

# Preparation and characterization of lanthanum silicon nitride

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Lanthanum silicon nitride ( $\text{LaSi}_3\text{N}_5$ ) powder has been prepared under the relatively mild conditions of 1400°C and 1 atm nitrogen. Chemical, X-ray diffraction, solid state nuclear magnetic resonance spectra, and morphological information on this powder is presented. The X-ray diffraction data and previously published information have been used to develop a more complete specification of the unit cell dimensions.  $^{29}\text{Si}$  magic-angle spinning nuclear magnetic resonance spectra of  $\text{LaSi}_3\text{N}_5$  show two chemical shifts at -64.5 and -56.5 p.p.m. These shifts reflect two electronically different "types" of silicon which have been attributed to the effects of quadrupolar  $^{139}\text{La}$  nuclei and their spatial arrangements around silicon atoms.

## 1. Introduction

The oxygen-free metal and nitrogen ternary derivatives of silicon are a potentially important class of materials that remain relatively unknown. Only a few of these have been prepared and characterized. This is in contrast to the metal-oxygen-nitrogen derivatives of silicon known as oxynitride glasses and sialon ceramics which have received considerable attention [1, 2] from the materials science community.

Among the ternary nitrides which have been reported are two groups classified as M-Si-N and M'-Si-N. Using this convention, M represents an alkali or alkaline earth element and M' a rare earth element. Examples of the M-Si-N group are  $\text{LiSi}_2\text{N}_3$  and polytypes of Be-Si-N [3-6], of which the known forms are  $\text{Be}_4\text{SiN}_4$ ,  $\text{Be}_9\text{Si}_3\text{N}_{10}$ ,  $\text{Be}_5\text{Si}_2\text{N}_6$ ,  $\text{Be}_{11}\text{Si}_5\text{N}_{14}$  and  $\text{BeSiN}_2$ . In the structure of the alkali and alkali earth metal silicon nitrides, the metal atoms substitute for silicon in the tetrahedra.

The only known compound from the second group of ternary nitrides (M'-Si-N) is lanthanum silicon nitride [7-9],  $\text{LaSi}_3\text{N}_5$ . The structure of  $\text{LaSi}_3\text{N}_5$  is uniquely different from the M-Si-N ternary nitrides. Here, the lanthanum atoms are located in interstitial positions and electrical neutrality is established by the presence of two different types of nitrogen [9]. The purpose of this manuscript is to report the results of our research into this unique and potentially important nitride material. This includes (1) the results of a new and less demanding method of preparation, (2) structural details obtained by X-ray diffraction (XRD) studies, and (3) characterization of  $\text{LaSi}_3\text{N}_5$  by solid-state  $^{29}\text{Si}$  nuclear magnetic resonance (NMR).

## 2. Experimental procedure

### 2.1. Sample analyses

Chemical compositions were determined in triplicate by Galbraith Laboratories (Knoxville, Tennessee,

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USA). Particle size distributions were determined via sedimentation techniques using a Sedigraph (Micromeritics, Norcross, Georgia, USA).

### 2.2. NMR spectroscopy

$^{29}\text{Si}$  NMR spectra were obtained at 39.6 MHz on a Varian XL200 NMR spectrometer equipped with Doty Scientific solids accessories. Data were acquired under magic-angle spinning (MAS) conditions using standard single-pulse techniques, a 90° pulse and a 180 sec pulse delay. Chemical shifts in p.p.m. are externally referenced relative to tetramethylsilane at 0 p.p.m.  $^{29}\text{Si}$  spin-lattice relaxation times ( $T_1$ ) were measured for the two peaks at -64.5 p.p.m. ( $T_1 = 28$  sec) and -56.5 p.p.m. ( $T_1 = 20$  sec). Because the delay between pulses is greater than five times the longest  $T_1$ , the 2:1 ratio of the integrated peak intensities is an accurate measure of their relative abundance in the  $\text{LaSi}_3\text{N}_5$  sample.

### 2.3. X-ray diffraction (XRD)

The XRD data were obtained on a Philips APD 3600 automated powder diffractometer. The lattice parameters for  $\text{LaSi}_3\text{N}_5$  were obtained by a least-squares analysis of the  $2\theta$  values of 24 reflections. These reflections were corrected for systematic errors by using silicon (NBS SRM 640a) as an internal reflection standard.

## 3. Results and discussion

### 3.1. Synthesis

Lanthanum silicon nitride ( $\text{LaSi}_3\text{N}_5$ ) has been previously synthesized by two methods. Inoue *et al.* [7] prepared  $\text{LaSi}_3\text{N}_5$  in the form of small single crystals by the reaction of  $\text{Si}_3\text{N}_4$  and  $\text{La}_2\text{O}_3$  at 2000°C under 50 atm pure nitrogen. Holcombe and Kovach [8] also prepared  $\text{LaSi}_3\text{N}_5$  by hot pressing  $\text{Si}_3\text{N}_4$  and  $\text{LaN}$  at roughly 1830°C under 270 atm nitrogen. Both of these

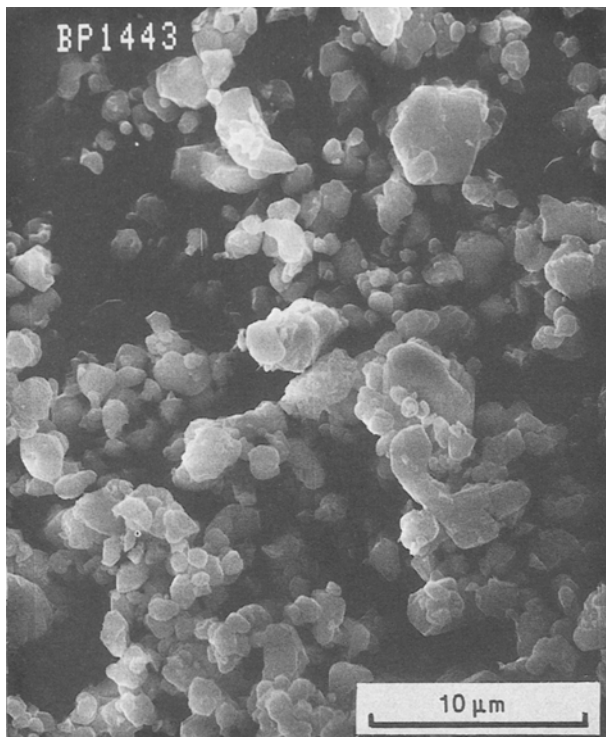


Figure 1 Scanning electron micrograph of  $\text{LaSi}_3\text{N}_5$  prepared at  $1400^\circ\text{C}$  and 1 atm nitrogen.

synthetic routes proceed under rather demanding conditions. In addition,  $\text{LaN}$  is moisture sensitive, making it a difficult starting material to handle.

We have developed the technology to prepare pure  $\text{LaSi}_3\text{N}_5$  powders using the relatively mild conditions of  $1400^\circ\text{C}$  and 1 atm nitrogen. The exact details of this procedure are currently under patent litigation and will be presented here at a later date. The  $\text{LaSi}_3\text{N}_5$  powders prepared via this route are very pure as evidenced by X-ray diffraction, nuclear magnetic resonance, and chemical composition. Chemical analyses repeatedly reveal the materials to have nitrogen contents (average 33.37 wt %) very close to theoretical (33.88 wt %). The analyses typically detected less than 1.5 wt % oxygen in the powders.

The physical properties of the  $\text{LaSi}_3\text{N}_5$  powders prepared under conditions of  $1400^\circ\text{C}$  and 1 atm nitrogen are given in Table I. The “as-prepared” powder is agglomerated, with a relatively broad particle size distribution and low surface area. However, this powder can be dispersed in liquid media and ball milled to a much finer powder as shown in Table I. The morphology of a batch of milled powder with an average particle size of  $2\ \mu\text{m}$  can be seen in the scanning electron micrograph shown in Fig. 1.

TABLE I Physical properties of  $\text{LaSi}_3\text{N}_5$  powders prepared under conditions of  $1400^\circ\text{C}$  and 1 atm nitrogen

Property	As-prepared	Ball-milled
Density ( $\text{g cm}^{-3}$ )	4.18	
Surface area ( $\text{m}^2 \text{g}^{-1}$ )	1.6	
Pore volume ( $\text{cm}^3 \text{g}^{-1}$ )	0.35	
Particle size distribution ( $\mu\text{m}$ ):		
67%	< 6.0	< 1.8
50%	< 4.8	< 1.5
33%	< 3.4	< 1.2

### 3.2. XRD analysis of $\text{LaSi}_3\text{N}_5$ structure

The original work [7, 9] on  $\text{LaSi}_3\text{N}_5$  reported structural parameters which were, unfortunately, only partially complete. In that work, the atomic positions of lanthanum and three nitrogens were reported, along with the unit cell dimensions. These values are given in Table II. In order to characterize fully this system, it is necessary to complete the structure data, including the atomic level positions of the silicon atoms. By interpolating the fractional coordinates from Fig. 1 of Inoue [9], we were able to fill in the data needed to describe the unit cell completely. These values are also given in Table II, although the accuracy of these data is not known. However, it was possible to calculate an XRD stick diagram from the structural data given in Table II. The stick diagram and a representative XRD pattern obtained from the powder of the present synthesis are given in Fig. 2. Note that fit is very good, indicating that the accuracy of the structural data given in Table II is good. These structural dimensions were also used to calculate unit cell dimensions, yielding values of  $a = 0.7855\ \text{nm}$ ,  $b = 1.1267\ \text{nm}$  and  $c = 0.4818\ \text{nm}$ . These values are, on average, only 0.24% larger than those originally reported [7].

### 3.3. NMR study of $\text{LaSi}_3\text{N}_5$

Solid-state NMR is fast becoming one of the more powerful tools available for the study of atomic level structure and chemistry in ceramic materials [10–12]. The  $^{29}\text{Si}$  NMR spectrum of  $\text{LaSi}_3\text{N}_5$  is given in Fig. 3. The spectrum shows two peaks at  $-64.5$  and  $-56.5$  p.p.m. and is free of typical silicon impurity signals such as  $\text{SiC}$  ( $\sim -20$  p.p.m.) and  $\text{Si}_3\text{N}_4$  ( $\sim -48$  p.p.m.). No carbon signal was detected in the analogous  $^{13}\text{C}$  NMR experiment (not shown) which indicates the absence of carbon impurities. Therefore, the  $^{29}\text{Si}$  and  $^{13}\text{C}$  NMR data reveal that the sample is very pure.

The presence of two peaks in the  $^{29}\text{Si}$  NMR spectrum of  $\text{LaSi}_3\text{N}_5$  (Fig. 3) indicates the presence of two “types” of silicon as distinguished by NMR. These two silicon “types” must be present in a 2:1 ratio which is reflected by the relative peak areas. The observation of two silicon peaks in a 2:1 ratio is consistent with the presence of three crystallographically distinct silicon sites [7, 9]. However, the assignment of these peaks is less obvious.

TABLE II Unit cell coordinates for  $\text{LaSi}_3\text{N}_5$ ; Space group  $P212121$ ,  $Z = 4^*$ ,  $a = 0.7839\ \text{nm}$ ,  $b = 1.1236\ \text{nm}$ ,  $c = 0.4807\ \text{nm}$

Atom	$x/a$	$y/b$	$z/c$
La*	0.061	0.168	0.008
Si1	0.661	0.658	-0.010
Si2	0.290	0.583	0.020
Si3	0.540	0.540	0.480
N1*	0.390	0.167	0.171
N2	0.352	0.488	0.300
N3*	0.158	0.078	0.542
N4*	0.293	0.294	0.662
N5	0.018	0.410	0.320

\*Fractional coordinates taken explicitly from [7].

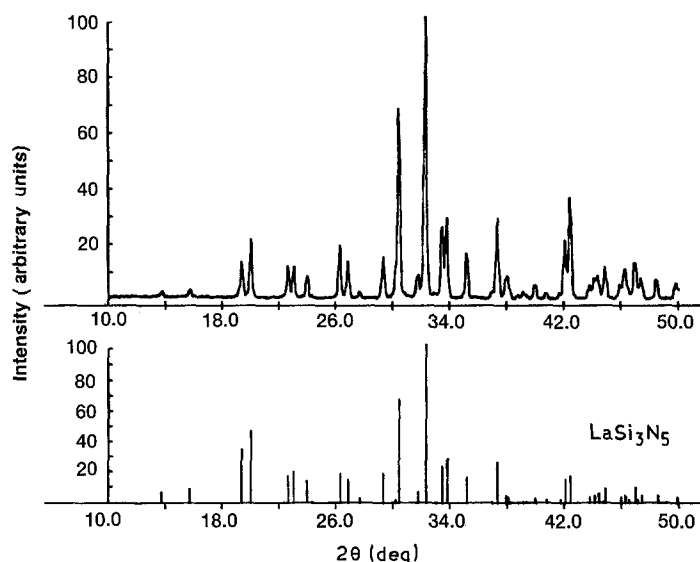


Figure 2 Representative XRD pattern of  $\text{LaSi}_3\text{N}_5$  and stick diagram calculated using the data from Table II.

The position, or chemical shift, of the peaks is indicative of the local electronic environment about the nucleus. Therefore, the two peaks reflect two inequivalent electronic environments. The local electronic environment is influenced by a number of factors including the bonding network and the identity of neighbouring nuclei. Thus, in order to assign the two NMR peaks, it is necessary to examine closely the structure of  $\text{LaSi}_3\text{N}_5$ .

In  $\text{LaSi}_3\text{N}_5$ , each silicon is tetrahedrally bound to four nitrogen atoms. Thus, it can be immediately inferred that the observed differences in chemical shift do not arise from simple differences in the nearest neighbour nuclei. However, there are two types of nitrogen in the structure [7, 9]. The first type, N, accounts for two-thirds of the nitrogens and is surrounded by three silicon atoms. The second type, N', is coordinated to two silicon and two lanthanum atoms.  $\text{SiN}_4$  tetrahedra exist as a 1:1:1 mixture of  $\text{SiNN}_3$ ,  $\text{SiN}_2\text{N}'_2$  and  $\text{SiN}_3\text{N}'$ . These different tetrahedra would account for the two  $^{29}\text{Si}$  peaks if, and only if, two of the three gave rise to the same chemical shift. This seems unlikely for the following reasons. Firstly, chemical shift effects are generally additive and vary smoothly with changes in structure. Secondly, if the larger peak at  $-64.5$  p.p.m. were made up of two overlapping peaks from silicon atoms in different chemical environments, one might expect

to see a double exponential  $T_1$  spin-lattice relaxation time. However, the signal at  $-64.5$  p.p.m. has a single exponential relaxation time.

Based on the above arguments, we can eliminate neighbouring nitrogens as the source for chemical shift differences. In other words, the two-peak pattern observed in Fig. 3 must arise from non-nearest-neighbour interactions. The most likely of these interactions would be expected to arise from surrounding silicon or lanthanum nuclei.

The first shell of neighbouring silicon nuclei appears as the surface of a sphere which is  $0.31 \pm 0.01$  nm from the silicon being examined. As mentioned previously, there are three crystallographically distinct silicon sites which are referred to as Si1, Si2 and Si3. Using the data from Table II we find that each silicon type has a different number of silicon neighbours along the 0.31 nm sphere. Si1 has five neighbours, Si2 has seven and Si3 has six. Arguments based on chemical shift additivity and spin-lattice relaxation (analogous to those used earlier for nitrogen) suggest that these differences are not responsible for the two-peak pattern in Fig. 3.

Finally, consider the effect of the surrounding lanthanum nuclei on each silicon. Examination of the  $\text{LaSi}_3\text{N}_5$  crystal structure reveals that the first shell of neighbouring lanthanum atoms appears as the surface of a sphere which is  $0.36 \pm 0.02$  nm from the silicon

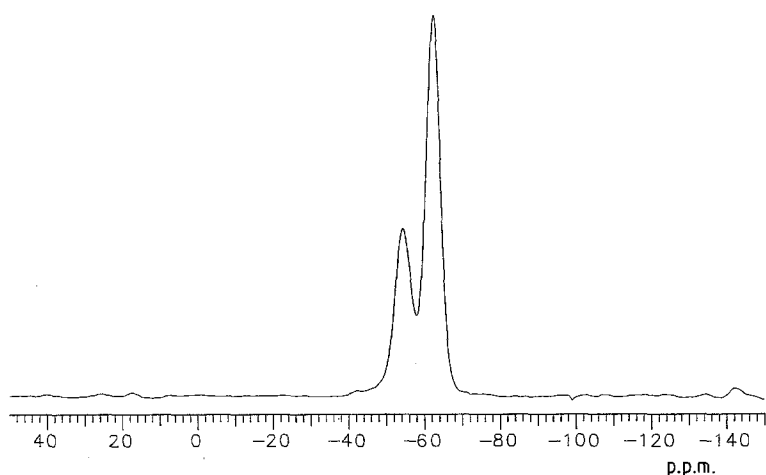


Figure 3  $^{29}\text{Si}$  NMR spectrum of  $\text{LaSi}_3\text{N}_5$ .

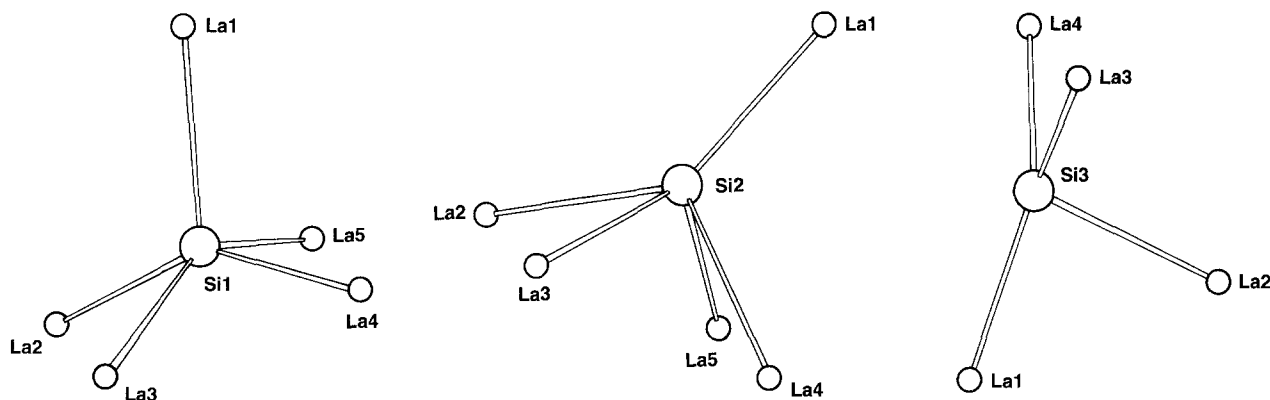


Figure 4 Nearest neighbour lanthanum coordination spheres surrounding each silicon type in  $\text{LaSi}_3\text{N}_5$ .

atom being examined. This lanthanum coordination sphere for each silicon type is illustrated in Fig. 4. Examination of the crystal and Fig. 4 reveals that Si3 has four lanthanum neighbours along the 0.36 nm surface. However, Si1 and Si2 have five. Therefore, the interaction of silicon with its neighbouring lanthanum atoms provides an attractive interpretation for the two-peak pattern in Fig. 3. Using this argument, the  $^{29}\text{Si}$  NMR peak at  $-64.5$  p.p.m. can be assigned to the silicon atoms (Si1 and Si2) with five nearest neighbour lanthanum atoms. Similarly, the peak at  $-56.56$  p.p.m. can be assigned to the silicon atom (Si3) with four nearest neighbour lanthanum atoms.

The inference that neighbouring lanthanum nuclei provide the dominant chemical shift determining interaction in  $\text{LaSi}_3\text{N}_5$  is further supported by the following argument. One of the most dominant forces affecting nuclear spins is the interaction with a quadrupolar nucleus. Both  $^{139}\text{La}$  and  $^{14}\text{N}$  are quadrupolar nuclei and possess a quadrupole moment due to a non-spherically symmetric electric field gradient at the nucleus. However, the quadrupole coupling constant of  $^{139}\text{La}$  is 13 times greater than that for  $^{14}\text{N}$  [13]. Thus, the lanthanum atoms in the system would be expected to produce the dominant quadrupolar interaction.

The "sphere of influence" argument used above to rationalize the chemical shifts of  $\text{LaSi}_3\text{N}_5$  reveals that the  $^{29}\text{Si}$  NMR chemical shift is sensitive to the influence of neighbouring lanthanum atoms. In addition, it indicates that the  $^{29}\text{Si}$  peaks reflect differences in the local electronic environment on a scale of nanometers. These results have major implications for studying the local structural environment of similar systems and for examining the effects of technologically significant processes (such as mechanical stress) on a new level of resolution.

#### 4. Conclusions

1. Lanthanum silicon nitride,  $\text{LaSi}_3\text{N}_5$ , powder of very high purity can be synthesized at the relatively mild conditions of  $1400^\circ\text{C}$  and 1 atm nitrogen.

2. The unit cell dimensions of  $\text{LaSi}_3\text{N}_5$  have been completely specified.

3. The  $^{29}\text{Si}$  NMR spectrum of this ternary metal-silicon nitride shows two chemical shifts at  $-64.5$  and  $56.5$  p.p.m. and the corresponding peak ratio is 2 : 1.

4. The chemical shifts in the  $^{29}\text{Si}$  NMR spectrum of  $\text{LaSi}_3\text{N}_5$  are caused by the quadrupolar  $^{139}\text{La}$  nuclei and their spatial arrangement around silicon which gives rise to two electronically different "types" of silicon atoms in this nitride material.

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