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Compound Formation and Melting Behavior in the *AB* Compound and Rare Earth Oxide Systems

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Compound formation in the systems of the covalent compounds BeO, AlN, and SiC with R_2O_3 (rare earth oxides) is described. Tentative phase diagrams of the AlN–Nd_2O_3 and AlN–Eu_2O_3 systems are presented. © 1990 Academic Press, Inc.

Introduction

The compounds BeO, AlN, and SiC (*AB* type) belong to the family of "Grimm-Sommerfeld compounds." These compounds crystallize in the same hexagonal wurtzite (*B*4) structure. Such a structure can be considered as being composed of two interpenetrating hexagonal close-packed sublattices, one of atoms *A*, the other of atoms *B* (*1*, *2*). *A* and *B* form interpenetrating tetrahedra AB_4 and BA_4, respectively. Increasing the valency of both elements increases the covalency of the bonds in the order BeO < AlN < SiC. This structure can be regarded as a tetrahedron network sharing corners, which leads to the possibility of forming salts such as acidic groups like SiO_2 with basic metal oxides. Some crystal chemistry data of these three compounds are listed in Table I, indicating the similarities and the differences between them.

In a previous paper, one of the authors (T. S. Yen) reported (*3*) the phase relationships in a series of the BeO–R_2O_3 systems (where R = La, Nd, Sm, Gd, Dy, Ho, Er, Yb, Lu, and Y) showing the formation of incongruently melting compounds or metastable compounds with a BeO : R_2O_3 mole ratio of 2 : 1 in all systems, and 2 : 3 in BeO–La_2O_3 and BeO–Nd_2O_3 systems, except 2BeO · La_2O_3, which is congruent.

Subsolidus phase relationships in the systems AlN–R_2O_3 (where R = Nd, Sm, Gd, Dy, Er, Yb, and Y) have been reported by these authors (*4*). The binary compounds with AlN : R_2O_3 mole ratio of 1 : 1 were found in the systems containing Nd and Sm. No compound, however, was found in the systems containing rare earth oxides with cations smaller than that of Gd. The

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TABLE I

CRYSTAL CHEMISTRY DATA FOR THE COMPOUNDS BeO, AlN, AND α-SiC

AB compounds	BeO	AlN	α-SiC[a]
Structure	B_4	B_4	B_4
Valence ratio of $A:B$	2:2	3:3	4:4
Structural element	$[BeO_4]$	$[AlN_4]$	$[SiC_4]$
Coordinations of $A:B$	4:4	4:4	4:4
Bond	Be–O	Al–N	Si–C
Bond length (Å)	1.65	1.87	1.89
Ionicity of bond	0.5	0.4	0.2

[a] Hexagonal wurtzite (B_4); β-SiC is zinc blende (B_3).

phase diagrams of these binary systems have not been presented.

No information has been reported on the SiC–rare earth oxide systems. Because of the crystal chemical similarities for the Grimm–Sommerfeld compounds, a comparison of the phase relationships in BeO, AlN, and SiC with the rare earth oxide systems should be very interesting. An understanding of compound formation in these three systems should also be highly important for the development of these three hard-to-sinter *AB* compounds as advanced ceramic materials.

Compound formation in the systems AlN–R_2O_3 (where R = La, Pr, and Eu) and SiC–R_2O_3 (where R = La, Nd, Sm, Eu, Gd, Dy, Er, and Y) was studied in the present work. The phase diagrams of AlN–Nd_2O_3 and AlN–Eu_2O_3 as typical systems were also determined.

Experimental

Starting powders used were AlN (Starck), SiC (Starck), and R_2O_3 (products of China, with purity better than 99.9%). All of the R_2O_3 powders were calcined at 1100°C for 1 hr before use. The compositions investigated were made by mixing the required amounts of the starting powders in an agate mortar under absolute alcohol as medium for 1.5 hr. The mixtures were dried and isostatically pressed under 300 MPa into small cylinders of 5 mm in diameter. These cylinders were used for the determination of phase changes during firing and melting behavior by DTA at a heating rate of 10°C/min and by visual observation. Hot pressing was also used to promote the solid state reaction of the samples. An automatic recording X-ray diffractometer with monochromatic Cu*Kα* radiation was used to analyze the phase compositions of the hot-pressed samples. The lattice parameters of compounds were measured with silicon as standard. Some samples after hot pressing were heat-treated in a protective environment (nitrogen for AlN- and argon for SiC-containing systems) at 1400°C for 24 hr in a Pt–Rh wiring furnace for the equilibrium studies. Equilibria were checked by X-ray diffraction studies.

Results and Discussion

1. Compound Formation

In the previous papers (*4–6*), the compounds Ce_2AlO_3N, Nd_2AlO_3N, and Sm_2AlO_3N (AlN : R_2O_3 = 1 : 1) had been reported to have the same tetragonal structure. In the present work, Pr_2AlO_3N and Eu_2AlO_3N were also found to have the same structure. The X-ray diffraction data of these compounds are listed in Table II. The lattice parameters of the above five compounds R_2AlO_3N (where R = Ce, Pr, Nd, Sm, and Eu) are summarized in Table III and Fig. 1. No compound was found in the systems of AlN–R_2O_3 with smaller ionic radii (high atomic weight) beyond Gd. The composition of AlN : La_2O_3 (1 : 1) was hot-pressed at 1400°C for 1 hr; no binary compound was found.

Compositions with equal mole ratio of SiC and R_2O_3 (R = La, Nd, Sm, Eu, Gd, Dy, Er, and Y) were hot-pressed in BN-coated graphite dies in an argon atmo-

TABLE II

X-RAY DATA FOR Pr_2AlO_3N, Nd_2AlO_3N, AND Eu_2AlO_3N

	Pr_2AlO_3N		Nd_2AlO_3N		Eu_2AlO_3N	
hkl	*d*(Å)	I/I_0	*d*(Å)	I/I_0	*d*(Å)	I/I_0
101	3.563	ms	3.55	s	3.529	s
004	3.150	m	3.12	s	3.098	ms
103	2.783	s	2.771	vs	2.747	vs
110	2.627	s	2.619	s	2.603	s
112	2.425	w	2.416	w	2.400	w
006/105	2.100	w	2.085	w	2.066	w
114	2.017	ms	2.006	ms	1.993	ms
200	1.8575	ms	1.850	m	1.841	ms
211	1.6471	m	1.641	w	1.632	w
116	1.6403	w	1.633	m	1.618	w
107	1.6200	m	1.611	m	1.596	m
204	1.6000	w	1.594	w	1.582	w
008	1.5750	vw	1.560	vw	1.549	vw
213	1.5449	ms	1.538	m	1.529	m
206/215	1.3913	w	1.385	w	1.374	w
118	1.3508	vw	1.343	vw	1.331	vw
220	1.3135	w	1.309	w	1.301	w
Tetragonal	$a = 3.715$ Å $c = 12.60$ Å		$a = 3.704$ Å $c = 12.505$ Å		$a = 3.682$ Å $c = 12.38$ Å	

sphere at 1650 and 1700°C. X-ray diffraction analyses of these hot-pressed samples indicated only the above-mentioned starting compounds; no evidence of binary compound formation was found. Some Sm-, Eu-, and Gd-containing samples after melting were devitrified at 1400°C in Ar for 24 hr in a Pt–Rh furnace. No new phase was found yet, indicating the difficulty of compound formation in the SiC–R_2O_3 systems.

TABLE III

LATTICE PARAMETERS OF THE COMPOUNDS R_2AlO_3N, WHERE R = Ce, Pr, Nd, Sm, AND Eu

	Lattice parameters (tetragonal)		
Compounds	*a* (Å)	*c* (Å)	References
Ce_2AlO_3N	3.736	12.72	(*6*)
Pr_2AlO_3N	3.715	12.60	Present work
Nd_2AlO_3N	3.704	12.505	(*4*)
Sm_2AlO_3N	3.690	12.371	(*4, 5*)
Eu_2AlO_3N	3.682	12.38	Present work

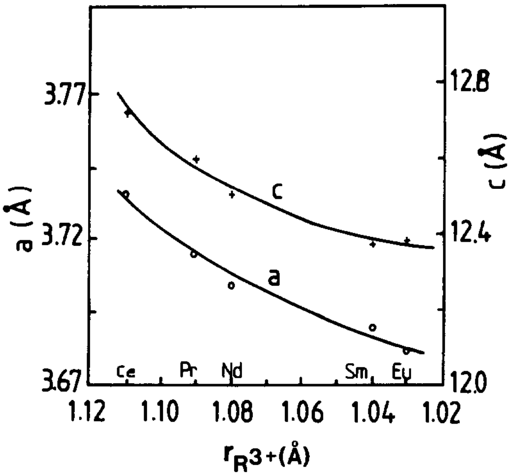

FIG. 1. Lattice parameters of R_2AlO_3N vs ionic radii of rare earths R.

Comparing with the BeO–R_2O_3 systems in which there exist two kinds of beryllates with mole ratios of 2 : 1 and 2 : 3 (BeO : R_2O_3), only one kind of R_2AlO_3N (where R = Ce, Pr, Nd, Sm, and Eu) was identified in AlN–R_2O_3 systems, but no compound was found in SiC–R_2O_3 systems. Such a tendency toward decreasing capability of salt compound formation may be related with increasing covalency and/or bond energy of the three Grimm–Sommerfeld-type compounds in the order of BeO < AlN < SiC.

In rare earth beryllates, there is only one type of bond Be–O (bond length 1.65 Å) in the acidic group $(BeO_x^{-2x+2})_n (x > 1)$ (*3*). However, if any salt compound forms for the AlN–R_2O_3 and SiC–R_2O_3 systems, two pairs of bonds, Al–N (1.87 Å) and Al–O (1.75 Å) and Si–C (1.89 Å) and Si–O (1.60 Å), should exist in the acidic groups $(AlNO_x^{-2x})_n (x > 0)$ and $(SiCO_x^{-2x})_n (x > 0)$, respectively. Therefore, the differences of bond lengths in the structural units of compounds would be 0, 0.12, and 0.29 Å for three kinds of salts investigated, respectively. The bigger the difference in the bond lengths, the larger the distortion of the tet-

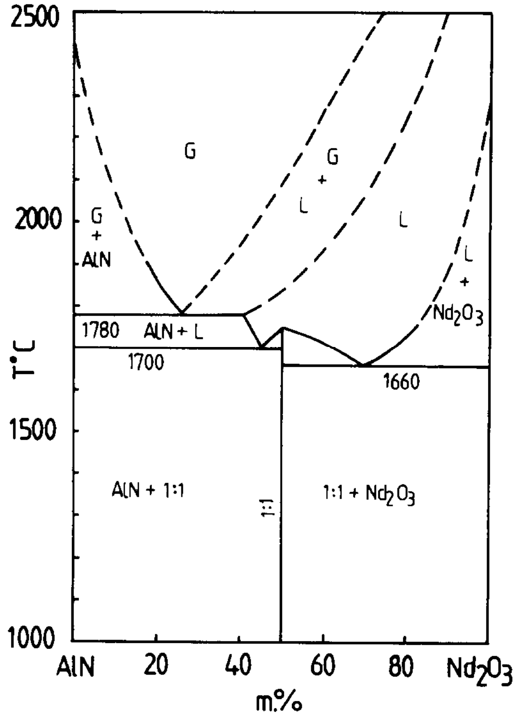

FIG. 2. Tentative phase diagram of the AlN–Nd_2O_3 system.

rahedron $[A(B, O)_4]$. Also, the stronger the covalency of the bonds, the more difficult it would be for such a distortion to occur, indicating that it would be much harder for the O^{-2} ion from R_2O_3 to enter into tetrahedron (SiC_4) than into (AlN_4). Obviously, there should be no problem for (BeO_4), forming the individual acidic group which separates the tetrahedron network $[A(B, O)_4]_\infty$. Thus, the tendency toward decreasing formability of salt compounds occurs in the order of BeO > AlN > SiC.

In addition, the light rare earths, as basic metal oxides, form salt compounds more easily with BeO and AlN as acidic compounds.

2. *Melting Behavior*

The melting behavior of the AlN–Nd_2O_3 and AlN–Eu_2O_3 systems was determined by visual observation and by DTA. The resulting tentative phase diagrams of both systems are presented in Figs. 2 and 3, respectively. The compound Nd_2AlO_3N melts congruently at 1750°C whereas the compound Eu_2AlO_3N melts incongruently at 1400°C into liquid and Eu_2O_3 with some $Eu_{1-x}O$ (7) caused by reduction.

For molten samples with compositions near to AlN, either big bubbles or large weight loss was observed, indicating the existence of regions of gas phase formation. It is evident that the reaction of R_2O_3 (where R = Nd and Eu) with AlN promotes the decomposition of AlN at high temperatures. The gas phase, as the products of the decomposition of AlN, would be composed of nitrogen and some gaseous oxides of aluminum or of the rare earth. The boundaries of the gas and/or liquid phase regions are suggested by dotted lines, because of the

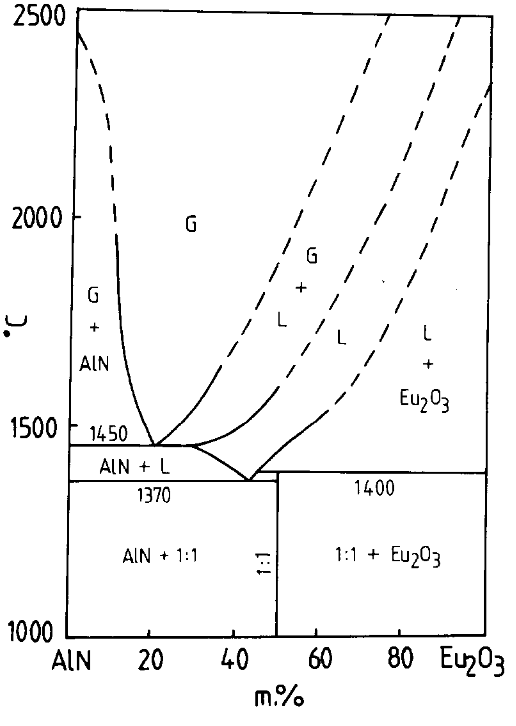

FIG. 3. Tentative phase diagram of the AlN–Eu_2O_3 system.

difficulties in the measurements. Except for the regions involving gas phase, the phase diagrams of both systems look like that of the BeO-containing systems (*3*), with steep liquidus ties from both end members. It is expected that the phase diagrams of the AlN-heavy rare earth (beyond Gd) oxide systems, as well as SiC–R_2O_3 systems, without any binary compound formation, will be simple binary ones with regions of a gas phase.

Conclusion

Salt compound formation in the systems of Grimm–Sommerfeld compounds, BeO, AlN, and SiC, having different degrees of covalent bonding, with R_2O_3 (rare earth oxides) was studied. The decreasing tendency for compound formation in systems containing BeO, AlN, to SiC was discussed. Tentative phase diagrams of the AlN–Nd_2O_3 and AlN–Eu_2O_3 systems were also presented which show a similarity to those of BeO–R_2O_3, having steep liquidus drops from both end members.

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