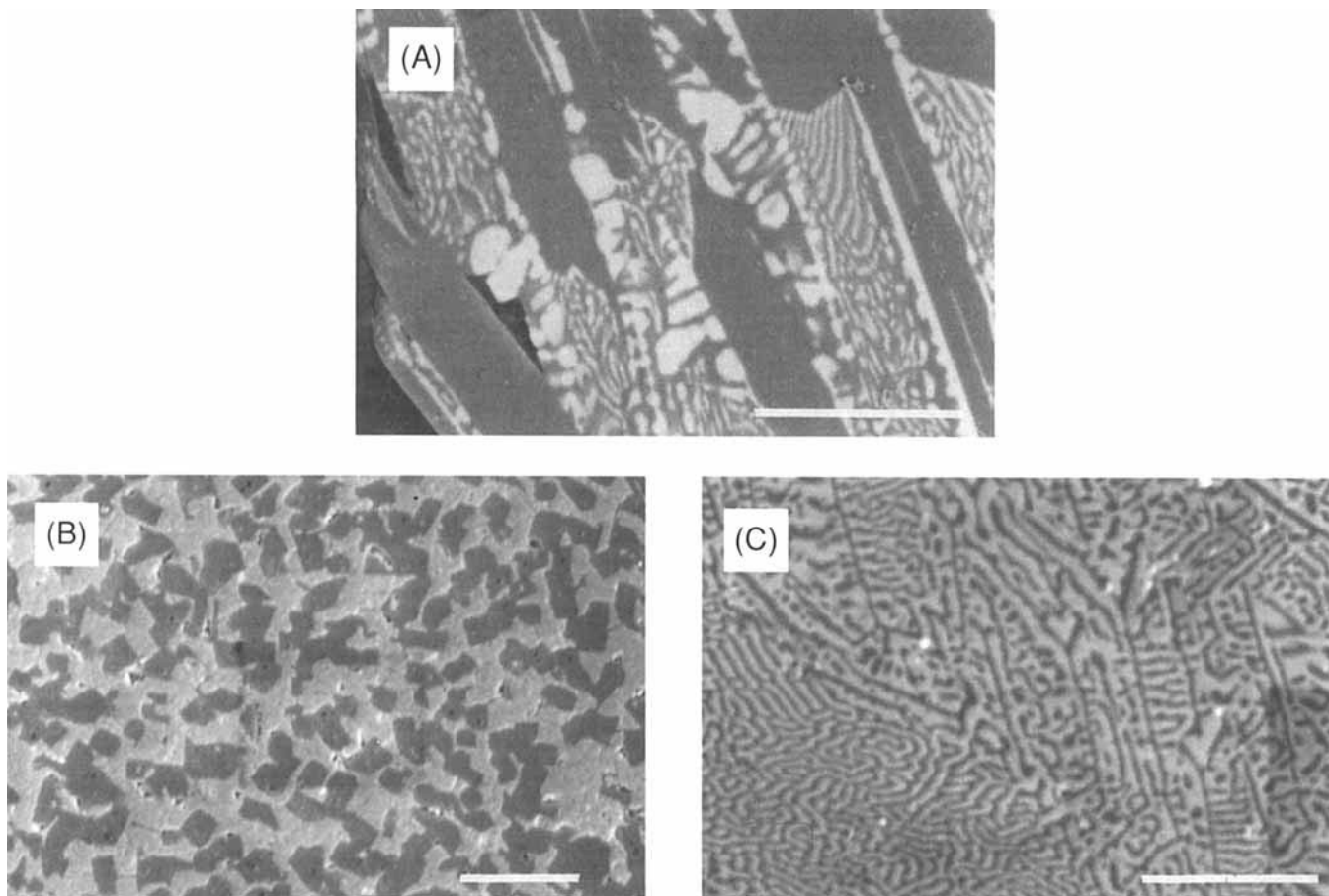
Fig. 5. SEM micrographs of samples in the Ce_2O_3–Al_2O_3 system: (A) 12 mol% Ce_2O_3. (Backscattered electron image) 1820°C, vacuum, 6 h, 5°C/min to 1100°C, furnace-quenched to RT. Eutectic matrix surrounding the elongated, dark α-alumina crystals. $CeAlO_3$ is also present in the sample. (B) 74 mol% Ce_2O_3. (Backscattered electron image) 1875°C, vacuum, 4 h, furnace-quenched. Dark $CeAlO_3$ grains, gray CeO_{2-x} matrix. (C) 79 mol% Ce_2O_3. 1940°C, vacuum, 3 h, furnace-quenched. Eutectic-like matrix of $CeAlO_3$ and CeO_{2-x} with large gray grains of CeO_{2-x}. (Bars = 10 μm.)

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.*[9] reported that they were able to water-quench their samples from temperatures in excess of 1900°C. Heating a 74-mol% Ce_2O_3–26-mol% Al_2O_3 sample (preequilibrated 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 $CeAlO_3$ and $[Ce_2O_3 + CeO_{2-x}]$ as shown in Fig. 5(B). The darker phase is $CeAlO_3$ in this picture. The other two compositions we studied in the Ce_2O_3-rich region of this system produced unique microstructures similar to that displayed in Fig. 5(C). Upon heating the 79-mol% and 83-mol% Ce_2O_3 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 $[Ce_2O_3 + CeO_{2-x}]$, whereas the darker phase was $CeAlO_3$.

Although our attempts to synthesize the orthorhombic R-compound[9] 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 100) of that phase, with the tentative lattice constants $a = 19.28$ Å, $b = 12.35$ Å, and $c = 6.37$ 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 Ce_2O_3–Al_2O_3 system reported by Mizuno *et al.*[9] had quite different lattice constants: $a = 9.538$ Å, $b = 5.850$ Å, $c = 15.205$ Å.

IV. Conclusions

The two binary compounds, $CeAlO_3$ and $CeAl_{11}O_{18}$, of the system Ce_2O_3–Al_2O_3 have been synthesized from the pure oxides CeO_2 and Al_2O_3. 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% H_2, and vacuum. $CeAlO_3$ was shown to be stable in a perovskite-like tetragonal structure, with the lattice constants $a = 3.763$ Å and $c = 3.792$ Å, in the atmospheres used in this study from room temperature to 1950°C. A new XRD pattern was suggested for $CeAlO_3$.

$CeAl_{11}O_{18}$ was synthesized from the oxides and was shown to be an incongruently melting compound, confirming the findings of the previous researchers. It decomposed into α-Al_2O_3 and a liquid phase at 1915° ± 25°C upon heating. An XRD pattern is suggested, for the first time, for the hexagonal compound $CeAl_{11}O_{18}$, with the lattice constants $a = 5.558$ Å and $c = 22.012$ Å.

The eutectic reaction between $CeAl_{11}O_{18}$ and $CeAlO_3$ was confirmed to occur at 1785° ± 15°C as reported by Mizuno *et al.*[9] Although it was almost impossible for us to form the single-phase $CeAl_{11}O_{18}$ 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% Ce_2O_3 (without any unreacted α-Al_2O_3), within a eutectic matrix of $CeAl_{11}O_{18}$ and $CeAlO_3$.

Eutectic-like microstructures, with submicrometer-sized lamellae, were observed, for the first time in any of the Ln_2O_3–$LnAlO_3$ (Ln: Lanthanide) systems studied, in the Ce_2O_3-rich (74–83 mol%) side of the Ce_2O_3–Al_2O_3 binary.

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