

## Subsolidus Phase Relationships in the Systems $Re$ -Al-O-N (Where $Re$ = Rare Earth Elements)

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Subsolidus phase relationships in the systems  $Re$ -Al-O-N (where  $Re$  = Ce, Pr, Nd, and Sm) were determined. A family of lanthanum aluminium oxynitrides,  $ReAl_{12}O_{18}N$ , with magnetoplumbite structure occurs, where the rare earth elements have large ionic radii ranging from La to Eu. The lattice parameters of these compounds were determined, and the results indicated that all these compounds have nearly the same value of  $a = 5.564 \text{ \AA}$ ,  $c = 22.00 \text{ \AA}$ , and  $c/a = 3.96 \text{ \AA}$ . © 1991 Academic Press, Inc.

### Introduction

Aluminium nitride is a covalent bonded compound with Grimm-Sommerfeld structure. Huang *et al.*'s work (1) showed that the covalency of the chemical bonding in Grimm-Sommerfeld compounds ( $AB$ )-BeO, AlN, and SiC varies considerably and has an effect on compound formation in the systems  $AB$ - $Re_2O_3$ . Increasing the valency of both elements ( $AB$ ) increases the covalency of the bonds in the order  $BeO < AlN < SiC$ . The tendency toward compound formation diminishes with the increasing atomic number of rare earth elements. The strong covalent bond in SiC leads to no reaction occurring in the systems  $SiC$ - $Re_2O_3$ . The decreasing covalency in BeO increases its ability to form compounds with a  $BeO:Re_2O_3$  (where  $Re$  = La, Nd, Sm, Gd, Dy, Ho, Er, Yb, Lu, and Y) mole ratio of 2:1 in all systems and 2:3 in  $BeO$ - $La_2O_3$  and  $BeO$ - $Nd_2O_3$  systems (2).

The covalency of AlN is weaker than that of SiC but stronger than BeO. The tendency toward compound formation in the systems  $AlN$ - $Re_2O_3$ , therefore, can be expected to rank between that of  $BeO$ - $Re_2O_3$  and  $SiC$ - $Re_2O_3$ , and that is proved by the formation of the compounds  $Re_2AlO_3N$  ( $Re$  = Ce, Pr, Nd, Sm, and Eu) (1). Their crystal structures ( $Re$  = La, Nd, and Sm) have been studied by R. Marchand (3, 4). The tendency toward compound formation diminishes also with increasing atomic number of the rare earth elements. Heavy rare earth elements after Gd are not able to form compounds with AlN, and  $Eu_2AlO_3N$  is the last member existing in the systems  $AlN$ - $Re_2O_3$ .

Similar chemical behavior of the light rare earth elements is also reflected in the compound formation between  $Al_2O_3$  and  $Re_2O_3$ , where the compounds  $ReAlO_3$  can be formed, and some other compounds, such as  $2Re_2O_3 \cdot Al_2O_3$  and  $Re_2O_3 \cdot 11Al_2O_3$  ( $\beta$ -

alumina), occur in some systems. However, the occurrence of these two compounds has not been observed by all investigators working on these systems (5–8). Therefore, from a chemical point of view, it is of interest to study the phase relationships among  $AlN$ ,  $Al_2O_3$ , and  $Re_2O_3$ .

On the other hand, many light rare earth oxides have been used as a sintering additive for  $Si_3N_4$  ceramics (9).  $Al_2O_3$  combined with  $AlN$  can be accommodated in  $\beta-Si_3N_4$  structure forming  $\beta$ -sialon. A thorough understanding of the effect of these compounds depends on the knowledge of the phase relationships in the systems  $Re-Si-Al-O-N$ . Therefore, the systems  $Re-Al-O-N$ , as a subsystem of  $Re-Si-Al-O-N$ , seem in order to be studied. With this aim, the phase relationships of the  $Nd-Al-O-N$  system (10) was first determined, and the results indicated that there exists a neodymium aluminium oxynitride,  $NdAl_{12}O_{18}N$ , with the same structure as  $EuAl_{12}O_{19}$ , which was reported to have similar structure as  $\beta$ -alumina (11). In fact,  $EuAl_{12}O_{19}$  possesses magnetoplumbite (MP) structure. A stoichiometric MP compound has a composition  $AB_{12}O_{19}$ , and a typical composition of  $\beta$ -alumina is  $AB_{11}O_{18}$  (11). Therefore, the  $\beta$ -alumina structure can be considered as a distorted MP structure with vacancies. The formation of  $NdAl_{12}O_{18}N$  increases the interest to understand the phase relationships in the other corresponding systems because the occurrence of the MP phases will provide information for the material design in the  $Re-Al-O-N$  and  $Re-Si-Al-O-N$  systems. For comparison, the results obtained for the  $Nd-Al-O-N$  system (10) are also summarized in this paper. The present work is more concerned with phase relationships and compound formation; compound structure will not be discussed.

## Experimental

The starting powders used were  $AlN$  (laboratory-made containing 1.4% O),  $CeO_2$ ,

$Pr_6O_{11}$ ,  $Nd_2O_3$ , and  $Sm_2O_3$  (all 99.9% pure, Shanghai Youlong products, calcinated at 1100°C before use), and  $Al_2O_3$  (99.99%, produced by decomposing ammonia alum). They were weighed and mixed in an agate mortar under absolute alcohol for 1.5 hr. The mixtures were dried and then pressed into disks of 20-mm diameter. The disks were isostatically pressed under 200 MPa prior to firing or straightly placed in a BN-lined graphite die for hot-pressing. The disks for the determination of phase composition were embedded in BN powder and fired. Hot-pressing under 20 MPa was employed for sample preparation for the determination of the composition of the nitrogen-containing MP compounds. The temperatures used for the determination of subsolidus phase relationships varied from 1450–1850°C, depending on which system and which phase region the compositions fell into. For instance, for composition C-1 (high Ce content) the temperature used was lower, because it melted at about 1650°C, but for the compositions with  $Re$  content less than 10 eq%, 1800–1850°C were needed. Both the pressureless sintering and hot-pressing were carried out in a graphite resistance furnace under mildly flowing nitrogen. The phase compositions and unit cell dimensions were identified and determined by the X-ray diffraction technique.

The starting compositions, firing conditions, and phase compositions obtained for the determination of the subsolidus phase relationships in the phase regions  $Re_2O_3-AlN-Al_2O_3$  ( $Re = Ce, Pr, \text{ and } Sm$ ) are listed in Tables I–III.

## Results and Discussion

### 1. Subsolidus Phase Relationships

The subsolidus phase relationships in the systems  $Re-Al-O-N$  ( $Re = Ce, Pr, Nd, \text{ and } Sm$ ) can be represented in Figs. 1 and 2. The compositions located in the triangles  $AlN-ReN-Re_2O_3$  could not be prepared because of the unavailability of the starting

TABLE I  
EXPERIMENTAL DATA FOR THE SYSTEM Ce-Al-O-N

No.	Composition (eq.%)				Firing cond. (Temp. (°C) for 1 hr)	Phase present
	Ce	Al	O	N		
C-1	75.68	24.32	91.89	8.11	1450	CeO <sub>2</sub> s; CAOm
C-2	66.67	33.33	66.67	33.33	H.P. 1550 H.P. 1700	CAOvs; CeO <sub>2</sub> w; Ce <sub>2</sub> O <sub>3</sub> w; AlNvw CAOs; CAONm; Ce <sub>2</sub> O <sub>3</sub> m; CeO <sub>2</sub> w; AlNtr.
C-3	37.04	62.96	51.85	48.15	1650	CAOvs; Ce <sub>2</sub> O <sub>3</sub> w; CeO <sub>2</sub> W; AlNw
C-4	19.35	80.65	70.97	29.03	1650	CAOvs; AlNm; MPm
C-5	15.38	84.62	97.44	2.56	1800	CAOs; MPs; Al <sub>2</sub> O <sub>3</sub> tr.
C-6	8.33	91.66	100	0	1800	MPvs; CAOvw
C-7	7.69	92.31	97.44	2.56	H.P. 1800	MPs
C-8	7.69	92.31	92.31	7.69	H.P. 1850	MPs
C-9	5.13	94.87	97.44	2.56	1850	MPs; Al <sub>2</sub> O <sub>3</sub> m
C-10	3.43	96.57	85.71	14.29	1850	MPs; SPs
C-11	3.19	96.81	93.62	6.38	1850	MPs; Al <sub>2</sub> O <sub>3</sub> s; SPm
C-12	2.82	97.18	59.15	40.85		MPs; Al <sub>2</sub> O <sub>3</sub> m; AlNw; SPvw

Note. CAO = CeAlO<sub>3</sub>, CAON = Ce<sub>2</sub>AlO<sub>3</sub>N, SP = aluminium oxynitride spinel, MP = MP phase (or  $\beta$ -alumina phase such as in C-6).

TABLE II  
EXPERIMENTAL DATA FOR THE SYSTEM Pr-Al-O-N

No.	Composition (eq.%)				Firing cond. (Temp. (°C) for 1 hr)	Phase present
	Pr	Al	O	N		
P-1	75.68	24.32	91.89	8.11	1650	PAOs; Pr <sub>2</sub> O <sub>3</sub> m
P-2	66.67	33.33	66.67	33.33	1700	PAONs; PAOm
P-3	37.04	62.96	51.85	48.15	1650	PAOvs; AlNm; PAONm
P-4	19.35	80.65	70.97	29.03	1650	PAOvs; AlNm; MPm
P-5	15.38	84.62	97.44	2.56	1650	PAOs; MPm
P-6	8.33	91.66	100	0	1800	MPvs; PAOvw
P-7	7.69	92.31	97.44	2.56	1800	MPs
P-8	7.69	92.31	92.31	7.69	H.P. 1800	MPs
P-9	5.13	94.87	97.44	2.56	H.P. 1850	MPs; Al <sub>2</sub> O <sub>3</sub> m
P-10	3.43	96.57	85.71	14.29	1850	MPs; SPs
P-11	3.19	96.81	93.62	6.38	1850	MPs; SPs; Al <sub>2</sub> O <sub>3</sub> m
P-12	2.82	97.18	59.15	40.85	1850	MPvs; Al <sub>2</sub> O <sub>3</sub> m

Note. PAO = PrAlO<sub>3</sub>, PAON = Pr<sub>2</sub>AlO<sub>3</sub>N, SP = aluminium oxynitride spinel, MP = MP phase (or  $\beta$ -alumina phase such as in P-6).

TABLE III  
 EXPERIMENTAL DATA FOR THE SYSTEM Sm-Al-O-N

No.	Composition (eq.%)				Firing cond. (Temp. (°C) for 1 hr)	Phase present
	Sm	Al	O	N		
S-1	75.68	24.32	91.89	8.11	1650	SAOs; Sm <sub>2</sub> O <sub>3</sub> m; SAONm
S-2	37.04	62.96	51.85	48.15	1650	SAOvs; SAONm; AlNw
S-3	19.35	80.65	70.97	29.03	1650	SAOvs; AlNm; MPm
S-4	15.38	84.62	97.44	2.56	1650	SAOvs; MPm; Al <sub>2</sub> O <sub>3</sub> w
S-5	8.33	91.66	100	0	1800	SAOvs; Al <sub>2</sub> O <sub>3</sub> s; MPtr.
S-6	7.89	92.11	94.74	5.26	H.P. 1800	MPvs; SAOvw
S-7	7.69	92.31	92.31	7.69	H.P. 1800	MPs
S-8	3.43	96.57	85.71	14.29	1800	MPs; SPs
S-9	3.19	96.81	93.62	6.38	1800	MPs; Al <sub>2</sub> O <sub>3</sub> s; SPm
S-10	2.82	97.18	59.15	40.85	1800	MPvs; Al <sub>2</sub> O <sub>3</sub> m; SPm; AlNw

Note. SAO = SmAlO<sub>3</sub>, SAON = Sm<sub>2</sub>AlO<sub>3</sub>N, SP = aluminium oxynitride spinel, MP = MP phase (or  $\beta$ -alumina phase such as in S-5).

materials *Re*N. The compositional range of aluminium oxynitride spinel has not been redetermined in the present work and was taken from the literature (13).

Like NdAl<sub>12</sub>O<sub>18</sub>N, single phase nitrogen-containing samarium MP compound only occurs at the composition SmAl<sub>12</sub>O<sub>18</sub>N, but single phase cerium and praseodymium MP compounds can be obtained in the composition range *Re*Al<sub>12-x</sub>O<sub>18</sub>N<sub>1-x</sub> (0 < x < 1). Except for that, the remaining parts of the phase relationships in these four systems are the same, as shown in Figs. 1 and 2.

In the present work, complete reaction forming Ce<sub>2</sub>AlO<sub>3</sub>N (14) was found to be difficult. Compositions C-1 and C-3, falling into the compatibility triangles Ce<sub>2</sub>O<sub>3</sub>-Ce<sub>2</sub>AlO<sub>3</sub>N-CeAlO<sub>3</sub> and Ce<sub>2</sub>AlO<sub>3</sub>N-CeAlO<sub>3</sub>-AlN, respectively, do not give Ce<sub>2</sub>AlO<sub>3</sub>N under the conditions used. Composition C-2 was exactly located at the starting 1:1 composition of Ce<sub>2</sub>O<sub>3</sub>:AlN, and Ce<sub>2</sub>AlO<sub>3</sub>N as a main phase only occurs at higher temperatures, around 1700°C. It seems that the complete reaction probably needs more reducing atmosphere than the atmosphere used in the present conditions, where a neu-

tral atmosphere N<sub>2</sub> was employed, which became slightly reducing at higher temperatures because of the graphite heating element used. However, under such conditions the compounds CeAlO<sub>3</sub> and Ce<sub>2</sub>O<sub>3</sub> · 11Al<sub>2</sub>O<sub>3</sub> can be produced, as has also been indicated by Levin and McMurdie (6) and M. Mizuno *et al.* (8), who used H<sub>2</sub> and Ar + 5% H<sub>2</sub> as the firing atmosphere, respectively. The formation of Pr<sub>2</sub>AlO<sub>3</sub>N is easier than Ce<sub>2</sub>Al

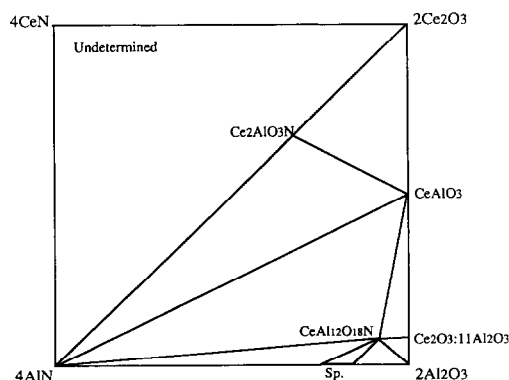


FIG. 1. Subsolidus phase relationships in the system *Re*-Al-O-N (*Re* = Ce, Pr).

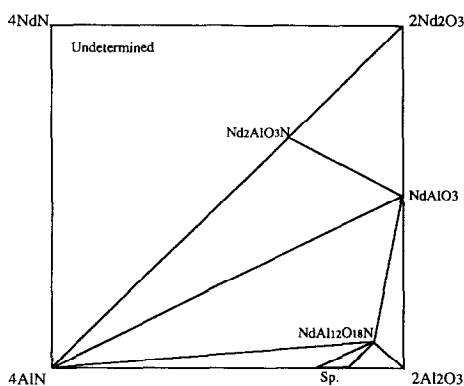


FIG. 2. Subsolidus phase relationships in the system  $Re\text{-Al-O-N}$  ( $Re = \text{Nd, Sm}$ ).

$\text{O}_3\text{N}$ , but a single phase was not obtained in the present work. The reason seems to be the same as that for  $\text{Ce}_2\text{AlO}_3\text{N}$ .

As a result, the subsolidus phase relationships in the  $\text{Ce}(\text{Pr})\text{-Al-O-N}$  systems contain three two phase regions,  $\text{Ce}(\text{Pr})\text{AlO}_3\text{-MP}$  phase,  $\text{MP phase-Al}_2\text{O}_3$ , and spinel-MP phase, and five three phase regions. The subsolidus phase relationships of  $\text{Sm-Al-O-N}$  are exactly the same as in the  $\text{Nd-Al-O-N}$  system.

## 2. Formation of the Compounds $\text{ReAl}_{12}\text{O}_{18}\text{N}$ and $\text{ReAl}_{11}\text{O}_{18}$

In the present work, the starting compositions at  $\text{LaAl}_{12}\text{O}_{18}\text{N}$ ,  $\text{EuAl}_{12}\text{O}_{18}\text{N}$ , and  $\text{GdAl}_{12}\text{O}_{18}\text{N}$  were explored as well, and the results showed that (except Gd) the other two elements La and Eu can form the pure magnetoplumbite phase. Therefore, the light rare earth elements from La until Eu with Pm not yet known have the same characteristics in forming nitrogen-containing magnetoplumbite phases.  $\text{EuAl}_{12}\text{O}_{18}\text{N}$ , like  $\text{Eu}_2\text{AlO}_3\text{N}$ , is the last member of the MP compounds  $\text{ReAl}_{12}\text{O}_{18}\text{N}$ . The X-ray diffraction patterns of the  $\text{ReAl}_{12}\text{O}_{18}\text{N}$  are the same, and nearly no significant difference can be detected. That is understood because the content of rare earth elements in these MP

compounds is too small to cause a noticeable difference in the unit cell dimensions. Thus,  $a = 5.564 \text{ \AA}$ ,  $c = 22.00 \text{ \AA}$ , and  $c/a = 3.96 \text{ \AA}$  can be represented to be the unit cell dimensions of  $\text{ReAl}_{12}\text{O}_{18}\text{N}$  ( $Re = \text{La} \rightarrow \text{Eu}$ ).

Lanthanide aluminium oxynitride with MP structure was first reported in 1988 by X. H. Wang *et al.* (15). During this time, our work on the  $\text{Nd-Al-O-N}$  system, which was published in 1989, was being carried out and the compound  $\text{NdAl}_{12}\text{O}_{18}\text{N}$  (called N-containing  $\beta$ -alumina) was independently found. These parallel work in both sides resulted in very similar results. Wang *et al.* (15) reported that the nitrogen-containing MP phases can be produced for  $Re = \text{La, Ce, Pr, Nd, Sm, Eu, and Gd}$ , among which only Sm- and Eu-containing compounds occur as single phase; the others are always contaminated with  $\text{ReAlO}_3$  and  $\text{Al}_2\text{O}_3$ . Composition  $\text{GdAl}_{12}\text{O}_{18}\text{N}$  gives a mixture of MP phase,  $\text{GdAlO}_3$ , and  $\text{Al}_2\text{O}_3$ . In our laboratory all the MP phases ( $Re = \text{La, Ce, Pr, Nd, Sm, and Eu}$ ) can be prepared as single phase and no  $\text{GdAl}_{12}\text{O}_{18}\text{N}$  is observed. However, it can be seen that the ability to form the MP compound diminishes with increasing atomic number of  $Re$  elements and ends at  $\text{EuAl}_{12}\text{O}_{18}\text{N}$  or  $\text{GdAl}_{12}\text{O}_{18}\text{N}$ , which, if it exists, has a narrow stability range.

As a comparison, samples with starting compositions  $\text{Re}_2\text{O}_3 : 11\text{Al}_2\text{O}_3$  for  $Re = \text{La, Ce, Pr, Nd, Sm, Eu, and Gd}$  were also made under the present conditions. The temperature used was  $1800^\circ\text{C}$ . The results showed that La, Ce, Pr, and Eu can form  $\beta$ -alumina phases contaminated by a small amount of  $\text{ReAlO}_3$ . It has been known that Eu is a multiple-valency element (+2 or +3) and the compound  $\text{EuAl}_{11}\text{O}_{18}$  does not exist. Therefore, the compound occurring in the  $\text{Eu}_2\text{O}_3\text{-Al}_2\text{O}_3$  system should have the composition  $\text{EuAl}_{12}\text{O}_{19}$ , which belongs to a MP compound (12). The formation of  $\text{EuAl}_{12}\text{O}_{19}$  under the present conditions can be attributed to the slightly reducing atmosphere, especially at high temperatures. Wang *et*

TABLE IV  
THE FORMATION OF  $ReAl_{12}O_{18}N$  AND  $ReAl_{11}O_{18}$

Compositions	La	Ce	Pr	Nd	Sm	Eu	Gd
$ReAl_{12}O_{18}N$ +	+	+	+	+	+	-	
$ReAl_{12}O_{18}N^*$	+	+	+	+	+	+	+
$ReAl_{11}O_{18}$	+	+	+	-	-	+^	-
$ReAl_{11}O_{18}^* +$	+	+	+	+^	+^	-	

Note. +, forming compounds; -, not forming compounds; \*, after Wang (15); +^, actual composition should be  $ReAl_{12}O_{19}$ .

*al.*(15) reported that lanthanum aluminates exist for *Re* = La, Ce, Pr, Nd, Sm, and Eu, except Sm and Eu, and all the other compounds are always contaminated with  $ReAlO_3$  and  $Al_2O_3$  (15). They also indicated that the pure Sm and Eu compounds occurring in the  $Re_2O_3$ - $Al_2O_3$  systems are  $ReAl_{12}O_{19}$ . Therefore, the compounds  $ReAl_{11}O_{18}$  with  $\beta$ -alumina structure exist within the lanthanum series to Pr or probably Nd. Unambiguously, nitrogen can enter the lattice to form MP structure, and the stability range of MP rare earth compounds is wider than the corresponding compounds with  $\beta$ -alumina structure. The narrow stability range of  $ReAl_{11}O_{18}$  is probably the reason for the conflicting results obtained by different researchers. The formation of the MP phase and the  $\beta$ -alumina phase, both observed in the present work, and those reported by Wang *et al.* (15), are summarized in Table IV.

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