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Journal of Solid State Chemistry 177 (2004) 2928–2932

JOURNAL OF SOLID STATE CHEMISTRY

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Silicon/aluminum and oxygen/nitrogen ordering in lanthanum U – phase ($La_3Si_3Al_3O_{12}N_2$)

Ahmet Koroglu,[a] Derek P. Thompson,[b,*] David C. Apperley,[c] and Robin K. Harris[c]

[a] Department of Physics, Science and Arts Faculty, University of Ondokuzmayis, Kurupelit, Samsun 55139, Turkey
[b] Advanced Materials Group, School of Chemical Engineering and Advanced Materials, University of Newcastle, Newcastle upon Tyne NE1 7RU, UK
[c] Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, UK

Received 10 July 2003; received in revised form 4 March 2004; accepted 4 April 2004

Abstract

High-resolution ^{29}Si, ^{27}Al, ^{15}N, and ^{17}O MAS NMR spectra have been obtained for both glass and crystalline samples of lanthanum U-phase, $La_3Si_3Al_3O_{12}N_2$. Previous X-ray single-crystal studies have shown that this phase is iso-structural with rare-earth gallogermanates of the type $Ln_3Ga_5GeO_{14}$, the atomic arrangement consisting of layers of [(Si,Al)(O,N)$_4$] tetrahedra in the x, y plane of the hexagonal unit cell, linked together in the z-direction by [AlO_6] octahedra, with rare-earth cations occupying the large holes in this network. However, previous studies obtained only a limited amount of information about cation and anion ordering, mainly deduced from bond-length data. NMR spectra have not only enabled the change in structure from glass to crystalline ceramic to be monitored, but have also given detailed ordering information about the latter, indicating partial disorder of both (Si,Al) and (O,N) on their respective sites in the tetrahedra.

Keywords: MAS NMR; Sialons; Lanthanum U-phase; Disorder

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1. Introduction

When metal oxides (MgO, Y_2O_3, Ln_2O_3) are used for the densification of silicon nitride ceramics, the metal oxide reacts with silicon nitride and its surface silica to form a eutectic liquid which promotes densification and then cools down to form an oxynitride glass. Heat treatment of these glasses at temperatures above the glass transition temperature results in crystallization, with multiphase products forming determined by the phase relationships in the particular metal sialon system at the heat-treatment temperature used. Certain glass compositions can be crystallized to give a single-phase nitrogen glass ceramic, and sialon U-phase is of this type. The phase was originally observed in low concentrations in the grain boundaries of α and β sialon ceramics densified with the lower atomic number rare-earth oxides [1] and later work showed it to occur for Ln = La–Dy, with La U-phase the most stable (melting point ≈1400°C). Although Grins et al. [2] gave U-phase the general formula, $Ln_3Si_{3-x}Al_{3+x}O_{12+x}N_{2-x}$, with $0<x<1$ and Ln with $Z \leqslant 62$, most samples in the current research had compositions similar to that given by Fernie et al. [1], i.e. $Ln_3Si_3Al_3O_{12}N_2$. The unit-cell dimensions of the hexagonal unit cell decrease with increasing atomic number of rare-earth cation as expected.

Crystal structure determination of U-phase (see Fig. 1; after Käll et al. [3]) has shown it to be isomorphous with $Ln_3Ga_5GeO_{14}$ [4], with an atomic arrangement consisting of individual [AlO_6] octahedra and $[(Si, Al)(O, N)_4]$ tetrahedra, present in the ratio 1:5, linked together in a three-dimensional network with the Ln atoms occupying the large interstices. Käll et al. [3] assumed that the octahedral cation was aluminum, and the surrounding six non-metals were oxygen; since X-ray diffraction was unable to distinguish silicon and aluminum or between oxygen and nitrogen, they were unable to give further details about the Si/Al and O/N ordering in tetrahedral sites.

The present paper describes the preparation of U-phase using ^{15}N and ^{17}O enriched starting materials

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*Corresponding author. Fax: +44-191-222-8563.
E-mail address: d.p.thompson@ncl.ac.uk (D.P. Thompson).

0022-4596/$ - see front matter
doi:10.1016/j.jssc.2004.04.001

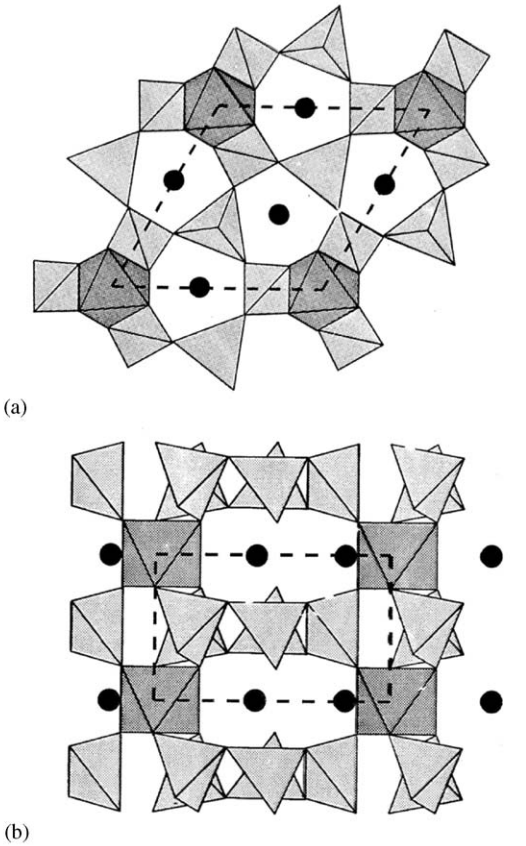

Fig. 1. Crystal structure of sialon U-phase projected down (a) [001] and (b) [$\bar{1}$20] (after Kall et al. [3]).

and presents ^{27}Al, ^{29}Si, ^{15}N, and ^{17}O MAS NMR spectra for this compound. These spectra are interpreted in relation to the crystal structure and the composition of U-phase.

2. Experimental

Lanthanum U-phase was prepared by melting followed by crystallization, using appropriate mixes of La_2O_3, SiO_2, Al_2O_3, and Si_3N_4 powders for the initial glass melting. La_2O_3 (99.9%) was supplied by Rare-Earth Products and alumina (Grade A17) was obtained from Alcoa, but the silica and silicon nitride powders were prepared in-house, appropriately doped with ^{17}O and ^{15}N, respectively. The preparation of ^{15}N-doped silicon nitride and ^{17}O-doped silica has been described elsewhere [5], and silicon nitride and silica prepared in this way were enriched to the extent of ca. 60% in ^{15}N and 20% in ^{17}O, respectively, in separate samples. Glasses were produced from the starting powders by melting at 1700°C in a tungsten element resistance furnace for half an hour followed by rapid cooling in a nitrogen atmosphere. Crystalline lanthanum U-phase was produced by heat treating the resulting glass at 1200–1250°C for 25 h. Samples were characterized by X-ray diffraction, using a Hägg–Guinier focusing camera and Cu$K\alpha_1$ radiation and showed only lanthanum U-phase in the products. ^{29}Si, ^{15}N, ^{17}O, and ^{27}Al MAS NMR spectra were recorded at 59.583, 30.400, 40.687, and 78.158 MHz, respectively, using a Varian Unityplus spectrometer and a Doty Scientific probe with zirconia rotors 7 mm in diameter (except for the ^{27}Al spectra for which a 5 mm o.d. rotor and corresponding probe were used). Acquisition conditions are given in the appropriate figure captions. Chemical shifts are quoted with respect to the ^{29}Si signal from tetramethylsilane, the nitrate group nitrogen in solid ammonium nitrate for ^{15}N (−5.1 ppm with respect to nitromethane), the oxygen in isotopically enriched water for ^{17}O, and 1 M $AlCl_3$ solution for ^{27}Al.

3. Results

The ^{29}Si NMR spectrum of $La_3Si_3Al_3O_{12}N_2$ glass appeared to show four overlapping peaks at −53, −60, −70, and −80 ppm (see Fig. 2(a)), and by analogy with the interpretation of previous sialon glass spectra [6–9], these are consistent with $[SiN_3O]$, $[SiN_2O_2]$, $[SiO_3N]$, and $[SiO_4]$ environments. After crystallization, the

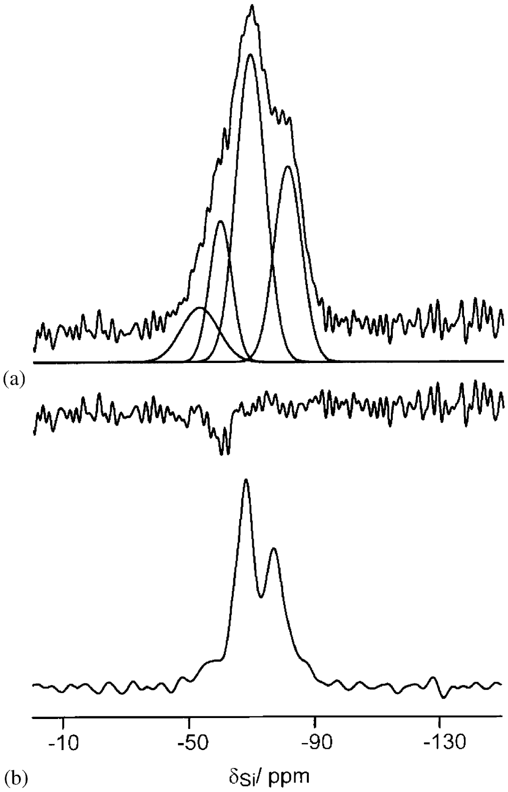

Fig. 2. The ^{29}Si MAS NMR spectrum of lanthanum U-phase showing (a) the precursor $La_3Si_3Al_3O_{12}{}^{15}N_2$ glass and (b) the final crystalline product. Spectrometer operating conditions: pulse angle 90°, recycle delay 120 s; number of transients 1182 and 500; spinning rates 5.5 and 4.8 kHz, for (a) and (b) respectively.

spectrum changed to show two peaks at −68 and −77 ppm in the intensity ratio 3:2 corresponding to [SiO_3N] and [SiO_4] environments (Fig. 2(b)). These results are consistent with a previous investigation [5], which reported peaks at −70 and −81 ppm for La–sialon U-phase in the intensity ratio 2:1. If the glass and crystalline spectra are compared, it can be seen that the overall center of gravity of the distribution is fairly similar, but the more nitrogen-rich environments in the glass have disappeared, leaving the [SiO_3N] and [SiO_4] peaks, which have shifted to slightly higher frequencies.

The ^{27}Al NMR spectrum of U-phase glass showed a single asymmetrical highly broadened peak with maximum intensity at 59 ppm (Fig. 3(a)), corresponding to an [AlO_4] environment. Probably the broadening on the low-frequency side arises, at least in part, from overlapped [AlO_5] and [AlO_6] environments, as generally observed in M–Si–Al–O–N glasses [5,10,11], though the shape may also be explained by quadrupolar effects. Crystallization of the glass into U-phase gave a spectrum with two peaks at −5 and 61 ppm (Fig. 3(b)) attributable to [AlO_6] and [$Al(O,N)_4$] environments, respectively. Because of the shape and breadth of the 61 ppm peak, it is impossible to determine precisely the relative amounts of [AlO_4] and [AlO_3N] environments. These results are in moderate agreement with previous work [5], which reported peaks at 11 and 50 ppm for crystalline U-phase. The shift of the former from the value of −5 ppm observed here may be due to $LaAlO_3$ impurity (traces of which are difficult to completely eliminate during crystallization), and the discrepancy in the four-coordinated peak position cannot be commented on reliably because of the large line width, but may be due to the presence of uncrystallized glass.

The ^{15}N NMR spectrum of lanthanum U-phase glass (Fig. 4(a)) showed two peaks at −227 and −302 ppm in the intensity ratio ca. 3.5:6.5, corresponding to [NSi_2] and [NSi_3] environments. Crystalline lanthanum U-phase also gave two peaks at −218 and −277 ppm but in the intensity ratio ca. 10:1 (Fig. 4(b)). This behavior is typical of crystallized oxynitride glass, which before crystallization exhibits both [NSi_3] and [NSi_2] environments [5,10], but the [NSi_3] environment disappears on crystallization. The weak −277 ppm peak for the crystalline material may perhaps be attributed to background noise.

The ^{17}O NMR spectrum of lanthanum U-phase glass (Fig. 5(a)) shows two or three peaks at 74, 168, and possibly 186 ppm, the first one corresponding to bridging oxygen sites. Crystalline U-phase showed a not dissimilar spectrum with two peaks at 102 and 170 ppm (the latter unsymmetrical), again corresponding to bridging and non-bridging sites, respectively (Fig. 5(b)) [12–15]. The peak at 168 ppm in the glass is

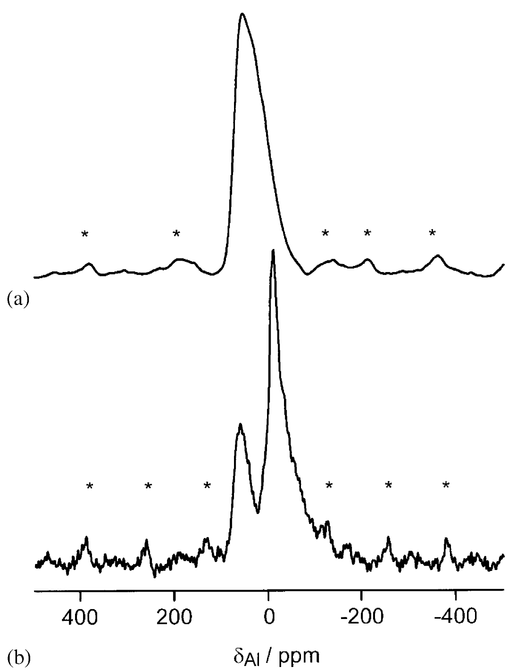

Fig. 3. The ^{27}Al MAS NMR spectrum of lanthanum U-phase showing (a) the precursor $La_3Si_3Al_3O_{12}{}^{15}N_2$ glass and (b) the final crystalline U-phase. Spectrometer operating conditions: pulse angle 15°; recycle delays, number of transients and spinning rates were 0.2 s, 8000, 11.6 kHz and 0.5 s, 3000 and 10.1 kHz, for (a) and (b) respectively. Spinning side bands/satellite transitions are indicated by asterisks.

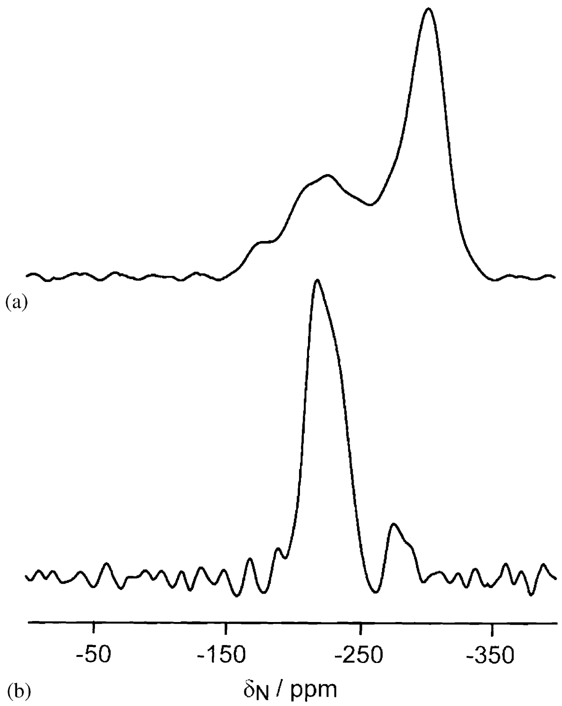

Fig. 4. The ^{15}N MAS NMR spectrum of (a) the precursor $La_3Si_3Al_3O_{12}{}^{15}N_2$ glass and (b) the final crystalline U-phase. Spectrometer operating conditions: pulse angle 45°; recycle delay 600 s; number of transients 110 and 100, spinning rates 3.67 and 4.27 kHz, for (a) and (b) respectively.

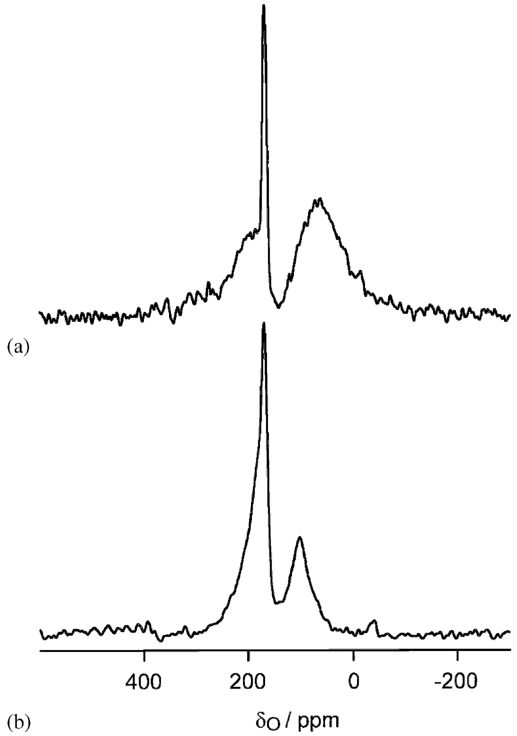

Fig. 5. The ^{17}O MAS NMR spectrum of (a) $La_3Si_3Al_3{}^{17}O_{12}N_2$ U-phase glass and (b) the final crystalline U-phase. Respective spectrometer operating conditions: pulse angles 32.7° and 18°; recycle delays 10.0 and 5 s; number of transients 500 and 1584; spinning rates 7.46 and 8.5 kHz.

quite sharp and in contrast to the broadened peaks shown by most nitrogen glasses. We are not in a position to give a convincing explanation for this peak, but we do not think it is an instrumental artifact. Possibly this peak is due to nano-size crystallites of lanthanum U-phase, too small to be observed by X-ray diffraction but nevertheless present after initial glass melting. Alternatively, it may arise from some non-framework mobile species.

4. Discussion

If it is assumed that the octahedral site in the crystalline U-phase structure is occupied by aluminum and the surrounding six non-metal atoms are all oxygen, then the remaining eight non-metal atoms in the unit cell, i.e. six oxygens plus two nitrogens, will form the corners of the two tetrahedra centered on triad axes, which will therefore be on average of the type $[(Si,Al)O_3N]$. On the assumption that the non-bridging non-metal in these tetrahedra (i.e., the one located on the triad axis) is oxygen, the remaining three non-metals would be O_2N, and there is no reason to suggest other than a random distribution. This would leave the other three tetrahedra in the cell to comprise two oxygens plus two $[O_{2/3}N_{1/3}]$ atoms, giving an overall composition of $[(Si,Al)O_{3.33}N_{0.67}]$, i.e., a mix of two $[(Si,Al)O_3N]$ and one $[(Si,Al)O_4]$ for the three tetrahedra. The five tetrahedra in the cell would therefore be four of the type $[(Si,Al)O_3N]$ and one of the type $[(Si,Al)O_4]$. The observed intensity ratio of ca. 3:2 between the $[SiO_3N]$ and $[SiO_4]$ NMR peaks corresponds to a more oxygen-rich result, and whereas this might infer that aluminum preferentially occupied the triad-centered tetrahedra, a more likely explanation is that the starting composition has lost some nitrogen during melting. The ^{27}Al NMR spectrum confirms the existence of octahedral and tetrahedral sites in the structure. The octahedral peak is strong, corresponding to $[AlO_6]$ units, and the tetrahedral peak probably consists of contributions from both $[AlO_4]$ and $[AlO_3N]$ tetrahedra, overlapping in the spectrum. From ^{17}O evidence (non-bridging resonance), the terminal non-metal atoms in crystalline U-phase are probably oxygen; this is supported by the ^{15}N spectrum, which showed no evidence for nitrogen going into these sites.

5. Conclusions

^{29}Si, ^{27}Al, ^{15}N, and ^{17}O MAS NMR spectra collected for sialon U-phase are broadly consistent with the proposed X-ray structure. The presence of octahedral aluminum is clearly demonstrated, but there is no evidence for strong ordering of silicon and aluminum in the remaining five tetrahedral sites. Both the ^{15}N and ^{17}O spectra support the non-bridging non-metal atom in triad-centered tetrahedra being oxygen and, assuming that the octahedral aluminum is surrounded by six oxygens, the nitrogen atoms are then randomly distributed in the remaining six non-metal sites.

Acknowledgments

We are grateful to the EPSRC for access to the solid-state NMR research service in the University of Durham Chemistry Department.

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