

Formation of α -sialons with dual modifying cations (Li + Y and Ca + Y)

ZHEN-KUN HUANG

Department of Materials Science and Engineering, The University of Michigan, Ann Arbor, MI 48109, USA

YAO-ZHONG JIANG

Department of Materials Science and Engineering, Tsinghua University, Haidian, Beijing 100084, People's Republic of China

TSENG-YING TIEN

Department of Materials Science and Engineering, The University of Michigan, Ann Arbor, MI 48109, USA

α -Sialon (α -Si₃N₄ solid solution) can be derived from α -Si₃N₄ with partial replacement of Si-N by Al-N and Al-O. Charge balance is maintained by introducing a "modifying cation" (lithium, calcium, yttrium or many rare-earth elements). Modifiers can occupy up to two interstitial sites in the (Si, Al)-N network unit cell, resulting in a formula of M_x(Si, Al)₁₂(O, N)₁₆ with *x* less than or equal to 2 depending on the valency of the M ion [1]. α -Sialon possesses high hardness and strength. However, the fabrication of α -Sialon is more difficult than that of β -Sialon because the higher nitrogen content in the α -Sialon compositions makes them difficult to densify completely. If two kinds of metal elements (e.g. yttrium and lithium, or yttrium and calcium) are used together as the "modifying cations", the formation and densification of such dual-cation α -Sialons would be completed more easily than single-cation α -Sialons, because the dual cations lower the eutectic temperature of the system. Some investigations of α -Sialons containing dual modifying cations have been reported [2-5]. Two mixed cations from lithium, calcium and neodymium can be accommodated in α -sialon structure [4]. A small amount of cerium can enter the large interstitial cages in α -Sialon structure with yttrium [2, 3]. A cation as large as strontium (ionic radius 0.113 nm) has entered the α -Sialon structure when mixed with yttrium and calcium [5].

In our previous work, phase relationships in the systems Si₃N₄-AlN-M_xO_y (M = lithium, magnesium, calcium, yttrium, neodymium, samarium, gadolinium, dysprosium, erbium or ytterbium) have been reported [6-10]. The α -sialon solubility area occurs along the composition lines Si₃N₄-M₉O:3AlN (M₉ = 2Li, 1Ca or 2/3Y (R)). Combining two composition lines, Si₃N₄-Y_{2/3}O:3AlN and Si₃N₄-Li₂O:3AlN or Si₃N₄-Y_{2/3}O:3AlN and Si₃N₄-CaO:3AlN, gives two quasi-ternary systems Si₃N₄-Li₂O:3AlN-Y_{2/3}O:3AlN and Si₃N₄-CaO:3AlN-Y_{2/3}O:3AlN (Figs 1 and 2), in which a single α -Sialon crystal with dual modifying cations should occur.

The present work studied the formation of α -Sialons with dual modifying cations in the Si₃N₄-Li₂O:3AlN-Y_{2/3}O:3AlN and Si₃N₄-CaO:3AlN-Y_{2/3}O:3AlN systems.

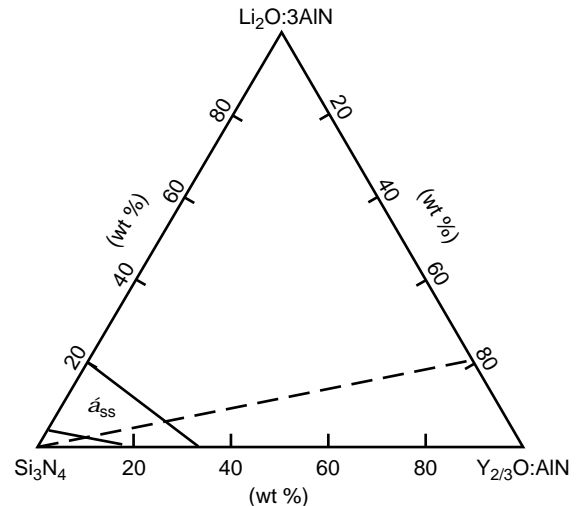


Figure 1 Tentative α (Li,Y)-Sialon region in the Si₃N₄-Li₂O:3AlN-Y_{2/3}O:3AlN system.

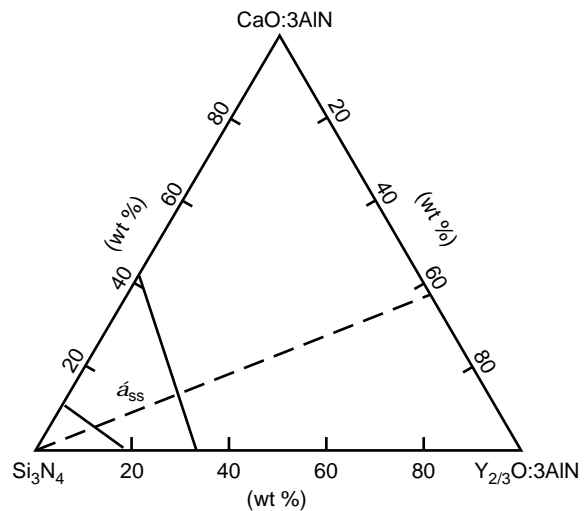


Figure 2 Tentative α (Ca,Y)-Sialon region in Si₃N₄-CaO:3AlN-Y_{2/3}O:3AlN system.

Si₃N₄ (UBE-10, Japan), AlN (MAN-05, Japan), Y₂O₃ (99.99%, Aldrich, USA), Li₂CO₃ (99.6%, Baker, USA) and CaCO₃ (. 99%, Baker, USA) were used as starting materials. Two series of compositions were chosen along the dashed lines in Figs 1 and 2 and are listed in Tables I-IV. They contain the same atomic amounts of lithium and yttrium in (Li, Y)_x(Si, Al)₁₂(O, N)₁₆ and calcium and yttrium in (Ca, Y)_x(Si, Al)₁₂(O, N)₁₆, respectively. Some

TABLE I Nominal compositions, hot-pressing conditions and densities for $\mathcal{A}(\text{Li},\text{Y})$ -Sialons

No.	Nominal compositions		Hot-pressing in N ₂ (8C/h)	Density (Mg m ⁻³)
	Formula	(Li,Y)O:3AlN (wt %)		
L1	Li _{0.15} Y _{0.15} Si _{11.1} Al _{0.9} O _{0.3} N _{15.7}	9.75	1750/1	3.257
L2	Li _{0.3} Y _{0.3} Si _{10.2} Al _{1.8} O _{0.6} N _{15.4}	19.04	1750/1	3.264
L3	Li _{0.4} Y _{0.4} Si _{9.6} Al _{2.4} O _{0.8} N _{15.2}	22.39	1750/1	3.288
L4	Li _{0.5} Y _{0.5} Si _{9.0} Al _{3.0} O _{1.0} N _{15.0}	30.76	1750/1	3.313
L5	Li _{0.6} Y _{0.6} Si _{8.4} Al _{3.6} O _{1.2} N _{14.8}	36.35	1700/1	3.332
L6	Li _{0.7} Y _{0.7} Si _{7.8} Al _{4.2} O _{1.4} N _{14.6}	41.78	1700/1	3.369
L7	Li _{1.5} Y _{0.5} Si _{7.5} Al _{4.5} O _{1.5} N _{14.5}	42.89	1700/1	3.221
L8	Li _{1.3} Y _{0.7} Si _{6.9} Al _{5.1} O _{1.7} N _{14.3}	48.80	1700/1	3.301

TABLE II Phase assemblages by XRD and cation ratios in $\mathcal{A}(\text{Li},\text{Y})$ -Sialons by EDS

No.	Composition			Phase assemblages by X-ray ^a	Cation ratio in \mathcal{A} by EDS				Actual wt % of (Li,Y)O:3AlN
	M	Li	Y		Li ^b	Y	Si	Al	
L1	0.3	0.15	0.15	$\mathcal{A}(\text{vs})$, $\mathcal{A}(\text{s})$					
L2	0.6	0.3	0.3	$\mathcal{A}(\text{vs})$	0.27	0.17	10.83	1.17	9.5
L3	0.8	0.4	0.4	$\mathcal{A}(\text{vs})$	0.39	0.31	10.04	1.96	20.6
L4	1.0	0.5	0.5	$\mathcal{A}(\text{vs})$	0.22	0.45	9.65	2.35	25.0
L5	1.2	0.6	0.6	$\mathcal{A}(\text{vs})$, AlN(tr.), J(tr.)	0.30	0.49	9.32	2.68	27.9
L6	1.4	0.7	0.7	$\mathcal{A}(\text{vs})$, M(m)					
L7	2.0	1.5	0.5	$\mathcal{A}(\text{vs})$, J(w), AlN(vw)					
L8	2.0	1.3	0.7	$\mathcal{A}(\text{vs})$, J(m)					

^aX-ray intensity, vs. s. m. w. vw. tr.; M, mililite; J, 2Y₂O₃ · Si₂N₂O.

^bBy calculation.

TABLE III Nominal compositions, hot-pressing conditions and densities for $\mathcal{A}(\text{Ca},\text{Y})$ -Sialons

No.	Nominal compositions		Hot-pressing in N ₂ (8C/h)	Density (Mg m ⁻³)
	Formula	(Ca,Y)O:3AlN (wt %)		
C1	Ca _{0.15} Y _{0.15} Si _{10.875} Al _{1.125} O _{0.375} N _{15.625}	12.32	1750/1	3.212
C2	Ca _{0.3} Y _{0.3} Si _{9.75} Al _{2.25} O _{0.75} N _{15.25}	23.87	1750/1	3.275
C3	Ca _{0.4} Y _{0.4} Si _{9.0} Al _{3.0} O _{1.0} N _{15.0}	31.17	1750/1	3.322
C4	Ca _{0.5} Y _{0.5} Si _{8.25} Al _{3.75} O _{1.25} N _{14.75}	38.18	1750/1	3.349
C5	Ca _{0.6} Y _{0.6} Si _{7.5} Al _{4.5} O _{1.5} N _{14.5}	44.91	1700/1	3.352
C6	Ca _{0.7} Y _{0.7} Si _{6.25} Al _{5.25} O _{1.75} N _{14.25}	51.38	1650/1	3.383
C7	Ca _{1.4} Y _{0.6} Si _{5.1} Al _{6.9} O _{2.3} N _{13.7}	64.25	1650/1	3.304

TABLE IV Phase assemblages by XRD and cation ratios in $\mathcal{A}(\text{Ca},\text{Y})$ -Sialons by EDS

No.	Compositions			Phase assemblages by X-ray ^a	Cation ratios in \mathcal{A} by EDX				Actual wt % of (Ca,Y)O:3AlN
	M	Ca	Y		Ca	Y	Si	Al	
C1	0.3	0.15	0.15	$\mathcal{A}(\text{vs})$, $\mathcal{A}(\text{w})$	0.12	0.2	10.75	1.25	14.3
C2	0.6	0.3	0.3	$\mathcal{A}(\text{vs})$	0.2	0.31	10.0	2.0	21.5
C3	0.8	0.4	0.4	$\mathcal{A}(\text{vs})$	0.25	0.38	9.5	2.5	26.4
C4	1.0	0.5	0.5	$\mathcal{A}(\text{vs})$, M(vw)	0.3	0.4	9.3	2.7	28.4
C5	1.2	0.6	0.6	$\mathcal{A}(\text{vs})$, M(w), AlN(w)	0.34	0.45	8.95	3.05	31.7
C6	1.4	0.7	0.7	$\mathcal{A}(\text{vs})$, M(m), AlN(m)					
C7	2.0	1.4	0.6	$\mathcal{A}(\text{s})$, AlN(s), M(vw)					

^aX-ray intensity, vs. s. m. w. vw; M, melilite.

compositions with higher lithium or calcium amounts located away from the dashed line were also chosen for comparison. The compositions were made by mixing the required amounts of the starting powders in an agate mortar under isopropyl alcohol for 1.5 h. Normally the formation of \mathcal{A} -Sialon can be completed around 1700 8C by hot-pressing. Therefore, dried mixtures were hot-pressed under a pressure of 25 MPa at 1650–1750 8C for 1 h in BN-coated graphite dies (diameter 20 mm \pm 5 mm)

in a graphite resistance furnace under a mild flow of nitrogen. The preparation of samples is the same as that reported in previous works [6–10]. After hot-pressing, the samples were polished. The densities of polished samples were measured by the Archimedeian method using water. The microhardness were measured by Vickers indentation under a load of 10 kg.

X-ray diffraction (XRD) was used for phase identification and the determination of lattice para-

meters. Energy dispersive spectroscopy (EDS) was used to analyse the cation atomic ratios in \mathcal{A} -Sialons. Lithium could not be detected by EDS because it is a light element. However, the amount of lithium can be calculated if the concentrations of the other cations are known. In $\mathcal{A}(\text{Li}, \text{Y})_x(\text{Si}, \text{Al})_{12}(\text{O}, \text{N})_{16}$, aluminium was added as both $\text{Li}_2\text{O}:3\text{AlN}$ and $\text{Y}_{2/3}\text{O}:3\text{AlN}$ with $\text{Li}:\text{Al} = 1:1.5$ and $\text{Y}:\text{Al} = 1:4.5$, respectively. For example, if Al_{total} is the total amount of aluminium detected, and Y_{total} is the amount of yttrium detected, then the amount of lithium, called Li_{total} , can be calculated by the equation $\text{Li}_{\text{total}} = 1/1.5[\text{Al}_{\text{total}} - 4.5 \text{Y}_{\text{total}}]$. Therefore, the atomic amount of lithium can be obtained from the cation ratios of $\text{Si}:\text{Al}:\text{Y}$ in \mathcal{A} -Sialon and then the formula of \mathcal{A} -Sialons with dual modifying atoms can be written.

Previous works [6–10] reported that the lower solubility limits (x) in all $\mathcal{A}\text{M}_x(\text{Si}, \text{Al})_{12}(\text{O}, \text{N})_{16}$ were near $x = 0.3$ cation per cell and the upper limits were 1.5(Li), 1.4(Ca) and 0.67(Y), respectively. By joining two lower limits and two upper limits of lithium and yttrium or calcium and yttrium, two tentative solubility areas of $\mathcal{A}(\text{Li}, \text{Y})$ - and $\mathcal{A}(\text{Ca}, \text{Y})$ -Sialon can be presented as in Figs 1 and 2, respectively.

Table I lists the nominal compositions, hot-pressing conditions and densities of $\mathcal{A}(\text{Li}, \text{Y})$ -Sialons. High density could be obtained by hot-pressing at 1700–1750 °C. The densities increase with increasing (Li,Y)O:3AlN content, except for two compositions (L7 and L8) which contain higher amounts of light element lithium. The phase assemblages analysed by X-ray diffraction (XRD) showed that only three compositions (L2, L3 and L4) formed single $\mathcal{A}(\text{Li}, \text{Y})$ -Sialon crystal phase (Table II). Other compositions with higher (Li,Y)O:3AlN formed \mathcal{A} as majority phase and AlN, melilite or J-phase as minority phases. The formation of the oxygen-rich J-phase should be caused by oxygen impurities in the starting Si_3N_4 and AlN powders. The lattice parameters of $\mathcal{A}(\text{Li}, \text{Y})$ -Sialons (Fig. 3) give the solubility limit of $\mathcal{A}(\text{Li}, \text{Y})$ with 15–30 wt% nominal (Li,Y)O:3AlN content. These lattice parameters are correspondingly higher than that of the single-cation $\mathcal{A}(\text{Y})$ with the same atomic amount of

yttrium [6], indicating lithium really entered into the $\mathcal{A}(\text{Li}, \text{Y})$ structure. The results of EDS analysis (Table II) show that the actual contents of (Li,Y)O:3AlN which entered the \mathcal{A} structure were lower than nominal ones. The atomic amounts of lithium and yttrium were not the same, indicating the actual compositions of $\mathcal{A}(\text{Li}, \text{Y})$ shifted from the dashed line. It is thought that lithium and yttrium can be accommodated in the \mathcal{A} structure in any mixed manner. From the experimental results, the actual solubility limit of $\mathcal{A}(\text{Li}, \text{Y})$ is 10–25 wt% (Li,Y)O:3AlN. This implies that the excessive lithium and yttrium should remain in the grain-boundary liquid. It seems the actual solubility limit of $\mathcal{A}(\text{Li}, \text{Y})$ -Sialon in the Si_3N_4 - $\text{Li}_2\text{O}:3\text{AlN}$ - $\text{Y}_{2/3}\text{O}:3\text{AlN}$ system is approximate to that predicted (Fig. 1).

For $\mathcal{A}(\text{Ca}, \text{Y})$ -Sialon, high density can be obtained by hot-pressing at 1650–1750 °C (Table III). The densities increase with increasing (Ca,Y)O:3AlN content except for C7 composition which contains the highest calcium in the composition series chosen. The phase assemblages analysed by XRD show two samples (C2 and C3) formed single $\mathcal{A}(\text{Ca}, \text{Y})$ crystal phase (Table IV). Other compositions with more calcium and yttrium formed $\mathcal{A}(\text{Ca}, \text{Y})$ as the majority phase and melilite and AlN as minority phases. The tendency to change the phase assemblages with the content of (Ca,Y)O:3AlN, $\mathcal{A} + \hat{a}$ (or \hat{a}) to \mathcal{A} to $\mathcal{A} + \text{M} + \text{AlN}$, is the same as that of single-cation $\mathcal{A}(\text{Y})$ -containing compositions occurring along the Si_3N_4 - $\text{Y}_{2/3}\text{O}:3\text{AlN}$ line [6]. The lattice parameters of $\mathcal{A}(\text{Ca}, \text{Y})$ increase with increasing (Ca,Y)O:3AlN, giving a solubility limit of $\mathcal{A}(\text{Ca}, \text{Y})$ with 15–48 wt% nominal (Ca,Y)O:3AlN (Fig. 4). These lattice parameters are correspondingly bigger than that of single-cation $\mathcal{A}(\text{Y})$ with the same atomic amount of yttrium [6], indicating calcium truly entered the $\mathcal{A}(\text{Ca}, \text{Y})$ structure. EDS analysis (Table IV) shows that the actual (Ca,Y)O:3AlN contents which entered the \mathcal{A} structure were also lower than nominal ones, corresponding to 15–32 wt% (see Fig. 5). This actual solubility limit of $\mathcal{A}(\text{Ca}, \text{Y})$ -Sialon in the Si_3N_4 - $\text{CaO}:3\text{AlN}$ - $\text{Y}_{2/3}\text{O}:3\text{AlN}$ system approximates to that predicted (Fig. 2). Furthermore the atomic

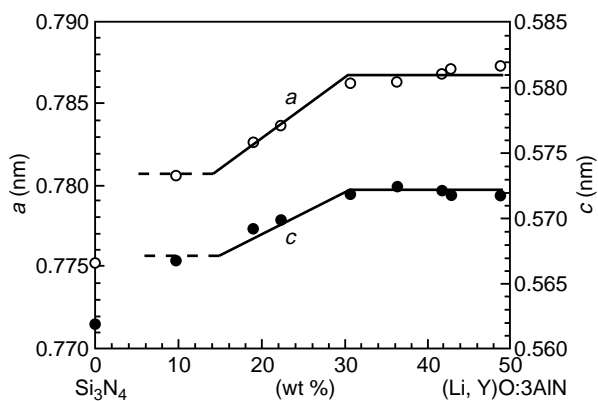


Figure 3 Lattice parameters of $\mathcal{A}(\text{Li}, \text{Y})$ -Sialons as a function of starting (Li,Y)O:3AlN in the samples.

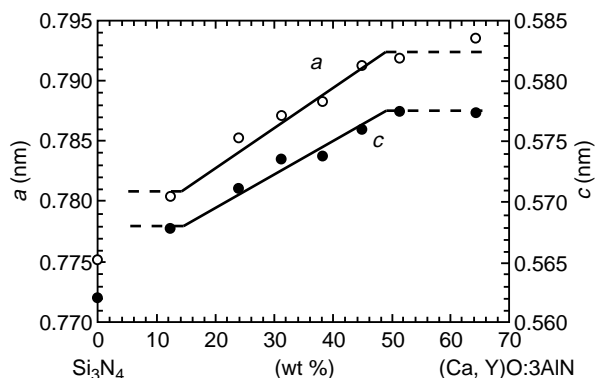


Figure 4 Lattice parameters of $\mathcal{A}(\text{Ca}, \text{Y})$ -Sialons as a function of starting (Ca,Y)O:3AlN in the samples.

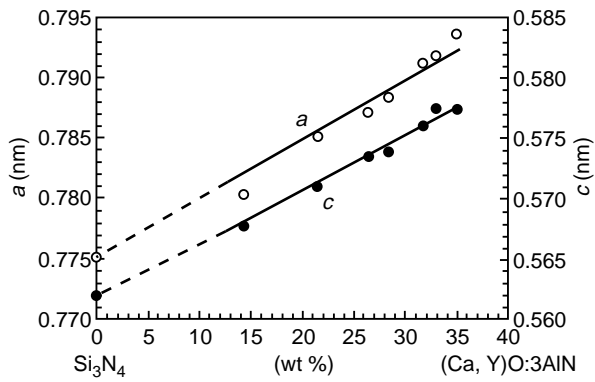


Figure 5 Lattice parameters of $\mathcal{A}(\text{Ca}, \text{Y})$ -Sialons as a function of the actual content of $(\text{Ca}, \text{Y})\text{O}:3\text{AlN}$.

amount of calcium in $\mathcal{A}(\text{Ca}, \text{Y})$ is about 0.1 lower than yttrium showing that there is more excessive calcium than yttrium remaining in the grain-boundary liquid except for forming other minority phases (e.g. mililite).

Fig. 6 shows scanning electron micrographs of samples L3 and C3. It is interesting that $\mathcal{A}(\text{Li}, \text{Y})$ -Sialon could form elongated, rod-shaped grains, whereas $\mathcal{A}(\text{Ca}, \text{Y})$ -Sialon is finer equiaxed. Table V lists the actual compositions and the lattice parameters of some typical dual-cation \mathcal{A} -Sialons obtained in the present work.

Both $\mathcal{A}(\text{Li}, \text{Y})$ - and $\mathcal{A}(\text{Ca}, \text{Y})$ -Sialons have very high hardness. The microhardness decreased with increas-

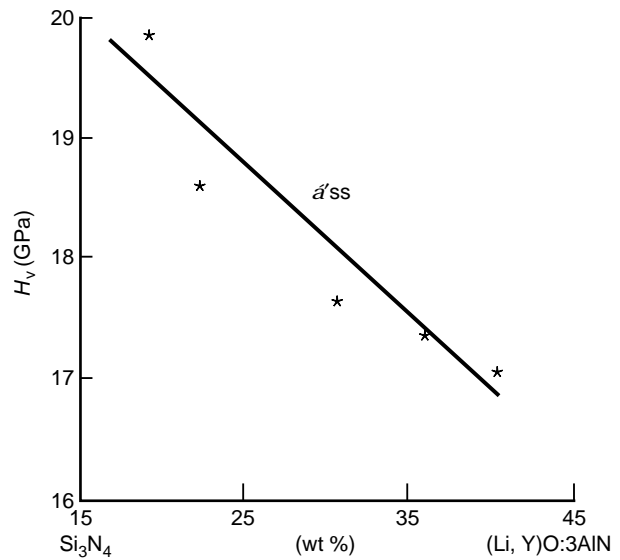


Figure 7 Microhardness as a function of nominal $(\text{Li}, \text{Y})\text{O}:3\text{AlN}$ in $\mathcal{A}(\text{Li}, \text{Y})$ -Sialon samples.

ing amount of $(\text{Li}, \text{Y})\text{O}:3\text{AlN}$ or $(\text{Ca}, \text{Y})\text{O}:3\text{AlN}$ as shown in Figs 7 and 8. The hardnesses of $\mathcal{A}(\text{Li}, \text{Y})$ -Sialons were a little higher than those of the corresponding $\mathcal{A}(\text{Ca}, \text{Y})$ -Sialons.

In summary, the formation of $\mathcal{A}(\text{Li}, \text{Y})$ - and $\mathcal{A}(\text{Ca}, \text{Y})$ -Sialons with dual modifying cations was studied. The solubility limit areas of $\mathcal{A}(\text{Li}, \text{Y})$ in Si_3N_4 - $\text{Li}_2\text{O}:3\text{AlN}$ - $\text{Y}_{2/3}\text{O}:3\text{AlN}$ system and $\mathcal{A}(\text{Ca}, \text{Y})$ in Si_3N_4 - $\text{CaO}:3\text{AlN}$ - $\text{Y}_{2/3}\text{O}:3\text{AlN}$ system

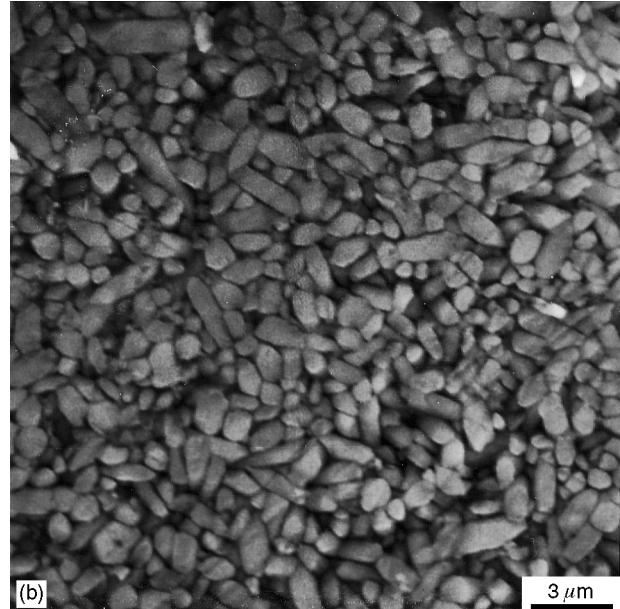
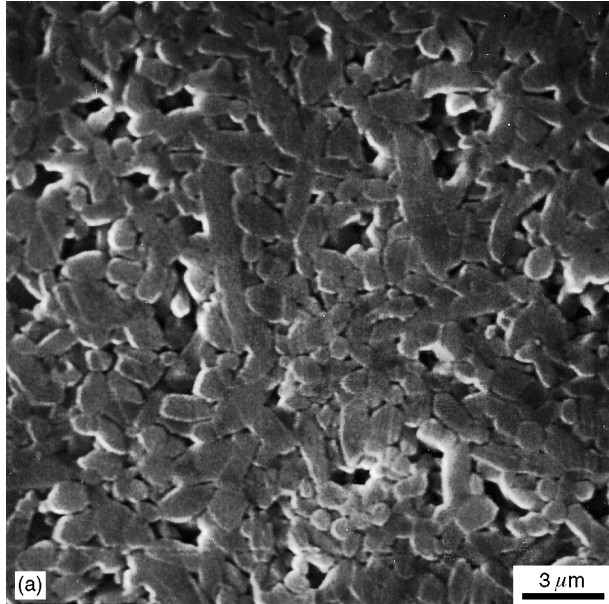


Figure 6 SEM photos of samples (a) L3 and (b) C3 hot-pressed.

TABLE V Lattice parameters of some \mathcal{A} -Sialons compositions

	a (nm)	c (nm)	c/a
$\text{Li}_{0.4}\text{Y}_{0.3}\text{Si}_{10.0}\text{Al}_{2.0}\text{O}_{0.7}\text{N}_{15.3}$	0.7837	0.5699	0.727
$\text{Li}_{0.22}\text{Y}_{0.45}\text{Si}_{9.64}\text{Al}_{2.36}\text{O}_{0.79}\text{N}_{15.21}$	0.7863	0.5719	0.727
$\text{Ca}_{0.20}\text{Y}_{0.31}\text{Si}_{10.0}\text{Al}_{2.0}\text{O}_{0.67}\text{N}_{15.33}$	0.7853	0.5711	0.727
$\text{Ca}_{0.25}\text{Y}_{0.38}\text{Si}_{9.5}\text{Al}_{2.5}\text{O}_{0.86}\text{N}_{15.14}$	0.7872	0.5735	0.728
$\text{Ca}_{0.3}\text{Y}_{0.4}\text{Si}_{9.3}\text{Al}_{2.7}\text{O}_{0.9}\text{N}_{15.1}$	0.7884	0.5738	0.728
$\text{Ca}_{0.34}\text{Y}_{0.45}\text{Si}_{8.95}\text{Al}_{3.05}\text{O}_{1.02}\text{N}_{14.98}$	0.7914	0.5761	0.728

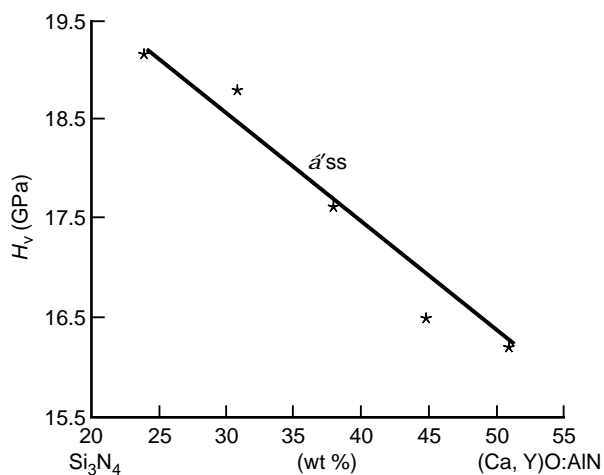


Figure 8 Microhardness as a function of nominal (Ca,Y)O:3AlN in \mathcal{A} (Ca,Y)-Sialon samples.

were determined to have 10–25 wt% (Li,Y)O:3AlN for \mathcal{A} (Li,Y)-Sialon and 15–32 wt% (Ca,Y)O:3AlN for \mathcal{A} (Ca,Y)-Sialon. High densities and high microhardnesses mean that all \mathcal{A} (Li,Y)- and \mathcal{A} (Ca,Y)-containing compositions investigated have good densification after hot-pressing.

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