

Oxygen/nitrogen ordering in lanthanum new phase ($\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$)

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Abstract

High-resolution ^{17}O NMR spectra have been collected for crystalline samples of lanthanum new phase, $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$. In conjunction with previously published ^{29}Si and ^{15}N spectra obtained for this phase, and in the light of the high-quality crystal structure data reported recently, a more detailed interpretation of the NMR spectra is presented than was possible in previous studies. The non-bridging oxygens in the structure are responsible for the single sharp peak seen in the ^{17}O spectrum at 188 ppm; the remaining oxygens, occupying bridging sites shared with nitrogen, show up only weakly on the ^{17}O spectrum as a broad diffuse band centered around zero ppm. The peak at -57.3 ppm on the ^{29}Si spectrum is believed to correspond to an overlap of $[\text{SiN}_4]$ and $[\text{SiON}_3]$ environments, with the -68.2 ppm peak corresponding to an $[\text{SiO}_2\text{N}_2]$ environment.

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1. Introduction

Magic-angle spinning (MAS) NMR has, during the last fifteen years, been successfully used as an adjunct to X-ray diffraction for characterizing ceramic materials, proving to be an extremely useful technique for obtaining detailed information about coordination, environment and order-disorder. In particular, it has been used to supplement structural information provided by low-reliability X-ray powder diffraction data in cases where single crystals are not available [1].

Early NMR studies on nitrogen ceramic materials examined ^{29}Si and ^{27}Al spectra for silicon nitride and related sialon derivatives [2–8]. More recently, this work has been extended to include ^{29}Si , ^{27}Al , ^{15}N and ^{17}O studies of metal silicon nitrides and a variety of metal sialon glasses and their crystalline derivatives [9–20]. It is obviously desirable to examine the environments round all the atoms in these structures, and, in the present work, the ordering of nitrogen and oxygen atoms is of particular interest. In order to prepare appropriate samples, isotopically enriched H_2^{17}O has been used in the present work to make Si^{17}O_2 , which has been

subsequently reacted with binary oxides and nitrides to form the oxynitride compounds under investigation.

The so called “new” phase in the La-Si-O-N system was originally assigned a composition $\text{La}_2\text{Si}_6\text{N}_8\text{O}_3$ on the basis of preparative evidence, and was first characterized by Mah et al. [22] in terms of a monoclinic unit cell of dimensions: $a = 18.0 \text{ \AA}$, $b = 4.86 \text{ \AA}$, $c = 7.90 \text{ \AA}$, $\beta = 114.5^\circ$. No similar mineral analogues could be identified, and Harris et al. [12] published a structure based on X-ray powder data (Fig. 1), showing it to have a composition of the type $\text{La}_3\text{Si}_8\text{O}_4\text{N}_{11}$ [9]. This work implied that two distinct silicon environments were present [6], either of the types $[\text{SiN}_4]$ and $[\text{SiON}_3]$ or $[\text{SiON}_3]$ and $[\text{SiN}_2\text{O}_2]$; as regards the non-metal atoms in the $\text{La}_3\text{Si}_8\text{O}_4\text{N}_{11}$ formula unit, four were believed to be nitrogen occupying $[\text{NSi}_3]$ sites, nine were mixed nitrogen/oxygen on $[(\text{O},\text{N})\text{Si}_2]$ sites, and the remaining two (consistent with Pauling’s rules [23]) were believed to be oxygen atoms occupying non-bridging sites co-ordinated to one silicon and three lanthanum atoms. ^{27}Al and ^{29}Si NMR studies, carried out by various groups [6,9,12,25] on both new phase and its Al-substituted derivative, supported these conclusions. However, Grins et al. [24] reported more detailed structural work on the Ce- and La- new phases ($\text{Ce}_3\text{Si}_{6.25}\text{Al}_{1.75}\text{N}_{9.25}\text{O}_{5.75}$ and $\text{La}_3\text{Si}_{6.5}\text{Al}_{1.5}\text{N}_{9.5}\text{O}_{5.5}$

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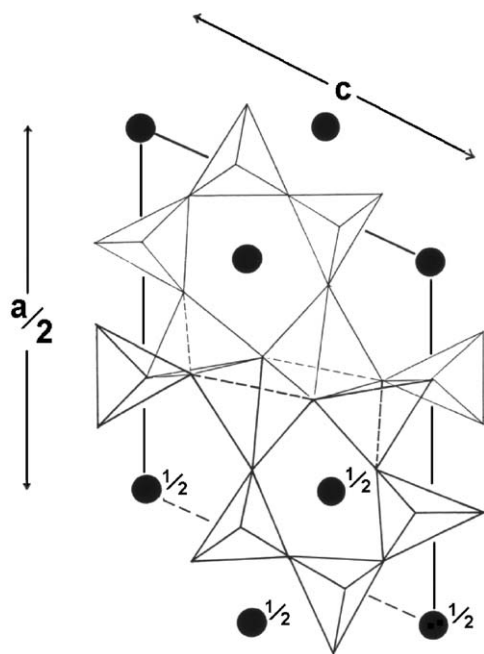


Fig. 1. [010] projection of the crystal structure of lanthanum new phase proposed by Harris et al. [23].

respectively) using a combination of single-crystal X-ray and time-of-flight neutron powder diffraction, respectively, and suggested that the original model of Harris et al. [12] was not completely correct. A comparison of the new structure (Fig. 2) with that of Harris et al. (Fig. 1) shows that the two structures are similar, but the Grins et al. cell has a doubling of the monoclinic c -axis due to periodic inversion of $[\text{Si}_2(\text{O},\text{N})_7]$ units [24].

The present work has prepared for the first time a ^{17}O -doped sample of La-New phase and obtained a ^{17}O MAS NMR spectrum for this sample. This is discussed along with the previous ^{29}Si and ^{15}N NMR data in the light of the new Grins et al. [24] structure model.

2. Experimental

The conventional route for producing ^{17}O -doped $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$ involves reacting mixtures of LaN , Si_3N_4 and $\text{La}_2^{17}\text{O}_3$. This is difficult because the compound LaN is not readily available and rapidly hydrolyses during processing. Samples were therefore prepared by reacting LaSi_3N_5 (prepared by carbothermal reduction and nitridation using $\text{La}_2\text{O}_3/\text{SiO}_2/\text{C}$ mixes) with Si^{17}O_2 . The preparation of ^{17}O -doped silica has been described elsewhere [23] and the same method was used here to give a silica product enriched to the extent of 20% in ^{17}O . Samples of new phase were prepared by reacting LaSi_3N_5 and the enriched Si^{17}O_2 at 1600°C in a carbon resistance furnace for 1 h under N_2 . These were characterized by X-ray diffraction, using a Hagg-Guinier focusing camera and $\text{CuK}\alpha_1$ radiation; no

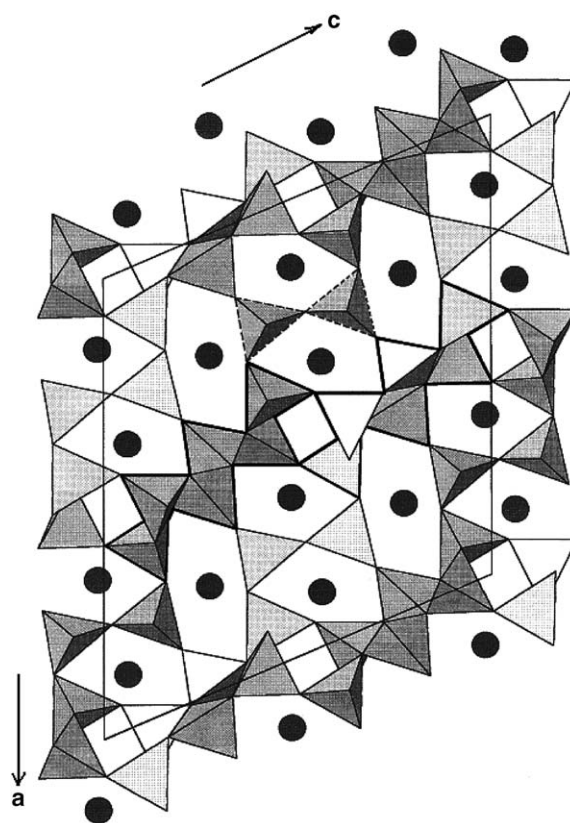


Fig. 2. The more detailed crystal structure of lanthanum new phase proposed by Grins et al. [24]. Two adjacent $[\text{T}_6\text{X}_{14}]$ units are outlined in bold type in the central part of the diagram, and one $[\text{T}_2\text{X}_7]$ unit adjacent to these has been dashed.

second phases were detected. The ^{17}O MAS NMR spectrum was recorded at 40.7 MHz using a Varian Unityplus300 spectrometer and a Doty Scientific probe with zirconia rotors 7 mm in diameter. Acquisition conditions are given in the figure captions. Chemical shifts are quoted with respect to the ^{17}O signal for enriched water.

3. Results and discussion

The structure of new phase by Grins et al., shown in Fig. 2, can be described as a three-dimensionally interlocked array of $[\text{SiN}_4]$ tetrahedra, with the lanthanum cations occupying the large interstices between these units. For the purposes of discussion it is convenient to distinguish between units of six tetrahedra (the $[\text{T}_6\text{X}_{14}]$ “ribbons” of Grins et al. [24]—outlined in bold), the central non-metal atoms in which are nitrogens in $[\text{NSi}_3]$ environments exactly as in silicon nitride, and $[\text{Si}_2(\text{O},\text{N})_7]$ units (the $[\text{T}_2\text{X}_7]$ units of Grins et al. [24]—dashed in Fig. 2) which link the $[\text{T}_6\text{X}_{14}]$ units together in the a - c plane. The latter are significant because the X-ray structure determinations suggest that the non-metal atoms projecting directly above or below

the two triangles representing the $[\text{Si}_2(\text{O},\text{N})_7]$ unit are oxygen, bonded only to a single silicon atom, i.e., in a non-bridging site. The ^{17}O NMR spectrum (Fig. 3) shows a single strong peak at 188 ppm, which by comparison with similar data for other oxynitrides [12] corresponds to a non-bridging environment as expected. However, there is also a very broad, but low-intensity peak located close to the origin of the spectrum, which related studies on oxynitride glasses [25] have shown corresponds to oxygen in a bridging environment. This is consistent with the crystal structure data which showed that only half the oxygen atoms in new phase occupied the $[\text{Si}_2(\text{O},\text{N})_7]$ non-bridging sites, leaving the remainder randomly distributed with nitrogen in bridging sites.

Dupree et al. [5] first reported the ^{29}Si spectrum of lanthanum new phase (Fig. 4(a)) and Harris et al. [9,23] also measured ^{15}N spectra (Fig. 4(b)). These authors showed that the ^{29}Si NMR spectrum had two peaks in a 3:1 intensity ratio at $\delta_{\text{Si}} = -57.3$ and -68.2 ppm, corresponding to two distinct silicon environments. However, they were unable to determine whether these corresponded to $[\text{SiN}_4]$ and $[\text{SiON}_3]$ or $[\text{SiON}_3]$ and $[\text{SiN}_2\text{O}_2]$ environments. ^{27}Al data [23], collected for an Al-substituted derivative, showed only the presence of [4]-coordinated aluminium, as expected, and this is consistent with both the X-ray crystal-structure determinations. The ^{15}N NMR spectrum [12] showed two bands centered at ca. 64 and ca. 126 ppm from the ammonium ion signal for NH_4NO_3 . Their intensities are in the ratio 4:7, which from considerations of both chemical shift and breadth were attributed to $[\text{NSi}_2]$ and $[\text{NSi}_3]$ environments, again in agreement with the nitrogen environments found from the X-ray crystal-structure work.

However, Fig. 2 suggests that there should be three silicon environments, $[\text{SiN}_4]$, $[\text{SiN}_3\text{O}]$ and $[\text{SiN}_2\text{O}_2]$.

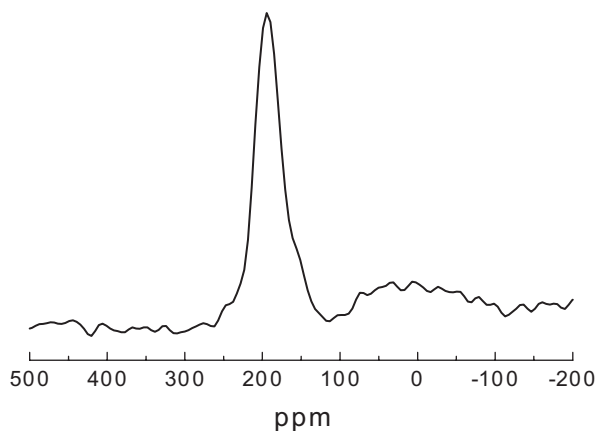


Fig. 3. ^{17}O NMR spectrum of La-new phase: Spectrometer operating conditions: pulse angle 20° ; recycle delay 10s; number of transients 3184; spinning rate 9 kHz.

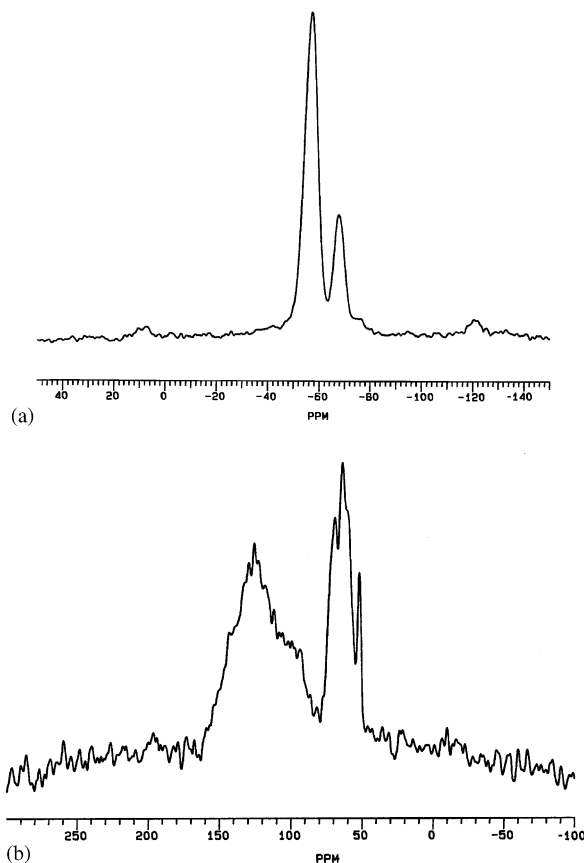


Fig. 4. (a) The ^{29}Si spectrum and (b) the ^{15}N spectrum of lanthanum new phase (after [6] and [12], respectively).

From the ordering scheme given by Grins et al. [24], which had four nitrogen atoms in the $[\text{NSi}_3]$ sites, two oxygens in non-bridging sites and the remaining seven nitrogens and two oxygens randomly distributed in bridging sites, the proportion of $[\text{SiN}_4]$ to $[\text{SiN}_3\text{O}]$ to $[\text{SiN}_2\text{O}_2]$ sites can be evaluated as 5:5:2. However this is not in agreement with the 3:1 intensity ratio observed for the -57.3 and -68.2 ppm peaks in the ^{29}Si spectrum, no matter what assumptions are made about pairs of peaks overlapping. A more likely way to account for the 3:1 ratio is in terms of the six silicon atoms in the $[\text{T}_6\text{X}_{14}]$ units and two in the $[\text{T}_2\text{X}_7]$ units. Because these units link together it is impossible to avoid the three silicon coordinations listed above, but the proportion of $[\text{SiN}_3\text{O}]$ can be minimized by including all the oxygen randomly in the non-metal sites of the $[\text{T}_2\text{X}_7]$ units, thereby making them of overall composition of $[\text{SiN}_2\text{O}_2]$ and generating an overall $[\text{SiN}_4]:[\text{SiN}_3\text{O}]:[\text{SiN}_2\text{O}_2]$ ratio of 4.4:1.6:2. If the chemical shifts of the $[\text{SiN}_4]$ and $[\text{SiN}_3\text{O}]$ tetrahedra are very similar (as has been observed for both the melilite and J-phases in the Y-Si-O-N system [16,21,26]), then a 2-peak spectrum with an intensity ratio of 3:1 would result.

4. Conclusions

The ^{17}O NMR spectrum for lanthanum new phase shows one sharp peak, corresponding to non-bridging oxygen sites, in agreement with the new X-ray crystal structure of Grins et al. [24] which showed that the non-bridging non-metal sites in the $[\text{T}_2\text{X}_7]$ units were occupied by oxygen. One additional weak and broadened peak was observed at a chemical shift close to zero ppm, corresponding to bridging oxygen present along with nitrogen in the non-metal sites linking together the $[\text{T}_6\text{X}_{14}]$ and $[\text{T}_2\text{X}_7]$ structural units.

The apparent 3:1 observed intensity ratio for the two peaks in the ^{29}Si NMR spectrum is most convincingly explained if it is the ratio between combined $[\text{SiN}_4]$ and $[\text{SiN}_3\text{O}]$ peaks and a separate $[\text{SiN}_2\text{O}_2]$ peak, which could arise if all the oxygen in the structure was present in the $[\text{T}_2\text{X}_7]$ units, giving the individual tetrahedra an overall composition of the type $[\text{SiN}_2\text{O}_2]$.

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