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Phase relationships in the system Si_3N_4–SiO_2–La_2O_3

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Phase relationships in the system Si_3N_4–SiO_2–La_2O_3 have been investigated after cooling from 1700° C. Two phases, $2Si_3N_4 \cdot La_2O_3$ (monoclinic) and $La_5(SiO_4)_3N$ (hexagonal), were identified; the other two phases in the system, $LaSiO_2N$ (monoclinic) and $La_4Si_2O_7N_2$ (monoclinic), were found to dissociate to $La_5(SiO_4)_3N$ and a glass after cooling from temperatures above 1650° C. The unit cells of $2Si_3N_4 \cdot La_2O_3$, $LaSiO_2N$ and $La_4Si_2O_7N_2$ have been determined and compared with those of preceding works. The results are discussed in relation to the intergranular phases observed when Si_3N_4 is sintered with La_2O_3 additions.

1. Introduction

Sintered silicon nitride is a candidate for engineering ceramics at high temperatures. The bonding between Si and N is basically covalent, so that the self-diffusion coefficient of Si and N [1] is too low to obtain fully dense materials without sintering aids. The densification of silicon nitride has been carried out with the addition of oxides. After reaction, the oxide is retained in intergranular phases, which cause strength degradation of the material at high temperatures. To improve the high-temperature strength, oxides with high melting temperatures, i.e., Y_2O_3 or Ln_2O_3 (lanthanide oxides), have been used as sintering aids.

Extensive investigations have been carried out in the system Si_3N_4–SiO_2–Y_2O_3 to clarify the relationships between sintering kinetics and the properties of sintered silicon nitride [2–5]. On the other hand, there are some uncertainties in the compositions and the structures of phases which appeared in the Si_3N_4–SiO_2–La_2O_3 system. The reason for this might be due to the fact that preceding investigators have been concerned only with the fitting of observed and calculated *d*-spacings of X-ray diffraction spectra [6–11].

In the present work, the space groups of lanthanum silicon oxynitrides were determined from electron diffraction patterns (for powders) and by X-ray methods (for single crystals). The X-ray powder diffraction patterns were indexed using the known crystal structures and from this information precise unit-cell dimensions were computed.

2. Experimental procedure

The starting materials used were Si_3N_4* (Si, 58.6 wt%; N, 37.9 wt%; Fe, 0.25 wt%; Al, 0.18 wt%; and O, 1.2 wt%), SiO_2† (99.9% pure) and La_2O_3‡ (99.99% pure). About 1.5 g of powder mixture was heated in a 10 mm diameter carbon die using a hot-pressing apparatus. In some compositions and at temperatures above 1600° C, liquid phases were squeezed out of the die by the applied pressure resulting in a change in the overall composition. The powder compact was therefore heated at a pressure of 20 MPa up to 1400° C and the temperature was then raised to 1700° C without pressure. The specimen was kept at 1700° C for 1 h and then allowed to cool.

The product was crushed for examination in a 1 MV electron microscope. The space group and unit-cell dimensions were determined from electron diffraction patterns. In the case of $La_4Si_2O_7N_2$, it

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was possible to grow single crystals by the floating-zone method [12] using a nitrogen over-pressure. The structure of this compound was determined from intensity measurements work on Weisenberg photographs.

Phase identification was carried out on powdered material using X-ray diffractometer. The diffraction spectra were indexed on the basis of the known crystal structures and the extinction rules. Precise unit-cell dimensions were calculated using X-ray powder data. The compositions of some phases were determined by electron-probe micro-analysis (EPMA) using either single-crystals or large-grained single-phase polycrystalline material.

Some of the phases which occurred as intergranular phases in Si_3N_4 sintered with La_2O_3 additions were prepared by heating the appropriate powder mixture under a pressure of 15 MPa at 1500 to 1700° C to determine the thermal expansion coefficient and melting temperature. The thermal expansion coefficient was measured using a dilatometer calibrated against fused silica in the range 20 to 1000° C.

3. Results and discussion

3.1. Phase relationships at 1700° C

Two compounds, $2Si_3N_4 \cdot La_2O_3$ and $La_5(SiO_4)_3N$ were observed in specimens prepared at 1700° C.

Wills *et al.* [6] showed that two compounds occurred on the Si_3N_4–La_2O_3 phase boundary in the Si_3N_4–SiO_2–La_2O_3 system. $2Si_3N_4 \cdot La_2O_3$ was reported to have an orthorhombic structure with $a = 1.6460$ nm, $b = 1.4524$ nm, and $c = 0.9624$ nm. $Si_3N_4 \cdot La_2O_3$ was reported to have a tetragonal structure with $a = 1.9487$ nm and $c = 1.3489$ nm. Marchand *et al.* [7] reported a compound of composition $Si_3N_4 \cdot La_2O_3$ with a tetragonal structure and unit-cell dimensions of $a = 0.789$ nm and $c = 0.511$ nm. Although they gave no X-ray diffraction spectra, they suggested that the structure was analogous to that of akermanite ($Ca_2MgSi_2O_7$, tetragonal with $a = 0.7846$ nm and $c = 0.5020$ nm).

The present work gave only one compound, $2Si_3N_4 \cdot La_2O_3$, along the Si_3N_4–La_2O_3 phase boundary. The space group of this compound was determined from electron diffraction patterns as $C2/c$ (monoclinic). X-ray diffraction data are shown in Table I. The X-ray spectra are quite similar to those of Wills *et al.* [6]. The unit-cell dimensions are $a = 1.8376$ nm, $b = 0.4873$ nm, $c = 1.5813$ nm and $\beta = 117.02°$. The structure is related to that of the $2Si_3N_4 \cdot La_2O_3$ described by Wills *et al.*: $a = a_0/\sin\beta$, $b = c_0/2$, $c = b_0$, when a_0, b_0 and c_0 are the dimensions of the unit cell of $2Si_3N_4 \cdot La_2O_3$ described in their work.

TABLE I X-ray diffraction spectra, *hkl* values, observed and calculated *d*-spacings and normalized line intensities, I/I_0, and unit-cell dimensions of $2Si_3N_4 \cdot La_2O_3$.

hkl	d_{obs}(nm)	d_{calc}(nm)	I/I_0
200	0.8177	0.8185	15
$\bar{2}02$	0.7196	0.7194	13
110	0.4671	0.4671	50
$\bar{4}02$	0.4549	0.4548	7
202	0.4435	0.4435	39
$\bar{1}12$	0.4148	0.4148	7
$\bar{2}04$	0.3952	0.3952	31
112	0.3678	0.3679	19
$\bar{4}04$	0.3596	0.3597	10
$\bar{6}02$	0.3054	0.3054	72
$\bar{3}14$	0.3028	0.3028	88
$\bar{1}14$	0.3006	0.3005	55
$\bar{5}12$	0.2935	0.2934	100
312	0.2894	0.2893	99
510	0.2717	0.2718	17
$\bar{5}14$	0.2700	0.2699	10
114	0.2650	0.2652	25
$\bar{3}15$		0.2648	
$\bar{4}06$	0.2612	0.2612	10
$\bar{2}06$	0.2590	0.2590	10
020	0.2436	0.2437	47
$\bar{6}06$	0.2395	0.2398	5
006	0.2346	0.2348	31
$\bar{7}12$	0.2295	0.2294	9
$\bar{7}14$	0.2260	0.2263	8
$\bar{8}02$		0.2259	
221		0.2257	
404	0.2216	0.2218	11
314	0.2216	0.2216	11
$\bar{1}16$	0.2216	0.2216	11
222	0.2135	0.2136	17
710	0.2109	0.2108	7
$\bar{2}24$	0.2075	0.2074	25
800	0.2045	0.2046	10
$\bar{7}16$	0.2037	0.2037	10
206	0.2026	0.2026	7
$\bar{4}24$	0.2017	0.2017	7
116	0.1996	0.1996	11
$\bar{6}08$	0.1933	0.1933	10
$\bar{4}25$	0.1904	0.1906	24
$\bar{6}22$		0.1905	
422	0.1890	0.1890	9
514	0.1841	0.1842	11
224		0.1840	
712	0.1824	0.1825	13
$\bar{5}18$		0.1825	

Monoclinic: $a = 1.8376$ nm, $b = 0.4873$ nm, $c = 1.5813$ nm and $\beta = 117.02°$.

Mah *et al.* [13] reported a compound of composition $2Si_3N_4 \cdot Ce_2O_3$ with a monoclinic structure and unit-cell dimensions: $a = 1.6288$ nm, $b = 0.4848$ nm, $c = 0.7853$ nm and $\beta = 91.544°$, which differs from the present results only in that the c repeat distance is halved. There are only three reflections with l odd, which are overlaps, out of a total 38 observed d-spacings in Table I. The indexing was carried out using the known crystal structure and the extinction rule, so that the reason for this might be attributed to the weakness of reflections with l odd.

It has been shown that $Si_3N_4 \cdot Ln_2O_3$ phases, where Ln is a lanthanide, occur with the akermanite structure if Ln is Y or a lanthanide metal of smaller ionic radius than Pr [14]. It is possible that there are no $Si_3N_4 \cdot Ln_2O_3$ phases in the system Si_3N_4–SiO_2–Ce_2O_3 [13] or Si_3N_4–SiO_2–La_2O_3 because of the large radius of the Ce^{3+} and La^{3+} ions. Lattice-imaging studies using a 1 MV electron microscope [15] revealed that the $2Si_3N_4 \cdot La_2O_3$ structure could be formed by a distortion of the akermanite structure accompanied by a change in composition. There is no mineral structure analogous to $2Si_3N_4 \cdot La_2O_3$. The composition of $2Si_3N_4 \cdot La_2O_3$ determined by means of EMPA was $Si_{5.7}La_{2.0}O_{2.9}N_{7.4}$ which is equivalent to $1.9Si_3N_4 \cdot La_2O_3$, which is, in turn, close to the suggested formula. The X-ray data of Wills *et al* [6] on $Si_3N_4 \cdot La_2O_3$ might correspond to those of $LaSiO_2N$, as shown later.

The reaction of $2Si_3N_4 \cdot La_2O_3$ with N_2, which took place by heating the compound under 50 atm N_2 pressure at 2000° C, formed a pure nitride, $LaSi_3N_5$ [16]. The space group of this phase was $P2_12_12_1$ (orthorhombic), and the unit-cell dimensions were $a = 0.7838$ nm, $b = 1.1236$ nm and $c = 0.4807$ nm.

The structure of $La_5(SiO_4)_3N$ is analogous to fluorapatite ($Ca_5(PO_4)_3F$, hexagonal $a = 0.9368$ nm and $c = 0.6884$ nm) [8, 17]. The unit-cell dimensions are given in Table II. It is likely that a solid solution exists between $La_5(SiO_4)_3N$ and $La_{4.67}(SiO_4)_3O$ [12] because of their similar structures.

The phase relationships in the system Si_3N_4–SiO_2–La_2O_3 at 1700° C are shown in Fig. 1. The relationships were obtained using specimens cooled to room temperature, so that Fig. 1 is not a true equilibrium diagram at 1700° C.

3.2. Unstable phases at 1700° C

There are two compounds on the line between La_2O_3 and Si_2N_2O, which are not observed in specimens cooled from 1700° C. Both are made by the reaction of La_2O_3 with equimolar mixtures of Si_3N_4 and SiO_2 at 1550° C.

TABLE II X-ray diffraction spectra, hkl values, observed and calculated d-spacings and normalized line intensities, I/I_0, and unit-cell dimensions of $La_5(SiO_4)_3N$.

hkl	d_{obs}(mn)	d_{calc}(nm)	I/I_0
110	0.4868	0.4860	5
200	0.4213	0.4209	20
111	0.4039	0.4038	17
002	0.3629	0.3629	11
102	0.3333	0.3332	29
210	0.3184	0.3182	29
211	0.2912	0.2914	100
112		0.2908	
300	0.2807	0.2806	26
202	0.2745	0.2748	13
220	0.2429	0.2430	5
310	0.2335	0.2335	5
311	0.2220	0.2223	5
302		0.2220	
222	0.2018	0.2019	20
312	0.1963	0.1964	14
213	0.1925	0.1926	25
321	0.1866	0.1866	10
410	0.1837	0.1837	16
402	0.1820	0.1821	21
004	0.1815	0.1814	17

Hexagonal: $a = 0.9721$ nm and $c = 0.7258$ nm

$LaSiO_2N$ occurs with the space group, $C2/c$ or Cc, as determined from electron diffraction patterns. The unit-cell dimensions are $a = 1.2695$ nm, $b = 0.7327$ nm, $c = 2.8558$ nm and $\beta = 90.81°$ and in fact, the cell is pseudo-hexagonal with $a = 0.7328$ nm and $c = 2.8558$ nm. The powder X-ray data are similar to those for $Si_3N_4 \cdot La_2O_3$ obtained by Wills, as shown in Table III. Morgan and co-workers [9, 18] suggested, on the basis of the data of Wills that $LaSiO_2N$ has pseudo-hexagonal unit cell with $a = 0.731$ nm and $c = 0.955$ nm. The unit-cell dimensions obtained in the present work had a repeat distance, c, that was three times greater than that in the unit cell suggested by Morgan. The smaller size of Morgan's cell might be related to the fact that the weak superstructure reflections corresponding to the larger cell were not included. The structure of $LaSiO_2N$ is analogous to pseudo-wollastonite structure ($SrGeO_3$, pseudo-hexagonal with $a = 0.7253$ nm and $c = 3.1446$ nm [19]). This phase tends to dissociate to $La_5(SiO_4)_3N$ and a glass when cooled from temperatures above 1650° C. The composition of the glass is inferred as shown in Fig. 1.

The other compound occurring on the La_2O_3–

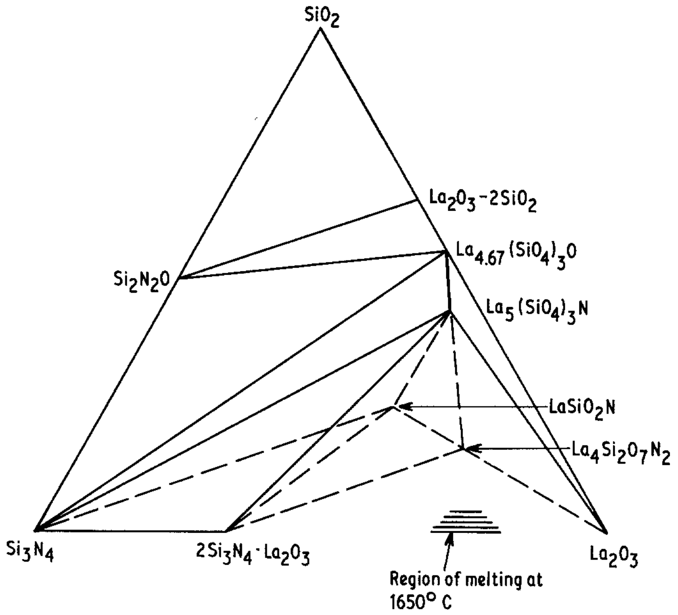

Figure 1 Phase relationships in the system Si_3N_4–SiO_2–La_2O_3 at 1700° C (dotted lines represent phase relationships at 1550° C).

Si_2N_2O joins is $La_4Si_2O_7N_2$. Wills *et al.* [6] have reported that this phase has a monoclinic structure with $a = 2.3948$ nm, $b = 1.0437$ nm, $c = 1.5538$ nm and $\beta = 113.53°$. Marchand *et al.* [7] showed that the unit cell of this compound was monoclinic with $a = 0.803$ nm, $b = 1.099$ nm, $c = 1.105$ nm and $\beta = 111.1°$. Thus, there are some possible ways in indexing X-ray powder data for a compound [10, 11].

More recently, single crystals of $La_4Si_2O_7N_2$ have been grown under a high N_2 pressure using the floating-zone method [12]. The space group was determined as $P2_1/m$ using a Weisenberg camera and the powder X-ray spectra are indexed as shown in Table IV. The calculated unit-cell dimensions are $a = 1.1151$ nm, $b = 1.0994$ nm, $c = 8.043$ nm and $\beta = 111.42°$, in good agreement with those of Marchand *et al.* [7]. The structure is analogous to cuspidine ($Ca_4Si_2O_7F_2$: monoclinic, $a = 1.093$ nm, $b = 1.057$ nm, $c = 0.757$ nm and $\beta = 110.07°$) and the composition determined by EPMA is $La_{4.0}Si_{2.0}O_{7.0}N_{1.9}$, in good agreement with the proposed formula.

TABLE III X-ray diffraction spectra, *hkl* values, observed and calculated *d*-spacings and normalized line intensities, I/I_0, and unit-cell dimensions of $LaSiO_2N$.

hkl	d_{obs}(nm)	d_{calc}(nm)	I/I_0
006	0.4767	0.4759	47
115	0.4215	0.4230	12
020	0.3663	0.3663	91
023	0.3423	0.3419	13
400	0.3179	0.3173	9
315	0.3063	0.3067	6
026	0.2907	0.2903	100
119	0.2815	0.2830	9
027	0.2727	0.2726	3
00.12	0.2379	0.2379	8
600	0.2114	0.2116	16
330		0.2115	
604	0.2018	0.2021	3
02.12	0.1996	0.1995	10
606	0.1927	0.1923	11
336		0.1928	
040	0.1832	0.1832	6

Monoclinic: $a = 1.2695$ nm, $b = 0.7327$ nm, $c = 2.8557$ nm and $\beta = 90.81°$.

3.3. The reaction of Si_3N_4 with La_2O_3

The sintering temperature of Si_3N_4 with La_2O_3 additions is 1700 to 1800° C. The heating of powder mixture of various Si_3N_4/La_2O_3 ratios at 1700° C results in the formation of $2Si_3N_4 \cdot La_2O_3$, $La_5(SiO_4)_3N$, and β-Si_3N_4 or a glass. The glass and $La_5(SiO_4)_3N$ are combined as a liquid at the reaction temperature, because the melting point of $La_4(SiO_4)_3N$ is about 1600° C, as shown below. An equi-molar mixture of Si_3N_4 and La_2O_3 heated to 1800° C at a rate of 30° C min^{-1} without applied pressure showed that there were three temperature regions in which chemical reactions took place, namely 1200 to 1250° C, 1400 to 1500° C and 1650 to 1750° C. The weight losses observed at 1650 to 1750° C when the powder mixture was heated under a pressure of 20 MPa occur because the liquid phase is squeezed out of

TABLE IV X-ray diffraction spectra and unit-cell dimensions of $La_4Si_2O_7N_2$.

hkl	d_{obs}(nm)	d_{calc}(nm)	I/I_0
001	0.7476	0.7488	6
020	0.5501	0.5497	2
200	0.5196	0.5190	2
210	0.4699	0.4694	19
$\bar{1}12$	0.3777	0.3777	3
220	0.3777	0.3774	3
130	0.3452	0.3456	3
310	0.3301	0.3301	21
$\bar{1}22$	0.3246	0.3246	100
022	0.3098	0.3094	19
221	0.3054	0.3059	15
112	0.3054	0.3047	15
230	0.2997	0.2994	22
320	0.2930	0.2928	26
$\bar{2}03$	0.2663	0.2661	3
$\bar{2}32$	0.2622	0.2623	7
410	0.2527	0.2526	2
$\bar{3}32$	0.2402	0.2405	3
$\bar{1}42$	0.2270	0.2269	5
312	0.2133	0.2134	11
$\bar{3}42$	0.2080	0.2081	4
123	0.2080	0.2080	4
510	0.2039	0.2040	18
$\bar{2}04$	0.2009	0.2011	12
$\bar{4}04$	0.1879	0.1878	14
$\bar{5}32$	0.1879	0.1877	14

Monoclinic: $a = 1.1151$ nm, $b = 1.0994$ nm, $c = 0.8043$ nm and $\beta = 111.42°$.

the die. The reactions occurring during heating were determined by X-ray diffractometry as

$$Si_3N_4 + La_2O_3 \xrightarrow[1200\text{ to }1250\,°\mathrm{C}]{} Si_3N_4 + (La_4Si_2O_7N_2 + LaSiO_2N)$$

$$\xrightarrow[1400\text{ to }1500\,°\mathrm{C}]{} LaSiO_2N + Si_3N_4$$

$$\xrightarrow[1650\text{ to }1750\,°\mathrm{C}]{} 2Si_3N_4\cdot La_2O_3 + \text{liquid}$$

$$\xrightarrow[20\,°\mathrm{C}]{} 2Si_3N_4\cdot La_2O_3 + La_5(SiO_4)_3N + \text{glass.}$$

The overall composition of the crystalline products observed at 1200 to 1500° C was away from that of the Si_3N_4–La_2O_3 phase boundary. This suggests the presence of non-crystalline solids in the materials, the composition of which might be on the $(2Si_2N_4\cdot La_2O_3)$–La_2O_3 phase boundary. The presence of $LaSiO_2N$ as the dominant product at 1500 to 1650° C explains why Wills *et al.* [6] suggested that this phase was $Si_3N_4\cdot La_2O_3$.

The reactions taking place when Si_3N_4 is sintered with small amounts of La_2O_3 are the same as those occurring in the Si_3N_4–$(2Si_3N_4\cdot La_2O_3)$–$La_5(SiO_4)_3N$ system because of the presence of surface silica on the Si_3N_4 powder. The amount of $2Si_3N_4\cdot La_2O_3$ and $La_5(SiO_4)_3N$ in the product is dependent on both the amount of La_2O_3 added and on the surface silica content of the starting silicon nitride powder.

TABLE V Linear thermal expansion coefficient and melting temperatures of intergranular phases in the system Si_3N_4–SiO_2–La_2O_3.

Compound	Linear thermal expansion coefficient ($\times 10^{-6}$ °C^{-1})	Melting temperature (° C)
$2Si_3N_4\cdot La_2O_3$	4.98	> 2000
$La_5(SiO_4)_3N$	10.1	≃ 1600
$Si_3N_4\cdot Y_2O_3$	5.60	≃ 1825 [2]

The linear thermal expansion coefficients and melting temperatures of $2Si_3N_4\cdot La_2O_3$ and $La_5(SiO_4)_3N$ are shown in Table V and compared with those of $Si_3N_4\cdot Y_2O_3$. Table V shows that $2Si_3N_4\cdot La_2O_3$ has better properties than those of $Si_3N_4\cdot Y_2O_3$. $La_5(SiO_4)_3N$ has a higher thermal expansion coefficient and lower melting temperature than $Si_3N_4\cdot Y_2O_3$ and is therefore undesirable as an intergranular phase. The presence of $La_5(SiO_4)_3N$ is inevitable in the production of high-density materials by liquid-phase sintering and, therefore, the amount of $La_5(SiO_4)_3N$ and glassy phase must be minimized to obtain materials with good high-temperature strengths.

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