JOURNAL OF MATERIALS SCIENCE 15 (1980) 2915–2920

A crystallographic study of a new compound of lanthanum silicon nitride, $LaSi_3N_5$

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A new compound of lanthanum silicon nitride, $LaSi_3N_5$ has been prepared by the reaction between Si_3N_4 and La_2O_3 under a 50 atm nitrogen pressure at 2000° C for 2 h. The space group is $P2_12_12_1$, $Z = 4$, $a = 7.838$ Å, $b = 11.236$ Å and $c = 4.807$ Å, $D_c = 4.6\,g\,cm^{-3}$. The crystal structure data and X-ray powder diffraction data are given. The characteristics of the structure have been noted and the similarities between $LaSi_3N_5$ and Si_3N_4 have been discussed in terms of the fundamental structural unit of SiN_4 tetrahedra.

1. Introduction

α- and β-Si_3N_4 consist of a fundamental structural unit of SiN_4 tetrahedra formed by sharing corners in a three dimensional net work [1, 2]. New ceramics which are composed of the fundamental unit of $Si(O,N)_4$ or $(Si,Al)(O,N)_4$ tetrahedra, the so-called "sialons", have been reported by Jack *et al.* [3, 4, 5]. The electrical neutrality in the sialon is maintained by the partial replacement of silicon by aluminium and by the replacement of nitrogen by oxygen. Recently, the crystal structure of yttrium silicon oxynitride has been discovered [6, 7]. The yttrium atom is located interstitially in the large space between the $Si(O,N)_4$-layers of the yttrium oxynitride structure as a result of the yttrium atom being too large for the site of the silicon atom which it has replaced. The electrical charge imbalance caused by yttrium is compensated for by the replacement of nitrogen with oxygen.

In this paper X-ray crystallographic data on a new compound, $LaSi_3N_5$, successfully synthesized, either by the reaction of Si_3N_4 and La_2O_3 powder under a 50 atm nitrogen pressure or directly by the reaction between Si_3N_4 and LaN powder directly, is reported and discussed. It has been revealed [8] that the large lanthanum atom is located in the centre of two pentagonal holes composed of 5 SiN_4 tetrahedra joined by sharing corners. In this structure, some of the nitrogen atoms are each co-ordinated with two silicon atoms and two lanthanum atoms rather than three silicon atoms. Electrical neutrality is maintained by these nitrogen atoms co-ordinating with lanthanum atoms instead of by the partial replacement either of silicon with aluminium or of nitrogen with oxygen. This is the first example of pure nitrogen ceramics in which a large size metallic atom is located, interstitially in a large structural hole without any replacement according to the $(Si,Al)(N,O)_4$ tetrahedra theory.

2. Synthesis

Powders of Si_3N_4 (from Advanced Materials Engineering Ltd, Gateshead, UK of 85% α, 15% β and of 99.6% purity) and La_2O_3 (from Shin-etsu Chemical Ltd, Japan of 99.9% purity) were used as the starting materials for the synthesis of $LaSi_3N_5$. The equimolecular mixture of Si_3N_4 (30.05 wt%) and La_2O_3 (69.95 wt%) was formed into a cylindrical specimen by a pressed mould, and then fired under a 50 atm pure nitrogen pressure at a temperature of 2000° C for 2 h using a pressure furnace. As a result of this heat-treatment, a great many single crystals grew on the surface of the heated cylindrical sample. These crystals

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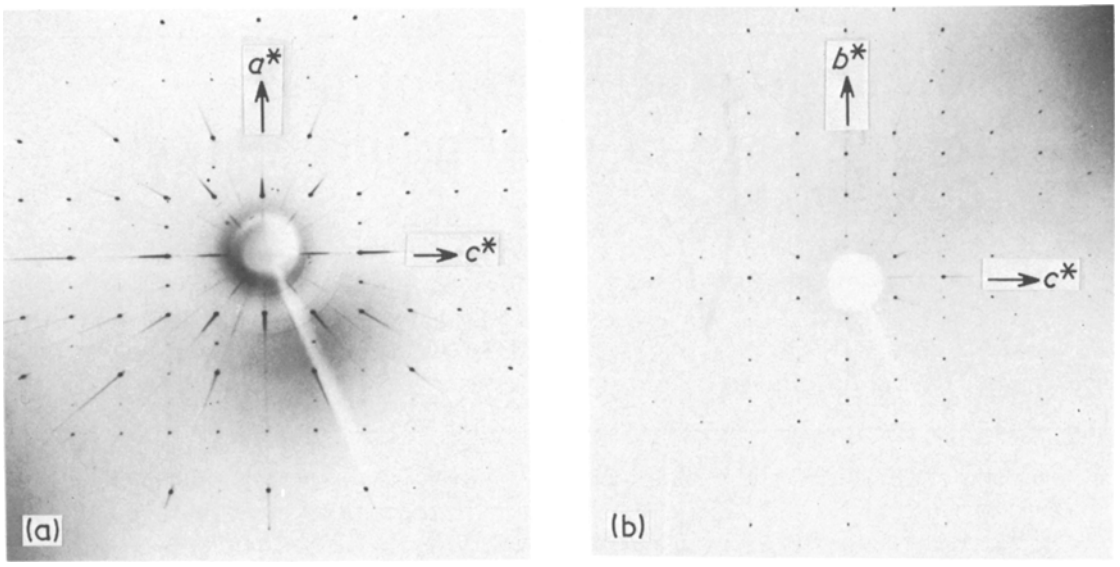


Figure 1 The precession photographs of $LaSi_3N_5$ single crystal taken by MoKα-radiation. (a) and (b) show ($h\,0\,l$) and ($0\,k\,l$) planes, respectively.

which appeared were transparent, were yellow in colour, had a rectangular shape and an average size of 0.4 mm in length and 0.02 mm in thickness.

3. Single-crystal data

A suitable crystal of dimensions 0.6 mm x 0.12 mm x 0.04 mm was selected under an optical microscope for the X-ray single-crystal analysis. The unit cell dimensions and its space group were revealed using a precession camera with Mo-radiation and a Weissenberg camera with Cu-radiation. The approximate unit cell dimensions were found to be $a = 7.84$ Å, $b = 11.25$ Å and $c = 4.81$ Å. The conditions limiting possible reflections are

$$h\,0\,0 \text{ for h} = 2n;$$

$$0\,k\,0 \text{ for k} = 2n;$$

$$0\,0\,l \text{ for } l = 2n.$$

On the basis of the systematic extinction [9]. the space group of this crystal can be identified as $P2_12_12_1$. The ($h\,0\,l$) and ($0kl$) reciprocal planes of this crystal are shown in Fig. 1a and b, respectively. Both pictures were taken by a precession camera with $\mu = 25°$ with 40 kV x 30 mA Mo-radiation.

The chemical composition of this crystal was confirmed by electron probe microanalysis and the results are given in Table I. The results indicate that the oxygen content was less than 0.67 wt % and that the atomic component ratio of La:Si:N was nearly 1:3:5. The oxygen originally included in the La_2O_3 of the starting material was replaced by nitrogen during the reaction at 2000° C under a 50 atm nitrogen pressure. The apparent chemical reaction which produces $LaSi_3N_5$ is

$$N_2 + La_2O_3 + 2Si_3N_4 = 2(LaSi_3N_5) + 3(O).$$

The specific gravity was measured using a heavy solution of a mixture of thallium formic acid and thallium malonic acid. The observed specific gravity D_o was 4.7 g cm^{-3}, while the calculated specific gravity of $4(LaSi_3N_5)$ is 4.6 g cm^{-3}. The molecular formula in the unit cell of this crystal can be represented by $(LaSi_3N_5)_4$.

X-ray diffraction data of a single crystal was collected on a Rigaku four-circle diffractometer with MoK_α radiation ($\lambda = 0.7107$ Å, made mono-

TABLE I The chemical composition of $LaSi_3N_5$ single-crystal determined by EPMA.

Element	Construction (wt %)
La	48.08
Si	28.92
O	0.67
N	20.93
Total	98.60

Atomic composition: $La_{1.00}Si_{2.97}N_{4.33}$
Molecular formula: $LaSi_3N_5$

TABLE II X-ray powder diffraction data of $LaSi_3N_5$. d_c, $2\theta_c$, $2\theta_o$, I_c and I_o represent the calculated planar spacing, calculated 2θ angle, observed 2θ angle, calculated diffraction intensity and observed diffraction intensity, respectively. I_c and I_o values are normalized with respect to the (1 3 1) plane reflection.

hkl	d_c (Å)	$2\theta_c$ (°)	$2\theta_o$ (°)	I_c (arb. units)	I_o (arb units)
1 1 0	6.43	13.78	13.80	5.8	5.0
0 2 0	5.62	15.77	15.80	5.9	5.0
1 2 0	4.57	19.44	19.42	27.6	23.0
0 1 1	4.42	20.09	20.10	41.4	36.0
2 0 0	3.92	22.69	22.65	18.7	15.0
1 1 1	3.85	23.10	23.10	19.1	14.0
2 1 0	3.70	24.05	24.04	12.4	9.0
1 3 0	3.38	26.35	26.38	22.1	26.0
1 2 1	3.31	26.91	26.89	14.8	16.0
2 0 1	3.04	29.38	29.30	16.5	24.0
2 1 1	2.93	30.40	30.42	70.2	76.0
0 4 0	2.81	31.83	31.82	7.5	7.0
1 3 1	2.76	32.35	32.34	100.0	100.0
2 2 1	2.67	33.51	33.48	23.2	21.0
1 4 0	2.64	33.87	33.89	27.7	27.0
3 1 0	2.54	35.23	35.20	15.2	13.0
0 0 2	2.40	37.38	37.36	25.8	25.0
3 2 0	2.37	37.94	37.90	4.3	5.0
2 3 1	2.36	38.11	38.10	4.9	5.0
3 3 0	2.14	42.13	42.13	17.0	15.0
1 2 2	2.13	42.46	42.48	15.1	21.0
3 2 1	2.12	42.50	42.48	17.9	21.0
0 5 1	2.04	44.46	44.46	6.6	5.0
1 3 2	1.96	46.31	46.30	5.3	5.0
4 1 0	1.93	47.03	47.02	10.5	18.0
0 6 0	1.87	48.57	48.57	5.6	5.0
0 4 2	1.83	49.89	49.89	4.5	5.0
4 0 1	1.81	50.23	50.20	7.1	5.0
1 4 2	1.78	51.32	51.33	15.5	22.0
3 4 1	1.78	51.36	51.33	12.5	22.0
3 1 2	1.75	52.31	52.30	9.1	6.0
2 6 0	1.69	54.24	54.22	4.6	7.0
3 2 2	1.69	54.32	54.22	5.4	7.0
2 6 1	1.59	57.79	57.80	14.2	8.0
4 4 1	1.52	60.70	60.70	3.7	6.0
0 7 1	1.52	60.78	60.70	6.8	6.0
1 3 3	1.45	64.28	64.20	13.1	14.0
5 2 1	1.44	64.64	64.64	13.0	8.0
2 7 1	1.42	65.74	65.70	6.2	5.0

chromatic by graphite). The 2θ–ω scanning mode was employed for the intensity measurements where $2\theta \leqslant 110°$, and 2594 independent non-zero reflections were collected. After the corrections for Lorentz, polarization and absorption effects, the necessary crystallographic calculations were carried out. The atomic positions of lanthanum and silicon were obtained by the Patterson method and the positions of nitrogen atoms were found by Fourier and differential Fourier synthesis. Finally, the crystal structure was refined by the full-matrix least-squares fit refinement program with anisotropic temperature factors giving a final value of $R = 0.046$ and $R_w = 0.067$.

In addition, the accurate unit cell dimensions were obtained from the 2θ values of 50 reflections measured using a Rigaku four-circle diffractometer with MoK_α radiation. The refinement calculation of the unit cell dimension was carried out by a least-squares fit computer program. The refined unit cell is

$$a = 7.838\,\text{Å}, b = 11.236\,\text{Å} \text{ and } c = 4.807\,\text{Å}.$$

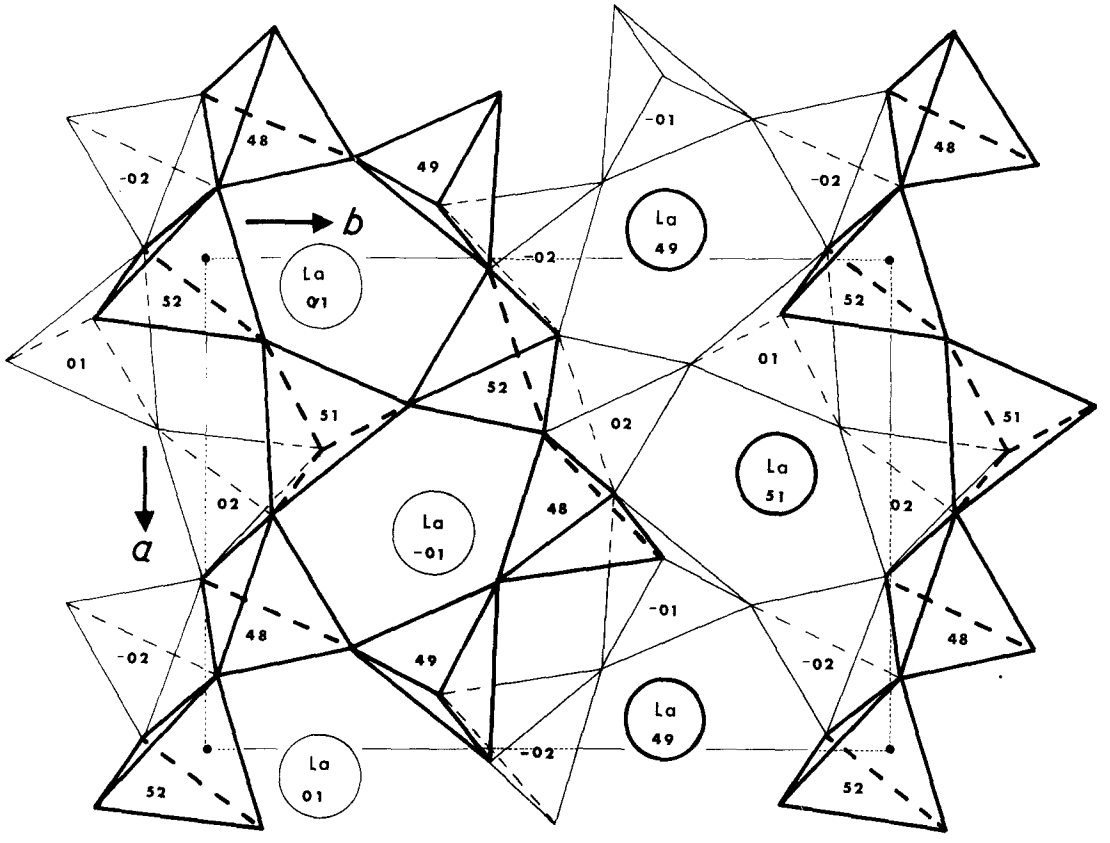


Figure 2 The crystal structure of $LaSi_3N_5$ projected on the (0 0 1) plane. A tetrahedron represents a SiN_4 tetrahedra and a circle denotes a lanthanum atom. The upside of half unit along *c*-axis is drawn by the bold lines.

4. Powder X-ray diffraction data

X-ray diffraction data was obtained from the powder sample which was made from the direct reaction of LaN and Si_3N_4 powders. In the synthesis procedure of the $LaSi_3N_5$ powder sample, lanthanum metal (from Nakarai Chemical Ltd, Japan, of 99.9% purity) was nitrated using nitrogen gas at between 750 and 900° C for 30 hours. The resulting lanthanum nitride, LaN, and silicon nitride, Si_3N_4, powder were mixed together in normal hexane using an agate mortar to prevent oxidation of the powder. This mixture was then heated at 1700° C for 30 minutes in a hot pressed furnace in a nitrogen atmosphere with a pressure of 150 kg cm^{-2}. The X-ray powder diffraction profiles of this powder sample synthesized from LaN and Si_3N_4 were identical to those of the powder samples of single crystals which were synthesized from La_2O_3 and Si_3N_4 under a 50 atm nitrogen pressure.

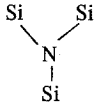
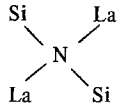
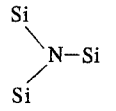
X-ray powder diffraction data was obtained using a Rigaku Geigerflex with CuK_α X-ray radiation and an Ni-filter with a scintillation counter detector scanning at $(2\theta - 1)°$ per minute. The X-ray reflections were collected in the range of 2θ from 10° to 70° and were then indexed by taking account of the unit cell dimensions obtained from the single crystal. The calculated planar spacings, the observed and calculated 2θ-values and their indices are given in Table II. The powder diffraction intensity I_c was calculated by taking account of the result of single crystal structure analysis. The calculated intensity I_c and the observed intensity I_o are also given in Table II.

5. Discussion

The (0 0 1) projection of the $LaSi_3N_5$ structure revealed by single-crystal structure analysis [8] is shown in Fig. 2. The lanthanum atoms are represented by circles and the silicon and nitrogen atoms are indicated by tetrahedra of SiN_4. The position of each atom along the *c*-axis is given by the two-digit number. The position of the tetrahedra is given in terms of the position of the silicon atoms. The characteristics of the structure are:

(a) $5SiN_4$ tetrahedra joined by sharing corners

TABLE III Comparisons of the characteristics of $LaSi_3N_5$ and Si_3N_4 structures.

Characteristic	$LaSi_3N_5$		Si_3N_4
Silicon atoms environment	Tetrahedrally co-ordinated with 4 nitrogen atoms, SiN_4		Tetrahedrally co-ordinated with 4 nitrogen atoms, SiN_4
	 and		
Nitrogen atoms environment	Co-ordinated with 3 silicon atoms	Co-ordinated with 2 silicon and 2 lanthanum atoms	Co-ordinated with 3 silicon atoms
Large hole composed of SiN_4 tetrahedra	Pentagonal hole of 5 SiN_4 tetrahedra joined by sharing corners		Hexagonal hole 6 SiN_4 tetrahedra joined by sharing corners
Modifying metallic atoms	La of interstitial site		–
Space group	$P2_12_12_1$		P31c for α-Si_3N_4 $P6_3$ for β-Si_3N_4
Unit cell	$a = 7.838$ Å, $b = 11.236$ Å, $c = 4.807$ Å		$a = 7.818$ Å, $c = 5.591$ Å for α-Si_3N_4 $a = 7.595$ Å, $c = 2.902$ Å for β-Si_3N_4
Mean Si-N distance	1.730 Å		1.732 Å for β-Si_3N_4 1.740 Å for α-Si_3N_4

nearly parallel to the (0 0 1) plane make a large pentagonal hole.

(b) The lanthanum atom is centrally located between the corresponding pentagonal holes which occur at one unit intervals along the c-axis.

(c) There are two types of nitrogen environment. In the first type, 8 nitrogen atoms (2/5 of all the nitrogen atoms in a unit cell) are each surrounded by 3 silicon atoms in a way similar to the silicon nitride structure. In the second type, 12 nitrogen atoms (3/5 of all the nitrogen atoms) are each co-ordinated with two silicon atoms and two lanthanum atoms.

The characteristics of $LaSi_3N_5$ structure are compared with those of α- and β-silicon nitride in Table III. $LaSi_3N_5$ and Si_3N_4 structures have several distinctive features: (a) the shape of rings composed of SiN_4 tetrahedra; (b) the nitrogen environment with cations; (c) the additional metal of La located interstitially; their unit cell dimensions; their space groups. However, consideration of the fundamental structural unit shows that there is quite a degree of similarity between $LaSi_3N_5$ and Si_3N_4. The fundamental unit of $LaSi_3N_5$, SiN_4 tetrahedra , is almost the same as that of Si_3N_4. There is neither replacement of silicon by aluminium nor replacement of nitrogen by oxygen atoms as in the (Si, Al) $(N, O)_4$ tetrahedra. The bond lengths between the silicon and nitrogen atoms of $LaSi_3N_5$ are also the same as those of α- and β-Si_3N_4, being 1.730 Å for $LaSi_3N_5$, 1.732 Å for β-Si_3N_4 [10], and 1.743 Å [11], 1.739 Å [12] and 1.738 Å [13] for α-Si_3N_4, respectively. The silicon environment co-ordinated with 4 nitrogen atoms and the nitrogen environment co-ordinated with 3 silicon atoms can be seen in the $LaSi_3N_5$ structure to be the same as the Si_3N_4 structure. Therefore, $LaSi_3N_5$ may be expected to have intrinsically the same properties as silicon nitride and be expected to form strong bonds with adjacent silicon nitride grains holding them tightly together.

The degree of ionization of La^{3+} is very high (93%) and lanthanum forms a strong bond with nitrogen. Consequently a mechanical high-strength property may be expected for this new compound. In addition, since the single crystal of $LaSi_3N_5$ grew at 2000° C in a nitrogen atmosphere, it can be expected to have a high-temperature strength similar to that of refractory materials.

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Received 20 March and accepted 29 April 1980.