

Evolution of crystalline aluminates from hybrid gel-derived precursors studied by XRD and multinuclear solid state MAS NMR

III. Lanthanum hexaluminate, $\text{LaAl}_{11}\text{O}_{18}$

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Abstract

A hybrid gel synthesis is described which produces crystalline lanthanum hexaluminate at 1200°C without the intermediate appearance of LaAlO_3 . XRD in conjunction with ^{27}Al and ^{139}La MAS NMR indicates that until the exothermic appearance of γ -alumina at about 900°C, the gel remains amorphous and contains Al in three types of site, one of which is characterised by an NMR resonance at 36 ppm. By 1200°C, the La ions have moved into the mirror planes between the γ -alumina blocks and the crystallinity of the $\text{LaAl}_{11}\text{O}_{18}$ which forms in an exothermic event at about this temperature continues to improve with further heating to 1350°C. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Aluminates having a layer structure consisting of spinel blocks separated by a cleavage plane containing larger ions are commonly called hexaluminates, and are typified by the two related structures β -alumina and magnetoplumbite. Where the large cation is Na^+ , as in Na β -alumina, the compounds possess excellent ionic conduction properties, but other uses for these compounds as fluorescent host materials, for lasers, nuclear waste disposal and for high temperature com-

bustion catalysis have also been proposed [1]. Recently, the cleavage properties of materials with the magnetoplumbite structure have been exploited as possible interface compounds to be interposed between the fibres and the matrix of fibre-reinforced oxide ceramic composites [2].

The structure and chemical composition of the hexaluminate phases is controlled by the nature of the ions within the cleavage layer, which has a mirror plane of symmetry.

In lanthanum hexaluminate, the size and charge of the La^{3+} mirror plane ion determines that this compound will adopt the magnetoplumbite structure, which differs from the structure of β -alumina in terms of its method of charge compensation. Lanthanum hexaluminate has been reported [3] to contain defects

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at both the Al and La sites associated with the mirror plane. The Al defects take the form of pairs of interstitial Al ions which are formed by a Frenkel mechanism and move into the mirror plane [3]. To avoid cation–cation interaction, the La site in the vicinity of these interstitial Al ions may either become vacant or be filled with an interstitial O atom [3]; the X-ray structure refinement [3] suggests the La vacancy is more likely.

The correct formula of lanthanum hexaluminate is $\text{La}_{1-x}\text{Al}_{12-y}\text{O}_{19-z}$, but there is disagreement in the literature [1] regarding the values of x , y and z (the lanthanum vacancy model predicts a nonstoichiometric formula of $\text{La}_{0.833}\text{Al}_{11.833}\text{O}_{19.0}$ [3]). For the sake of brevity we use the generic formula $\text{LaAl}_{11}\text{O}_{18}$ throughout this paper.

$\text{LaAl}_{11}\text{O}_{18}$ can be synthesised by solid state reaction between the oxides [4]; the reaction proceeds via LaAlO_3 , which then reacts very slowly with further Al_2O_3 at 1650°C . Sol–gel synthesis using an alumina sol and La acetate is reported [5] to provide an improved yield of product at the lower calcining temperature of 1450°C . The present work draws on previous experience with hybrid (organic/inorganic) gel preparations of other aluminates using aluminium alkoxide as one of the reactants [6,7] which suggests that a similar synthesis may have the advantage of product crystallisation at even lower temperatures. As in the previous work [6,7], a combination of thermal analysis, X-ray powder diffraction and solid state multinuclear nuclear magnetic resonance spectroscopy (MAS NMR) was used to monitor the changes taking place in such a hybrid $\text{LaAl}_{11}\text{O}_{18}$ gel during its thermal transformation and crystallisation. ^{27}Al MAS NMR spectroscopy has been widely used to study the atomic environments in gels and other poorly crystalline phases, but ^{139}La NMR spectroscopy has generally been much less useful because of the large quadrupole interaction in this heavy nucleus (spin 7/2) which broadens the spectra by a factor of about 30 by comparison with ^{27}Al in sites of similar distortion [8]. A frequency-swept spin-echo NMR technique has been successfully used to obtain ^{139}La spectra of La_2O_3 and some La perovskites [9], but a true MAS NMR spectrum has previously been obtained only for LaAlO_3 [8] where the La is in a symmetric site coordinated to 12 oxygens.

The aim of the present work is to prepare $\text{LaAl}_{11}\text{O}_{18}$ from a hybrid gel system and to study its thermal transformation to the crystalline phase, with particular attention to changes in the environments of Al and La which were monitored by XRD and solid state MAS NMR spectroscopy throughout the thermal treatment.

2. Experimental

2.1. Gel preparation

Reagent grade Al-sec-butoxide was dissolved in 2-propanol at a concentration of 4 mol l^{-1} and stabilised by the addition of 38 mol% acetylacetonate, calculated on the basis of the Al content. The calculated amount of reagent grade lanthanum acetate was dissolved in this solution with vigorous stirring, the whole preparation being carried out under an argon atmosphere until the onset of gelation. The suspension was peptized by the addition 65% HNO_3 (60 ml l^{-1} of solution) and the pH set to 6–7 to obtain a clear sol. This sol was then exposed to air at 60°C to obtain the gel, from which the solvent was removed under vacuum at $40\text{--}60^\circ\text{C}$ in a drying oven. This removal of the organic residues at low temperatures was hoped to lead to the formation of a well-ordered structure at an early stage, and to the crystallisation of $\text{LaAl}_{11}\text{O}_{18}$ at lower temperatures than previously reported.

Thermal analysis was carried out on the dried gel in flowing air (50 ml min^{-1}) at a heating rate of $10^\circ\text{C min}^{-1}$ using a Rheometrics STA 1500 thermoanalyser.

Aliquots of the gel were heated in air in platinum crucibles for 60 min in a pre-heated electric muffle furnace, then examined by XRD using a Philips PW1700 computer-controlled diffractometer with a graphite monochromator and Co $K\alpha$ radiation. Solid state ^{27}Al and ^{139}La MAS NMR spectroscopy was carried out at 11.7T using a Varian Unity 500 spectrometer and a 5 mm high-speed Doty MAS probe spun at 10–12 kHz, with the following acquisition conditions: ^{27}Al : spectra acquired at 130.245 MHz using a 15° pulse of $1\text{ }\mu\text{s}$ and a recycle time of 1 s, the spectra referenced to $\text{Al}(\text{H}_2\text{O})_6^{3+}$. ^{139}La : spectra acquired at 70.270 MHz using a Hahn spin-echo pulse sequence with 16-step phase cycling [10], a refocusing interval of $100\text{ }\mu\text{s}$, a pulse recycle time of 0.1 s and a

spectral width of 1 MHz. Typically 150,000–250,000 transients were acquired, and the spectra were referenced to a 1 M LaCl_3 solution.

3. Results and discussion.

The DSC and TG traces of $\text{LaAl}_{11}\text{O}_{18}$ gel are shown in Fig. 1.

The gel loses its volatile components (solvents and alcohol by-products) in several exothermic stages below 450°C , the total mass loss associated with these exotherms being 60% up to 420°C (Fig. 1). After the loss of the volatiles, the gel remains X-ray amorphous up to the temperature of the next exothermic event at about 936°C . At this temperature, broad XRD reflections corresponding to $\gamma\text{-Al}_2\text{O}_3$ appear in the XRD trace (indicated by asterisks in Fig. 2D). A broad exotherm at 1237°C accompanies the crystallisation of $\text{LaAl}_{11}\text{O}_{18}$; the XRD trace of this phase indicates that its poor crystallinity at 1200°C (Fig. 2(E)) improves markedly on heating to 1350°C (Fig. 2(F)), and corresponds well to the pattern of hexagonal

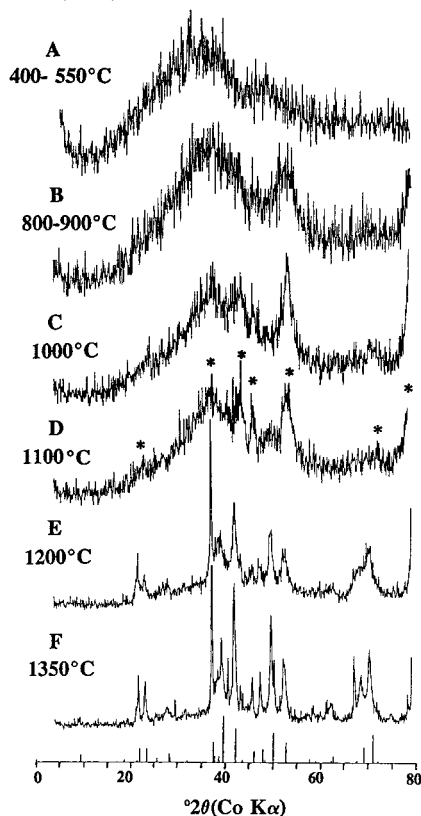


Fig. 2. X-ray powder diffractograms of $\text{LaAl}_{11}\text{O}_{18}$ gel heated at the indicated temperatures for 60 min. Asterisks indicate the position of $\gamma\text{-Al}_2\text{O}_3$ reflections (PDF no. 10-425). Lower diagram: hexagonal $\text{LaAl}_{11}\text{O}_{18}$ diffraction pattern (PDF no. 33-699).

$\text{LaAl}_{11}\text{O}_{18}$ (PDF no. 33-699) shown at the bottom of Fig. 2. However, some of the observed XRD peaks, notably the major 017 reflection at $d = 2.64 \text{ \AA}$, remain broad and poorly developed even after heating to 1350°C . A small trace of crystalline $\alpha\text{-Al}_2\text{O}_3$ is also detectable at this temperature, resulting from the thermal transformation of a slight excess of $\gamma\text{-Al}_2\text{O}_3$.

The ^{27}Al MAS NMR spectra of the unheated and heated gels are shown in Fig. 3.

The spectrum of the unheated gel (Fig. 3A) shows that most of the Al is located in at least two octahedral sites, the partially resolved lineshapes of which suggest multiple sites rather than a quadrupolar profile. Heating to 550°C converts a significant proportion of these octahedral sites to a mixture of tetrahedral (chemical shift 63 ppm) and a site characterised by a resonance at 34–36 ppm (Fig. 3B) which has been

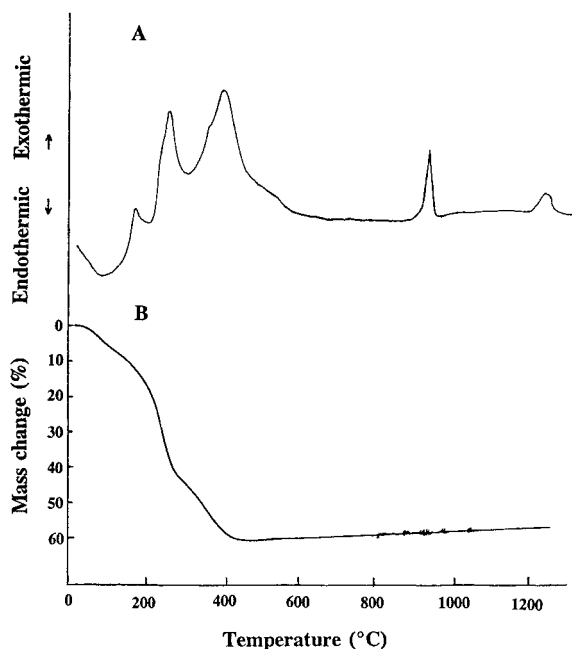


Fig. 1. Thermal analysis traces of hybrid $\text{LaAl}_{11}\text{O}_{18}$ gel in flowing air (50 ml min^{-1}), heating rate $10^\circ\text{C min}^{-1}$: (A) DSC trace; (B) TG trace.

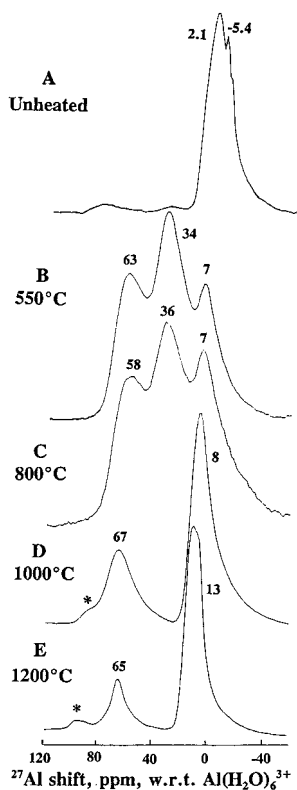


Fig. 3. $11.7T$ ^{27}Al MAS NMR spectra of $\text{LaAl}_{11}\text{O}_{18}$ gel, unheated and heated at the indicated temperatures. Asterisks indicate spinning side bands.

noted in other aluminate gels [6,7], amorphous aluminosilicate minerals and glasses. This site has previously been attributed either to Al in 5-fold coordination with oxygen, or to Al in a distorted tetrahedral environment such as occurs in the vicinity of the oxygen tricluster defects found in aluminosilicates such as mullite [11]. The formation of tricluster defects provides a charge balancing mechanism for the tetrahedral substitution of Al for Si in aluminosilicates but this is unlikely to be the case in the present system. Although the structure of some magnetoplumbite hexaluminates containing divalent cations is known to contain one pentacoordinated Al site which might at first sight provide an explanation for the 36 ppm NMR resonance, the X-ray refinement [3] suggests that in the lanthanum compound this site is better described as distorted tetrahedral, and furthermore, the 36 ppm site is not present in the samples containing crystalline hexaluminate. Some of the dis-

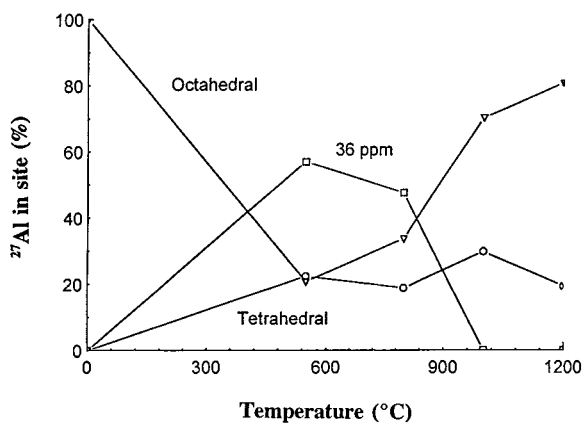


Fig. 4. Changes in the ^{27}Al site occupancies of $\text{LaAl}_{11}\text{O}_{18}$ gel as a function of heating temperature.

torted tetrahedral sites are randomly vacant because of their proximity to the interstitial Al pairs [3], and may correspond to the slight shoulder observed at about 45 ppm in samples which have just begun to crystallise (Fig. 3D). By analogy with mullite gels, therefore, the 36 ppm resonance could correspond to the distorted tetrahedral Al site prior to its incorporation in the interstitial Al defect structure in the region of the mirror plane. Curve-fitting and integration of the ^{27}Al NMR spectra indicates that both the tetrahedral and 36 ppm resonances grow at the expense of the initial octahedral peaks, the 36 ppm resonance reaching a maximum at 550°C before decaying away abruptly by 1000°C (Fig. 4).

Most of the 36 ppm resonance is converted to octahedral sites at 1000°C (Fig. 4) with a small increase in the tetrahedral intensity also apparent. The ^{27}Al spectrum at this temperature resembles that of $\gamma\text{-Al}_2\text{O}_3$ determined under the same conditions and at the same field strength (tetrahedral and octahedral shifts of 66 and 7.6 ppm respectively, tetrahedral/octahedral ratio = 0.63) but with slightly less tetrahedral Al (observed ratio = 0.42). After the appearance of crystalline $\text{LaAl}_{11}\text{O}_{18}$ at about 1200°C (Fig. 3E), the observed tetrahedral/octahedral ratio is 0.24, in good agreement with the value of 0.23 expected by Dupree et al. from the crystal structure [8]. The position of the octahedral peak in this phase (13 ppm) is slightly downfield of that found by Dupree et al. working at the lower field strength of 360 MHz [8]. The present octahedral resonance may also show

signs of structure, as observed by those authors, who were however unable to decide whether this was due to a poorly resolved quadrupole lineshape or to the presence of more than one slightly different octahedral Al sites [8].

The ^{27}Al NMR spectra therefore suggest that on losing its volatile constituents, the $\text{LaAl}_{11}\text{O}_{18}$ gel contains three types of Al co-ordination. The site characterised by a resonance at 36 ppm may represent the precursor to either the distorted tetrahedral site adjacent to the mirror plane, or to the interstitial Al Frenkel defect pairs which have been suggested to adopt a square pyramidal configuration [3] when the $\text{LaAl}_{11}\text{O}_{18}$ structure is eventually established. However, in the final structure, the total number of Al atoms in these distorted tetrahedral and interstitial sites (7.3% and 2.6% of the total Al sites respectively [3]) is much less than the occupancy of the 36 ppm sites, which reaches a maximum of 57% at 550°C. Most of the 36 ppm sites in the gel eventually become the octahedral atoms of the γ -alumina spinel structure blocks after their crystallisation at about 1000°C. The concomitant appearance of the interstitial defect may be indicated by the slight upfield asymmetry of the tetrahedral resonance (Fig. 3D and E).

Typical ^{139}La MAS NMR spectra of the unheated and heated gels are shown in Fig. 5.

All the ^{139}La spectra are typically broad, especially before crystallisation, as is expected for distorted polyhedral La environments with varying La–O bond lengths [8]. In the non-crystalline samples (<900°C) the centre-of-gravity (COG) of the peak envelope tends to be negative with respect to LaCl_3 solution, but with a detectable trend towards more positive shift values with increased heating temperatures (Fig. 6), suggesting a decrease in shielding of the La as the solvent and by-products are removed from the gel. Although the unheated and 550°C spectra (Fig. 5A and B) are noisy, they may contain an indication of two components, a narrower (less shielded) and a broader (more shielded) resonance; the latter appears to persist to at least 900°C (Fig. 5C). On crystallisation of the gel at about 1000°C, the ^{139}La peak envelope becomes markedly narrower and adopts a more deshielded shift value, which however becomes slightly more shielded as the La moves into its final position in the mirror plane of the $\text{LaAl}_{11}\text{O}_{18}$ (Fig. 6). The significance of these shift values is unknown

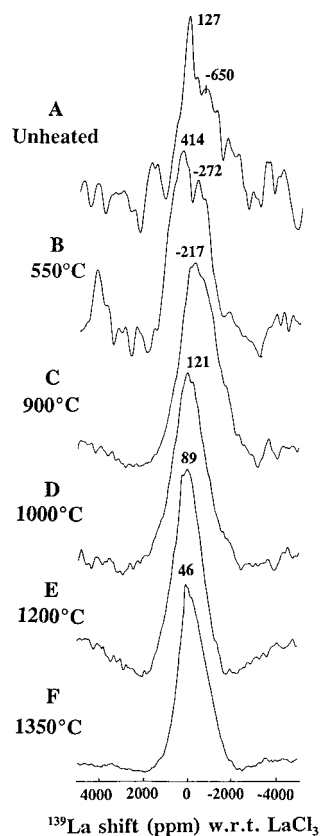


Fig. 5. 11.7T ^{139}La MAS NMR spectra of $\text{LaAl}_{11}\text{O}_{18}$ gel unheated and heated at the indicated temperatures.

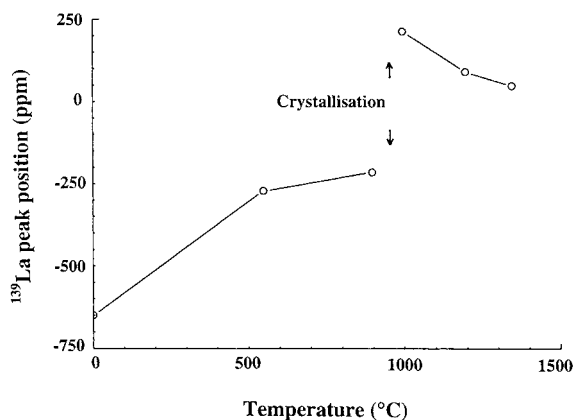


Fig. 6. Change in the position of the COG of the ^{139}La MAS NMR resonance as a function of heating temperature.

because of the paucity of tabulated ^{139}La data for known compounds; those which have been reported to date have considerably more positive isotropic chemical shifts (425 ppm for La_2O_3 [9], 425–443 ppm for the perovskites LaCrO_3 and $(\text{La},\text{Sr})\text{CrO}_3$ [9], 4230 ppm for LaCoO_3 [9] and 375 ppm for LaAlO_3 [8]). The comparatively symmetrical LaO_{12} environment of the latter gives rise to a comparatively sharp MAS line with a quadrupolar peak shape [8]. However the less positive shifts found in all the present samples, including crystalline $\text{LaAl}_{11}\text{O}_{18}$, suggest that in all these samples the La is more shielded than in the La perovskites. The considerable difference in the ^{139}La shift between LaAlO_3 and the present $\text{LaAl}_{11}\text{O}_{18}$ is interesting, since in both phases the La occurs in a 12 coordinated polyhedron; in the latter, however, the La site is less symmetrical with six of the 12 oxygens at a distance of 2.71 Å and the other six further away, at a distance of 2.78 Å. The ^{139}La spectra suggest that the La ions begin to migrate progressively into the structure at about the temperature at which the spinel regions are established ($>1000^\circ\text{C}$), but these movements are sluggish, as would be expected for a large tripositive species.

4. Conclusions

1. Hybrid gel synthesis of $\text{LaAl}_{11}\text{O}_{18}$ using aluminium sec-butoxide and lanthanum acetate in acetylacetonate and 2-propanol produces a product which thermally transforms via γ -alumina to the crystalline hexaluminate at 1200°C without the appearance of LaAlO_3 .
2. After the exothermic removal of the volatiles in several steps up to about 420°C , the gel is X-ray amorphous, and remains so until the exothermic appearance of poorly crystalline γ -alumina at 900 – 1000°C . The Al ions occur in the amorphous phase

in three types of site (octahedral, tetrahedral and a site characterised by an NMR resonance at 36 ppm). The latter attains its maximum Al occupation at about 550°C but disappears abruptly at the onset of γ -alumina crystallisation at 1000°C .

3. At 1000 – 1200°C the La ions begin to move into the mirror planes between the spinel blocks with the concomitant formation of charge-compensating Al defects. The crystallinity of the $\text{LaAl}_{11}\text{O}_{18}$, the appearance of which coincides with a small exothermic event at about 1200°C , continues to improve on heating to 1350°C .

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