Journal of the European Ceramic Society **15** (1995) 349–355

0955-2219/95/$9.50

Subsolidus Phase Relationships in the Systems Ln_2O_3–Si_3N_4–AlN–Al_2O_3 (Ln = Nd, Sm)

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(Received 14 April 1994; revised version received 14 July 1994; accepted 1 August 1994)

Abstract

Subsolidus phase relationships in the systems Ln–Si–Al–O–N where Ln = Nd and Sm have been determined. Forty-four compatibility tetrahedra were established in the region Ln_2O_3–Si_3N_4–AlN–Al_2O_3. Within this region, $LnAlO_3$ and M'-phase ($Ln_2Si_{3-x}Al_xO_{3+x}N_{4-x}$) are the only two important compounds which have tie lines joined to β-sialon and AlN polytypoid phases. α-Sialon coexists with the M' phase.

1 Introduction

It is well known that metal oxides are necessary for the densification of silicon nitride ceramics. During sintering, the metal oxide additives and silicon nitride (which unavoidably contains a small amount of silica as an impurity), form an eutectic melt which aids densification. The liquid composition affects the resulting microstructure and hence the properties of the final ceramics; it also determines the nature of grain-boundary crystalline phases after heat-treatment.

The importance of using rare earth oxides for the densification of silicon nitride ceramics has been recognized during recent years. Not only are they very effective for densification, either singly, or in combination with yttria, but also they can be accommodated in the α-sialon lattice, thus providing an opportunity for decreasing the transient liquid phase content after sintering, and hence reducing the amount of residual grain boundary glass. Therefore, phase relationships in Ln–Si–Al–O–N systems are of particular interest. The determination of a whole system, represents a very large amount of work and most previous studies have been restricted to the sub-systems Ln–Si–O–N,[1] Ln–Al–O–N (Ln = Ce, Pr, Nd and Sm)[2] and some planes involving α- and β-sialon.[3,4] In oxygen-rich compositions, there exist two five-component phases,[5–7] U-phase ($Ln_3Si_{3-x}Al_{3+x}O_{12+x}N_{2-x}$) and W-phase ($Ln_4Si_9Al_5O_{30}N$), which have no corresponding counterparts in the Y–Si–Al–O–N system. In the Ln_2O_3–Si_3N_4–AlN–Al_2O_3 sub-system where Ln = Sm, Nd, four compounds: Ln–melilite, $LnAlO_3$, Ln_2AlO_3N and MP ($LnAl_{12}O_{18}N$) have been identified (Fig. 1). The Ln–melilite phase extends into a five-component system, with Si and N being substituted by Al and O to form a solid solution, M', with a range of homogeneity from $x = 0$ to 1 in the formula $Ln_2Si_{3-x}Al_xO_{3+x}N_{4-x}$.[8,9] Work at Shanghai[2] on Ln–Al–O–N systems has shown that the nitrogen-containing magnetoplumbite phase of formula $LnAl_{12}O_{18}N$ is unstable in the pure oxide system.

The purpose of the present work is to complete the study of phase relationships in the region of the Ln–Si–Al–O–N systems defined by the four end-members Si_3N_4, AlN, Al_2O_3 and Ln_2O_3 (Ln = Nd,Sm). This region includes the phases α-sialon, β-sialon and AlN polytypoids, and covers the range of compositions used for the design and processing of commercial multi-phase sialon ceramics.

2 Experimental Procedure

The present paper is the result of two work programmes carried out separately at Shanghai Institute of Ceramics and the University of

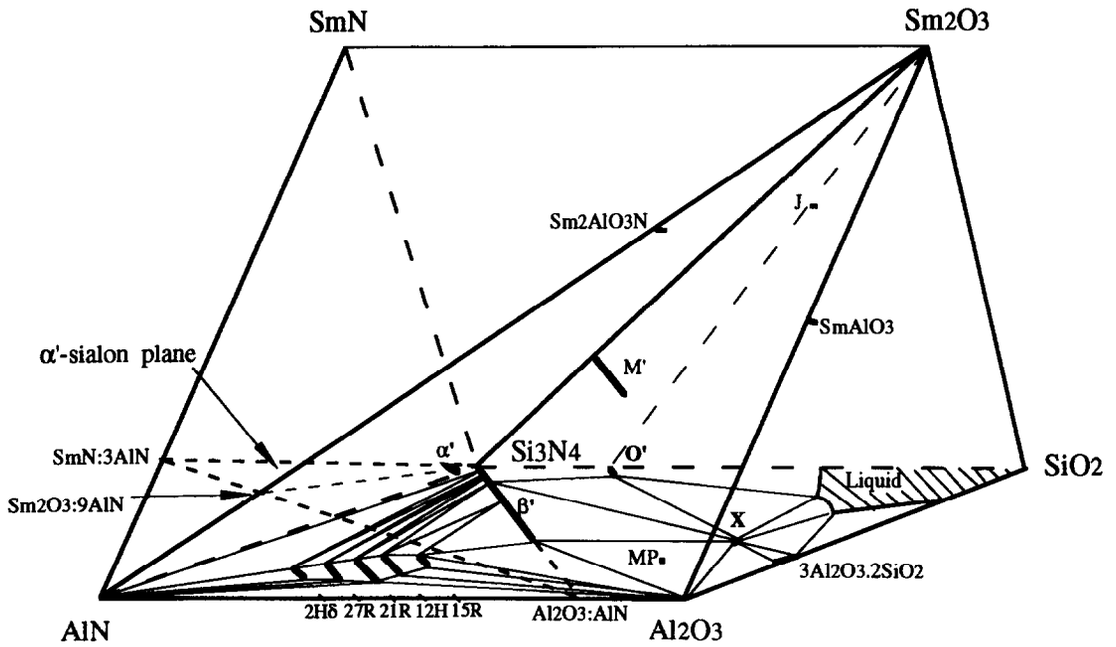

Fig. 1. Representation of Sm(Nd)–SiAlON system showing phases occurring in the region bounded by Si_3N_4, $Sm(Nd)_2O_3$, Al_2O_3 and AlN, and Si–Al–O–N behaviour diagram at 1700°C.

Newcastle. The symbols '#' and '*' are used to represent the experiments carried out at Shanghai and Newcastle, respectively. The starting powders used were α-Si_3N_4 (Starck H1# and Starck LC10*), AlN (supplied by Zhuzhou Institute of Hard Metal Alloys#, containing 1·2% oxygen and Starck Grade B*), Al_2O_3 (99·99%, produced by decomposing ammonium alum# and Alcoa A17*), Nd_2O_3 (99·9%, Yaolung Chemical Works, China# and 99·9%, Aldrick Chemical Co. Ltd*) and Sm_2O_3

Table 1. Compositions studied in the system Si_3N_4–AlN–Al_2O_3–Nd_2O_3

No.	*Compositions (wt%)*				*Firing*	*Phases present*	*Heat*	*Phases present*
	Si_3N_4	*AlN*	*Al_2O_3*	*Nd_2O_3*	*(°C-h)*		*treat.*	
1#	70·75	7·08	8·00	14·17	HP1750-1	β_6s; M'm		
2#	57·19	10·58	18·08	14·16	HP1750-1	β_{15}s; 12Hw	1350-24^	β_{15}s; As; 12Hvw
							1550–5	β_{15}s; 12Hw
3#	55·22	17·25	0·84	26·69	HP1750-1	M'vs; α's; 21Rvw		
4#	53·26	17·99	2·08	26·67	HP1750-1	M'vs; α's; 21Rw; β'vw		
5#	25·95	3·79	23·58	46·68	1500–2	Avs; β'w		
6#	19·75	16·90	27·55	35·65	1550–2	As; 15Rm		
7#	19·61	3·64	6·19	70·56	1700–2	M'vs; Jvw		
8#	14·45	35·30	14·05	35·12	1750–2	M'vs; 21Rm; α'w		
9#	11·77	6·52	—	81·71	1600–2	Jvs; M's		
10#	11·77	—	13·95	74·28	1550–2	As; M's; Hw		
11#	11·77	33·26	—	54·97	1700–2	M'vs; AlNw		
12#	10·57	37·51	43·09	8·74	1750–2	15Rs; MPm; Al_2O_3 vw		
13#	9·77	5·71	14·20	70·31	1550–2	Avs; M's; Hvw		
14#	9·17	41·07	40·95	8·74	1700–2	MPs; 21Rs		
15#	6·10	50·00	—	43·90	1650–2	M's; AlNs; Jm		
16#	4·88	—	13·95	81·17	1600–2	Avs; M's; Jw; Hw		
17#	4·88	6·52	—	88·60	1600–2	Ns; Js; Nd_2O_3s		
18#	80·00	—	4·65	15·35	1700–1	βvs; aw; M'vw	1350–24	βs; Hm; αvw
							1550–5^	βvs; M's; αvw
19*	75·91	1·09	1·85	21·15	1800–1	βvs; M'w	1550·5	M'vs; βs
20*	59·73	16·78	1·52	21·97	1750–1	M's; α'm; 12Hvw	1550–5	M'vs; α'm; 21Rw; βvw
21*	43·75	29·73	6·53	19·99	1750–1	M's; α'm; 21Rw	1550–5	M'vs; α'm
22*	36·96	9·60	23·88	29·56	1600–1	β_{20}s; 15Rm	1350–24	Avs; β_{20}m; 15Rvvw
23*	28·04	17·81	42·61	11·54	1600–1	β_{50}vs; 15Rm; 12Hvw	1150–24	β_{50}vs; Us; 15Rm
							1350–24^	β_{50}s~; As; 15Rm; MPm
24*	26·55	4·91	22·39	46·15	1550–1	M'w 12Hvw	1350–24	Avs; β_{35}W~
25*	14·06	38·89	11·91	35·14	1750–1	M'vs; Am; AlNw; Uvw		

^Used for establishing phase relationships; ~ containing some β' with smaller unit cell dimensions; α = α–Si_3N_4; α'=α-sialon; β = β–Si_3N_4; β', β_6,β_{15}...=β-sialon; A = $LnAlO_3$; N = Ln_2AlO_3N; MP = $LnAl_{12}O_{18}N$; M' = $Ln_2Si_{3-x}Al_xO_{3+x}N_{4-x}$; J = $Ln_4Si_2O_7N_2$; H = $Ln_{10}(SiO_4)_6N_2$; U = $Ln_3Si_3Al_3O_{12}N_2$ (all Ln here represents Nd).

Table 2. Compositions studied in the system Si_3N_4–AlN–Al_2O_3–Sm_2O_3

No.	*Compositions (wt%)*				*Firing*	*Phases present*	*Heat*	*Phases present*
	Si_3N_4	*AlN*	Al_2O_3	Sm_2O_3	*(°C-h)*		*treat.*	
1*	80·00	—	4·52	15·48	1700–1	βvs; M'vw	1350–24	βs; Hm
							1550–5^	βvs; M'w
2*	75·77	1·06	1·81	21·36	1700–1	M'vs; βs; αvw	1550–5	M'vs; βs
3*	70·64	7·07	7·97	14·32	1700–1	β_6s; α'm; M'w	1350–24	β_6s; As; α'w; M'w
							1550–5^	$\beta_6$vs; M's; α'vvw
4*	59·38	16·69	1·49	22·44	1750–1	M's; α'm; β'vw	1550–5	M's; α'm; 21Rvw
5*	57·08	10·56	18·05	14·31	1700–1	β_{13}s; α'w; 12Hvw	1350–24^	β_{13}s; As
							1550–5	β_{13}vs; 12Hw
6*	43·46	29·66	6·49	20·39	1750–1	M's; α'm; 21Rw	1550–5	M's; α'm; 21Rw
7*	36·57	9·50	23·63	30·30	1550–3	β_{20}s; 15Rm	1150–24	Uvs; β_{20}m; 15Rm; $SmSiO_3$?
							1350–24^	Avs; β_{20}m
8*	28·05	17·81	42·51	11·63	1600–1	β_{50}vs; 15Rm	1150–24	β_{50}vs; Us; 15Rm
							1350–24^	Avs; β_{50}S~; MPm; 15Rw
9*	26·56	4·91	22·01	46·53	1600–1	β_{20}s; 15Rm	1150–24	Uvs; β_{20}m; 15Rm; $SmSiO_3$?
							1350–24^	Avs; β_{20}m; Uvw
10*	13·91	38·89	11·91	35·29	1750–1	M'vs; As; AlNw; 27Rvw		
11*	11·82	—	—	88·18	1650–1	Jvs		
12*	9·46	–	2·55	87·99	1650–1	Jvs		
13*	4·73	6·31	—	88·96	1550–1	Avs; Js; Sm_2O_3w		
14*	4·73	—	13·57	81·70	1550–1	Avs; Js; Sm_2O_3w		
15#	10·58	37·44	42·98	9·00	HP1750–1	15Rvs; MPw		
16#	9·17	41·00	40·84	8·99	HP1750–1	12Hvs; MPw; Aw		
17#	3·55	4·21	6·79	85·45	1600–2	Ns; Jm		

All the symbols have the same meaning as in Table 1 except Ln (here Ln represents Sm).

(99·9%, Yaolung Chemical Works, China# and 99·9%, Aldrick Chemical Co. Ltd*). The oxygen contents of the nitride powders were taken into account in calculating the compositions. The starting powders were weighed out and ground in absolute alcohol# or isopropanol* using an agate pestle and mortar. The mixed powders were dried and pressed into pellets 10 mm in diameter and were then isostatically pressed under a pressure of 200 MPa. The specimens prepared at Shanghai were fired in a graphite-resistant furnace with a rather slow cooling rate (~50°C/min) whilst those at Newcastle were fired in graphite-resistant or tungsten element furnaces both of which could be cooled down to room temperature very quickly (~100°C/min). A nitrogen atmosphere was used in all cases. The specimens with the compositions near liquid phase region were prepared in Shanghai and then heat-treated in Newcastle. The heat-treatment was carried out either in a tungsten element furnace (at 1150–1450°C) or in a molybdenum element furnace (at 1550°C). All specimens were examined by X-ray diffractometry# or using a Hägg–Guinier focusing camera*. Only specimens showing less than 3% weight loss after firing were used for data analysis.

3 Results

Twenty five Nd-containing compositions and 17 Sm-containing compositions in the region bounded by Si_3N_4, AlN, Al_2O_3 and Ln_2O_3 were studied to establish compatibility relationships. The binary tie lines established were based on the results listed in Tables 1 and 2. In the region explored, the same phases were observed in both systems, but it was noted that melting temperatures were lower in the samarium system and consequently, at a given temperature, the size of the

Table 3. Subsolidus compatibility tetrahedra in the systems Si_3N_4–AlN–Al_2O_3–Ln_2O_3 (R = Nd and Sm)

Al_2O_3–β_{60}–15R–MP	Al_2O_3–15R–15R'–MP
Al_2O_3–15R'–12H'–MP	Al_2O_3–12H'–21R'–MP
Al_2O_3–21R'–AlN–MP	15R–15R'–12H–12H'–MP
12H–12H'–21R–21R'–MP	21R–21R'–27R–27R'–MP
27R–27R'–$2H^{\delta}$–$2H^{\delta'}$–MP	$2H^{\delta}$–$2H^{\delta'}$–AlN–MP
21R'–27R'–AlN–MP	27R'–$2H^{\delta'}$–AlN–MP
AlN–$2H^{\delta}$–MP–$LnAlO_3$	$2H^{\delta}$–27R–MP–$LnAlO_3$
27R–21R–MP–$LnAlO_3$	21R–12H–MP–$LnAlO_3$
12H–15R–MP–$LnAlO_3$	β_{60}–15R–MP–$LnAlO_3$
β_{60}–Al_2O_3–MP–$LnAlO_3$	β_{60}–β_{25}–15R–$LnAlO_3$
β_{25}–15R–12H–$LnAlO_3$	β_{25}–β_{10}–12H–$LnAlO_3$
β_{10}–12H–$LnAlO_3$–M'	β_{10}–12H–21R–M'
α'–β_0–β_{10}–M'	α'–β_{10}–21R–M'
α'–β_{10}–β_8–21R	α'–β_8–21R–27R
α'–β_8–β_5–27R	α'–β_5–27R–$2H^{\delta}$
α'–β_5–β_2–$2H^{\delta}$	α'–β_2–$2H^{\delta}$–AlN
α'–β_2–β_0–AlN	α'–AlN–$2H^{\delta}$–M'
α'–$2H^{\delta}$–27R–M'	α'–27R–21R–M'
M'–12H–21R–$LnAlO_3$	M'–21R–27R–$LnAlO_3$
M'–27R–$2H^{\delta}$–$LnAlO_3$	M'–$2H^{\delta}$–AlN–$LnAlO_3$
M'–AlN–$LnAlO_3$–J	M'–AlN–J–M
AlN–$LnAlO_3$–J–Ln_2AlO_3N	$LnAlO_3$–J–Ln_2AlO_3N–Ln_2O_3

MP = $LnAl_{12}O_{18}N$; M' = $Ln_2Si_{3-x}Al_xO_{3+x}N_{4-x}$; J = $Ln_4Si_2O_7N_2$; 15R, 12H, 21R, 27R, $2H^{\delta}$ are those on the Si-rich end of AlN polytypoids; 15R', 12H', 21R', 27R', $2H^{\delta'}$ are AlN polytypoids on the Al-rich end.

liquid-forming region is larger. Based on the much more extensive knowledge of phase relationships in the Y–Si–Al–O–N system[10–13] and other information in the literature listed above, 44 compatibility tetrahedra were established in this region for both Nd and Sm (Table 3).

As indicated in this table, tie lines exist between the compound $LnAl_{12}O_{18}N$ and all the AlN polytypoid phases as well as β_{60} (the maximum limit of the β-sialon solid solution). The compound $LnAlO_3$ was found to be compatible with β-sialon in the range $\beta_{10}(z = 0{\cdot}8)$–$\beta_{60}$, and also with the Si-rich terminal compositions of the AlN polytypoid phases. Compatibility tetrahedra are also formed between α-sialon, the Si-rich ends of the AlN polytypoid ranges (from AlN to 21R) and M'-phase. M' was also found to have tie lines with β-sialon from $\beta_0(\beta\text{-}Si_3N_4)$ to β_{10}, forming two $\alpha' + \beta'$ containing compatibility tetrahedra α'–β_0–β_{10}–M' and α'–β_{10}–21R–M'. $LnAlO_3$–AlN polytypoid and α'–β' two-phase regions are represented graphically in Figs 2–4. In the present work, α-sialon is considered as a point composition and its detailed solid solution range has not been determined.

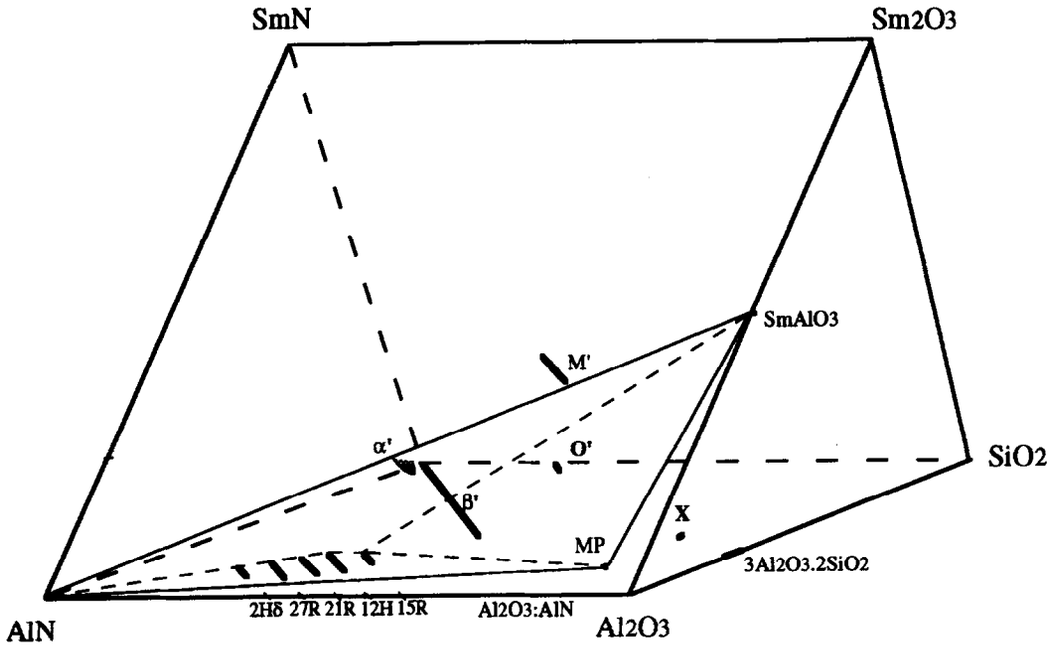

Fig. 2. Sm(Nd)AlO_3 is compatible with all polytypoid phases (Si-rich terminal), AlN and Sm(Nd)$Al_{12}O_{18}N$ (MP-compounds) forming five compatibility tetrahedra: Sm(Nd) AlO_3–15R–MP–12H; Sm(Nd)AlO_3–12H–MP–21R; Sm(Nd)AlO_3–21R–MP–27R; Sm(Nd) AlO_3–27R–MP–2Hδ and Sm(Nd)AlO_3–2Hδ–MP–AlN.

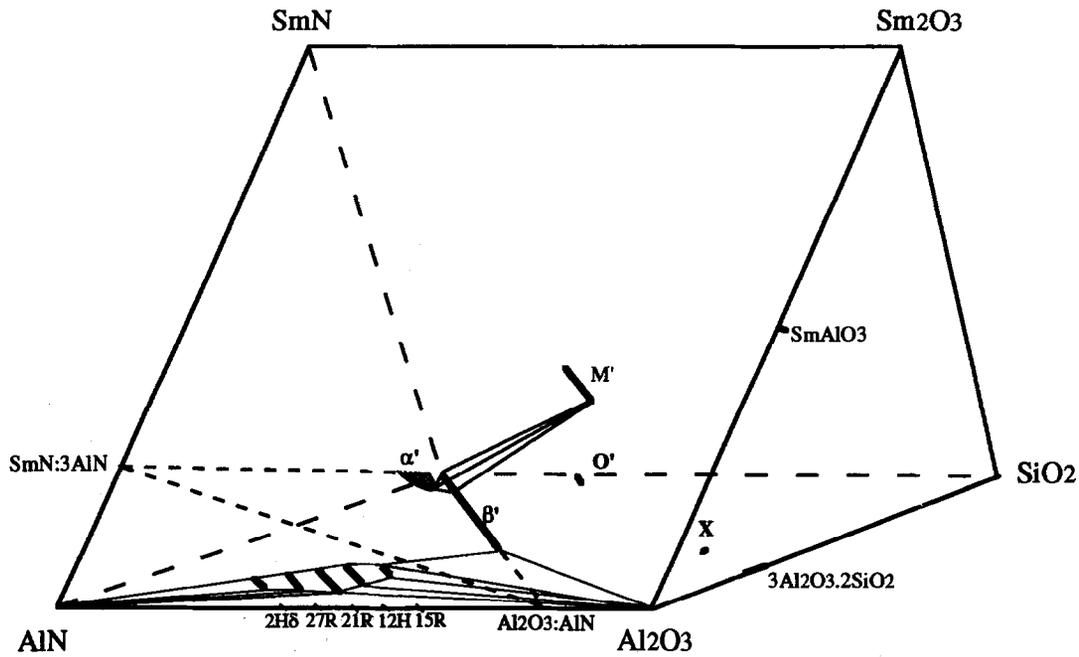

Fig. 3. M'(melilite solid solution) is compatible with β-sialon (β_0–β_{10}) and α-sialon forming α'–β'–M' compatibility tetrahedron.

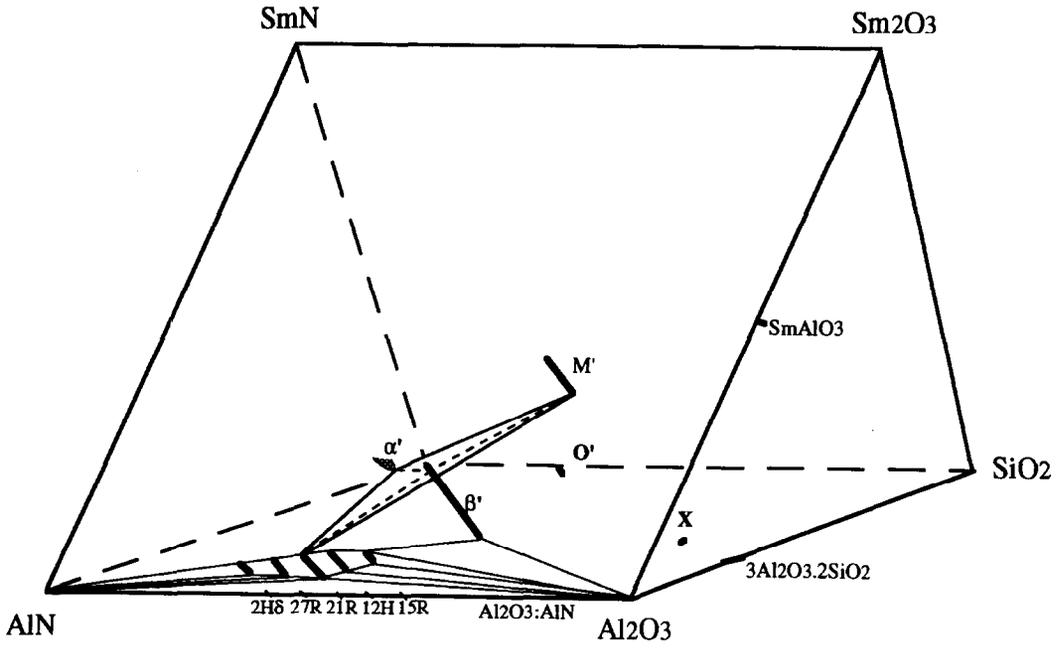

Fig. 4. Compatibility tetrahedron α'–β–21R–M'.

4 Discussion

Previous work in the Nd-system[4] showed that at 1700°C, the liquid phase region in this system intersects the β-sialon–$NdAlO_3$ plane (Fig. 5). Moreover, $NdAlO_3$ does not appear in nitrogen-rich compositions on this plane. These observations are in contrast to the behaviour of YAG ($Y_3Al_5O_{12}$) in the β-sialon–YAG system. The appearance of 12H polytypoid phase on the β-sialon–$NdAlO_3$ plane implies that it must be in equilibrium with a liquid phase of more silica-rich composition than those on the plane. Recently, heat-treatment studies of Ln–Si–Al–O–N (Ln = La–Yb) glasses,[14] have indicated that the resulting crystalline phases vary with the composition of the glass, the atomic number (i.e. ionic radius) of the rare earth element and with the heat-treatment temperature. In the Nd- and Sm-systems, at lower temperatures (1000–1200°C), wollastonite ($LnSiO_2N$) and U-phase are the main crystalline phases formed from glasses in equilibrium with mixed α + β sialons, and with increasing temperature, $LnAlO_3$ appears. U-phase, of composition

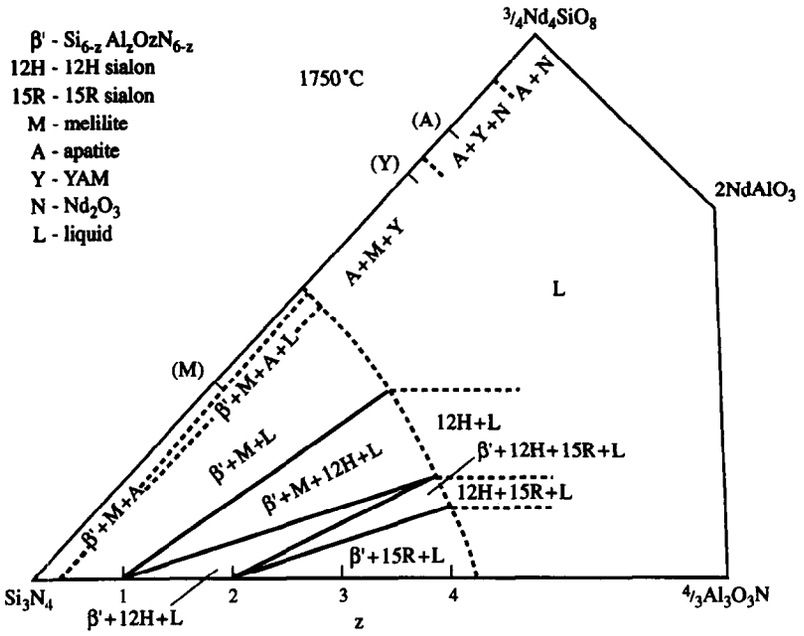

Fig. 5. Phase relationships of β'–$NdAlO_3$ plane at 1750°C.

$Ln_3Si_{3-x}Al_{3+x}O_{12+x}N_{2-x}$, where $O < x < 1$, is a crystallization product of Ln–Si–Al–O–N glasses in equilibrium with β-sialon, heated in the range 950–1400°C. The stability of this phase increases with cation size, and the melting point is around 1390°C.[6]

In the region studied, $LnAlO_3$, M'-phase and U-phase were the main phases observed after heat-treatment in the temperature range 1150–1550°C. Suitable devitrification temperatures for the formation of $LnAlO_3$ are in the range 1250–1450°C. At lower temperatures (1150–1250°C), U-phase occurred instead. In the oxygen-rich compositions explored in the present work, U-phase always occurred after heat-treatment (or even after firing in the Shanghai furnace, which has a slower cooling rate). The occurrence of U-phase in the region studied can not be considered as an equilibrium phase under subsolidus temperature conditions and is only an incompletely recrystallized form of the liquid phase. In Si_3N_4-rich compositions, M'-phase often occurs after sintering, increasing in amount after further heat-treatment at $\approx$1550°C. This is because the composition of M' is nearer to the liquid phase region and therefore M' phase dissolves into the melt during firing. The crystallization temperature for M' is about 1550°C. In establishing subsolidus phase relationships, the judgement on the correct equilibrium phases under subsolidus temperature conditions can sometimes be a difficult problem. Using phase assemblages observed at the same temperature for all conditions studied might lead to mistaken results, since different compositions may need different temperatures to fully crystallize the liquid phase.

In the present work, all starting compositions were designed to fall on supposed tie lines or into supposed compatibility triangles. For examples, in the Sm system, compositions Nos 2, 3 and 5 were on the lines between M' ($Ln_2Si_2AlO_4N_3$) and β-Si_3N_4, β-sialon ($z = 1$) and β-sialon ($z = 2$) respectively; Nos 1, 8 and 9 were on composition lines between $SmAlO_3$ and Si_3N_4, β-sialon ($z = 4$) and β-sialon ($z = 2$), respectively. If the expected phases were obtained after heat-treatment under a particular set of conditions, then equilibrium was believed to have been achieved. Based on this philosophy, compositions marked with the symbol '^' in Tables 1 and 2 were believed to have achieved equilibrium and were used to establish the subsolidus phase relationships. Composition No. 1 (Table 2) only gave M' and apatite ($Sm_{10}(SiO_4)_6N_2$) after heat treatment at 1350 and 1550°C, which indicated that the supposed tie line β-Si_3N_4–$SmAlO_3$ does not exist. In composition No.5(Table 2), the absence of M' phase implies that M' is not compatible with β_{13}. The coexistence of β-sialon with M' was found to be restricted to the range β_0–β_{10}. From the X-ray diffraction data of M' and β-sialon, it seems that Nd- and Sm-melilite ($Ln_2O_3.Si_3N_4$) has priority over β-Si_3N_4 in accommodating Al and O (thereby forming M' phase) and therefore the tie lines between melilite and β-sialon do not run parallel. The oxygen-containing α-sialon phase occurring in the present samples is believed to have a composition close to the oxygen-rich limit of the α-sialon homogeneity range in these systems; this phase is also compatible with M'.

α-sialon, 12H and 15R sometimes occurred in compositions located on the β-sialon–$LnAlO_3$ and β-sialon–M' planes, and decreased in amount or even disappeared after heat-treatment. This is partly because the liquid phase in these compositions shifts in composition with temperature, and also because some $\alpha \rightarrow \beta$ sialon transformation occurs in these samples.[15] J-phase ($Ln_4Si_2O_7N_2$) should occur in compositions along the line joining Ln_2O_3 to Si_2N_2O, but it always appears at the composition $3Ln_2O_3$:Si_3N_4, just as in the Y–Si–Al–O–N system. This could be attributed to the unavoidable existence of a silica layer on the surface of silicon nitride. In the Y–Si–Al–O–N system, J-phase forms a continuous solid solution with YAM ($Y_4Al_2O_9$). In the present work J-phase solid solution (J') was never observed. Composition Nos 11 and 12 (Table 2) were designed to produce J- and J'-phase and the X-ray data did not show visible differences in d-values between these two J-phases.

Of the 44 compatibility tetrahedra established in the present work, the following six which involve α-, β-sialon and AlN-polytypoids (which could be used as reinforcement phase for α', β' or α'-β' because of its fibre-like morphology) and the promising grain boundary phases M' and $LnAlO_3$, are the most useful for the design of multi-phase sialon ceramics. They are: α-sialon–β_0–β_{10}–M'; α-sialon–β_{10}–21R–M'; β_{25}–15R–12H–$LnAlO_3$; β_{25}–β_{10}–12H–$LnAlO_3$; β_{10}–12H–$LnAlO_3$–M' and β_{10}–12H–21R–M'.

5 Conclusions

Subsolidus phase relationships in the systems Ln_2O_3–Si_3N_4–AlN–Al_2O_3 (Ln = Nd, Sm) have been determined. Forty-four compatibility tetrahedra have been established in this region. $LnAlO_3$ coexists with β-sialon, approximately from β_{10} ($z = 0{\cdot}8$) to β_{60}($z = 4$). The liquid phase crosses the tie line between $LnAlO_3$ and β-sialon at firing temperatures (1600–1700°C) and therefore β-sialon–$LnAlO_3$ two-phase materials can only be

obtained after heat-treatment in the range 1250–1450°C. The coexistence of M' with β-sialon is restricted to the range β_0–β_{10}. α-Sialon is also compatible with M'. The compatibility tetrahedra α-sialon–β_0–β_{10}–M'; α-sialon–β_{10}–21R–M'; β_{25}–15R–12H–$LNAlO_3$; β_{25}–β_{10}–12H–$LnAlO_3$; β_{10}–12H–$LnAlO_3$–M' and β_{10}–12H–21R–M' are the most useful for the design and processing of multi-phase sialon ceramic materials.

Acknowledgement

This work was supported by NNSF (National Natural Science Foundation, China) and the ALCS (Academic Link with China Scheme) programme of the British Council, UK.

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