Evolution of crystalline aluminates from hybrid gel-derived precursors studied by XRD and multinuclear solid state MAS NMR IV: Calcium dialuminate, $CaAl_4O_7$ and calcium hexaluminate, $CaAl_{12}O_{19}$

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Abstract

X-ray amorphous calcium aluminate gels of dialuminate and hexaluminate composition were prepared, the former by two methods, and their thermal crystallisation was monitored by thermal analysis, X-ray powder diffraction and ^{27}Al MAS NMR. Both gel compositions lose a large amount of solvent and organic by-products below 600°C, forming amorphous precursors with ^{27}Al NMR spectra containing resonances corresponding to tetrahedral and octahedral sites, and another site with a peak at 36–39 ppm. The dialuminate gel crystallises abruptly at 900°C to the essentially phase-pure compound containing Al predominantly in two distorted tetrahedral environments. The hexaluminate gel crystallises exothermically at 900°C to γ-alumina spinel, containing only tetrahedral and octahedral Al. The magnetoplumbite structure of the hexaluminate phase appears in an exothermic reaction at 1160°C, this phase-pure reaction product containing Al atoms in one tetrahedral and two distinguishable octahedral sites. The first ^{43}Ca MAS NMR spectra of the crystalline dialuminate and hexaluminate are also reported. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

A number of crystalline and glassy (amorphous) calcium aluminates are known, spanning a range of Ca:Al compositions. Crystalline $CaAl_4O_7$ has extremely good resistance to thermal shock, and has been proposed as a refractory material [1]. Other calcium aluminate glasses have desirable infrared transmission properties which make them potentially useful for optical fibre applications [2], while others are photosensitive, with possible applications as optical information storage devices [3]. Calcium hexaluminate, $CaAl_{12}O_{19}$, has shown promise as an interface phase in fibre-reinforced ceramic oxide composites because of its preferred basal-plane cleavage properties [4].

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In addition to their practical applications, two of the calcium aluminates are of particular interest because of their structural characteristics, especially the coordination state of their Al. Calcium dialuminate, $CaAl_4O_7$, has a crystal structure related to that of the feldspar minerals, but contains two different tetrahedral Al sites [5]. Unlike the feldspars, this compound contains no tetrahedral silicon atoms to provide a charge balancing mechanism, which may therefore be achieved by sharing one oxygen atom per molecular unit between three Al tetrahedra, forming the 'tricluster' defect which is also a characteristic of the aluminosilicate mullite [6]. In the case of mullite, this tricluster unit has been postulated [7] as the source of a ^{27}Al MAS NMR resonance at about 30–35 ppm in amorphous precursors, as an alternative to the suggestion that this is a pentacoordinated Al site. Changes in the ^{27}Al NMR spectra during the evolution of the tricluster sites of calcium dialuminate during its crystallisation from the gel are therefore of considerable interest. A ^{27}Al MAS NMR study of a number of $CaO–Al_2O_3$ glasses which included two compositions $CaO:Al_2O_3$ <1 has shown [8] some evidence of a resonance near 35 ppm in these glasses, whose compositions however were not as alumina-rich as $CaAl_4O_7$. Other compositions in the $CaO–Al_2O_3$ glassy system have also been investigated by ^{27}Al MAS NMR [9].

Calcium hexaluminate, $CaAl_{12}O_{19}$ (hibonite) has the magnetoplumbite crystal structure [10] in which the calcium occurs in cleavage planes located between blocks of Al_2O_3 spinel structure containing 20 octahedral Al and two tetrahedral Al per unit cell. The remaining two Al atoms per unit cell are associated with the cleavage plane, and are suggested to be in irregular five-coordinated environments. The behaviour of the Al in this phase during its structural evolution from the gel is therefore of interest for the light it may shed on the general question of unusual Al environments in both amorphous and crystalline aluminates.

The aim of the present work was to investigate the changes in structure and atomic environment in hybrid gels of calcium dialuminate and hexaluminate composition during their thermal conversion to the crystalline compound using several complementary experimental methods (thermal analysis, X-ray powder diffraction and solid state MAS NMR).

Solid state ^{27}Al MAS NMR is a powerful tool which has been exploited in studies of the thermal evolution of other amorphous and poorly crystalline aluminate phases [11–13]. The present compounds also provide an opportunity for [43]Ca NMR, but because the natural abundance of this nuclide is extremely low (0.135%) such studies have previously necessitated expensive enrichment procedures, rendering them impractical. The recent availability of very large (14 mm) MAS probes has made natural abundance [43]Ca MAS NMR practicable [14], and in the course of the present study this technique was used for the first time to probe the atomic environment of the Ca atoms in the crystalline phases derived from $CaAl_4O_7$ and $CaAl_{12}O_{19}$ gels, designated below as CA2 and CA6, respectively.

2. Experimental

CA2 and CA6 gels were prepared by the Pechini mixed metal citrate method as adapted by Cinibulk [15], in which the aluminium source was an ethanolic solution of $Al(NO_3)_3·9H_2O$ also containing 2 mol of citric acid per mole of nitrate. The required amount of $Ca(C_2H_3O_2)_2·H_2O$ and 1 mol of ethylene glycol were added and the mixture refluxed for 6 h to secure polyesterification of the mixed-cation citric chelates to form a brittle resin-like gel.

A second preparation of CA2 gel was also made by a adapting a method of Mazza and Vallino [16]. A solution of $Al(NO_3)_3·9H_2O$ and $Ca(NO_3)_2·4H_2O$ was made with 10 wt.% glycerol and a small amount of distilled water, and heated at 150°C to decompose the nitrates. Further heating at 400°C was required to completely remove the nitrogen oxides and completely oxidise the organic compounds. The product was X-ray amorphous.

Thermogravimetric analysis was carried out on the dried gels in static air at a heating rate of 5°C min^{-1} using a Netzsch STA 429 thermobalance. Differential scanning calorimetry was carried out in static air at a heating rate of 5°C min^{-1} using a Netszsch DSC 404. Thermal analysis experiments were carried out on both the dried gels and gels pre-fired at 600°C for 1 h to remove the large amount of organic material present.

Aliquots of the gels were heated in air in platinum crucibles for 60 min in a pre-heated electric muffle

furnace at a number of temperatures determined from the thermal analysis results, then examined by XRD using a Philips PW1700 computer-controlled diffractometer with a graphite monochromator and Co Kα radiation. Solid state ^{27}Al MAS NMR spectroscopy was carried out at 14.1 T using a Chemagnetics Infinity spectrometer and a 3.2 mm high-speed MAS probe in which the sample was spun at 18 kHz. The spectra were acquired at 156.374 MHz using a 15° pulse of 0.5 μs and a recycle time of 1 s, and were referenced by using the secondary standard of the AlO_6 resonance of $Y_3Al_5O_{12}$ at 0.7 ppm. Natural abundance ^{43}Ca MAS NMR spectra of the crystalline products $CaAl_4O_7$ and $CaAl_{12}O_{19}$ were acquired at 14.1 T using a 14 mm probe spun at about 2 kHz (for CA2) and a 9.5 mm probe spun at about 3 kHz (for CA6). The spectra were acquired at 40.388 MHz using a pulse corresponding to π/10–π/8, with a recycle delay of 1 s (for CA2) and 0.7 s (for CA6). Typically, 750 000 transients were acquired in each spectrum and the shifts were referenced to saturated $CaCl_2$ solution.

3. Results and discussion

Fig. 1 shows the DSC and TG curves of the citrate method CA2 and CA6 gels. The TG curve of the glycerol method gel (not shown) was similar in all respects to that of the citrate method gel. Large mass losses associated with the removal of solvent and organic by-products of the gel synthesis are recorded up to about 600°C (Fig. 1A and B); these losses in CA2 and CA6 were 82.9 and 86.9%, respectively. No further mass loss was recorded in the CA6 gel up to 1350°C, but CA2 showed a further 2% loss between 900 and 1000°C (inset of Fig. 1). The removal of such a large amount of water and organic material produced in both gels, large endothermic effects at about 250°C and exothermic effects at about 500–700°C. In order to concentrate the samples and enhance the more interesting thermal events at higher temperatures, the gels were pre-fired at 600°C for 1 h and the DSC traces re-determined (Fig. 1C–E). Under these conditions, the citrate and glycerol-derived CA2 gels show three high-temperature exotherms, but with differences in their recorded temperatures (Fig. 1C and D). In the same temperature range, CA6 shows a major exotherm at 900°C with a small shoulder at
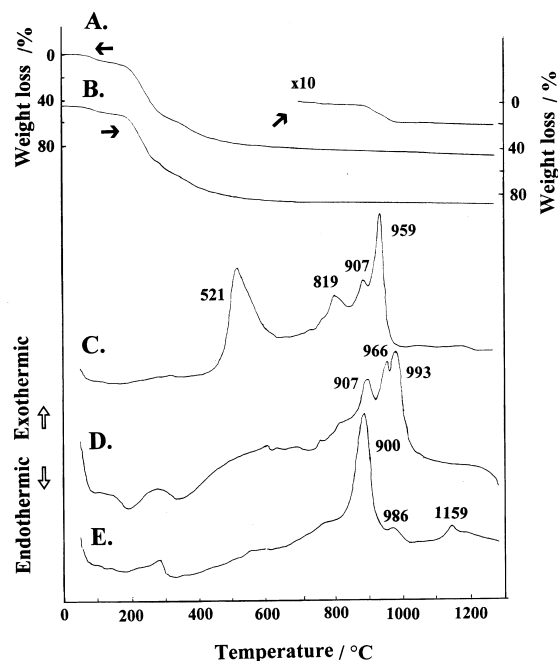

Fig. 1. Thermal analysis curves of CA2 and CA6 gels in static air, at a heating rate of 5°C min^{-1}: (A) TG curve of citrate-derived CA2; (B) TG curve of citrate-derived CA6; (C) DSC curve of citrate-derived CA2 pre-fired at 600°C for 1 h; (D) DSC curve of glycerol-derived CA2 pre-fired at 600°C for 1 h; (E) DSC curve of citrate-derived CA6 pre-fired at 600°C for 1 h.

986°C and another small exotherm at 1159°C (Fig. 1E).

The X-ray diffractograms of the unheated and heated CA2 gels prepared by the citrate method (Fig. 2) show that up to 800°C the material is X-ray amorphous, with the position of the larger of the two broad maxima in the unheated gel shifting from about 25°2θ (Co Kα) to about 35°2θ on heating to 800°C (Fig. 2B).

The XRD patterns indicate that the exotherm at about 900°C is associated with the abrupt crystallisation of $CaAl_4O_7$, the pattern of which appears after heating at 900°C superimposed on a background hump arising from a small amount of a residual amorphous phase (Fig. 2C). The transformation of this amorphous residue to $CaAl_4O_7$, which is complete by 1000°C (Fig. 2D) coincides with the 2% mass loss recorded in this temperature interval, but the reason for the different thermal behaviour of this part of the sample is not obvious from these data. The product formed at
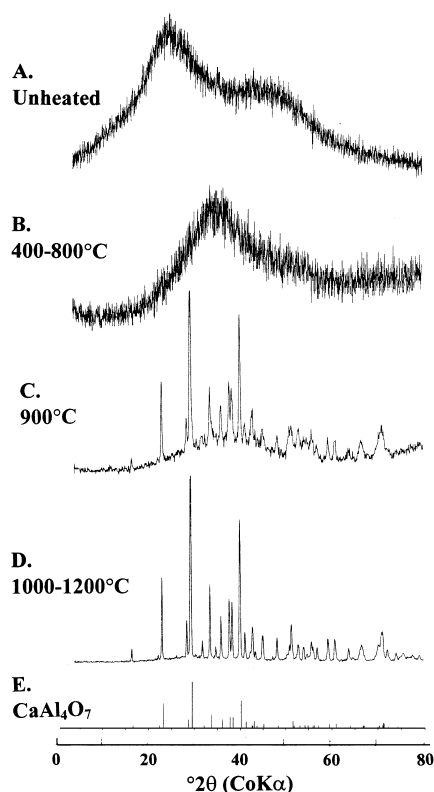
Fig. 2. X-ray powder diffractograms of CA2 citrate-derived gel for: (A) unheated; (B) 400–800°C; (C) 900°C; (D) 1000–1200°C heated for 60 min; (E) $CaAl_4O_7$ diffraction pattern (PDF no. 23-1037).
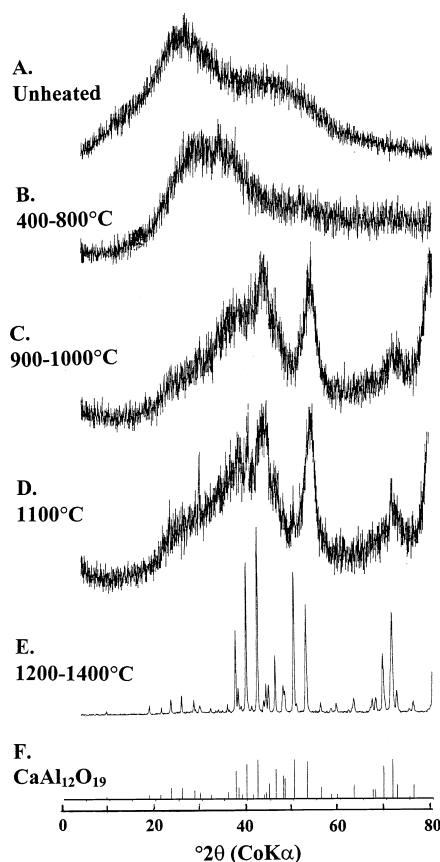

Fig. 3. X-ray powder diffractograms of CA6 citrate-derived gel for: (A) unheated; (B) 400–800°C; (C) 900–1000°C; (D) 1100°C; (E) 1200–1400°C all heated for 60 min. Asterisks indicate the position of γ-alumina reflections (PDF no. 33-699). (F) $CaAl_{12}O_{19}$ diffraction pattern (PFD no. 7-85).

1000°C is crystalline and almost phase-pure, the only indication of the presence of an intermediate being a small peak at 35°2θ. Further heating to 1200°C produces little improvement in the crystallinity of the product, which has an XRD pattern conforming closely to PDF no. 23-1037 (Fig. 2E). The small peak at 35°2θ slowly disappears on prolonged heating at 1400°C. Similar thermal and XRD behaviour was found for the CA2 gel prepared by the glycerol method. In this case, however, the transformation to crystalline $CaAl_4O_7$ was more abrupt; the XRD trace at 900°C was still fully amorphous but the gel had fully crystallised by 1000°C. A possible explanation is that this sample is similar to the residual amorphous component of Fig. 2C which transformed with similar abruptness just below 1000°C. If this is the case, the difference between the two CA2 preparations may be in their degree of homogeneity.

The XRD traces of unheated and heated CA6 gels are shown in Fig. 3. The unheated gel shows an amorphous XRD trace (Fig. 3A) identical to that of unheated CA2 gel (Fig. 2A) with a similar shift in the maximum of the broad diffuse hump on heating to 800°C (Fig. 3B). Heating to 900°C, in the region of the first high-temperature exotherm, results in the appearance of broad new reflections corresponding to the major lines of γ-alumina spinel (PDF no. 10-425). Thus, the 900°C exotherm corresponds to the formation of the spinel building blocks into which the calcium ions will later migrate to form the magnetoplumbite structure. A similar sequence was found during the formation of magnetoplumbite-type lantha-

num hexaluminate $LaAl_{11}O_{18}$ [13] and in lanthanum aluminates of other compositions [17]. The crystallinity of the spinel units, as evidenced by the sharpness of the XRD reflections, improves only slightly on heating to 1100°C (Fig. 3D), but above the temperature of the 1159°C exotherm, the highly crystalline hexaluminate phase $CaAl_{12}O_{19}$ suddenly appears. Heating to 1400°C produces little improvement in the crystallinity of the product, which has an XRD pattern identical to PDF no. 7-85 (Fig. 3F). As was found for the CA2 gels, this synthesis method produces a crystalline monophasic product with no evidence of intermediates or secondary phases, by contrast with the results of Cinibulk [15] who reported the formation of small amounts of intermediate $CaAl_4O_7$ during the heat treatment of CA6 gels prepared by this method.

3.1. ^{27}Al MAS NMR spectroscopy

3.1.1. $CaAl_4O_7$

Fig. 4 shows a typical series of ^{27}Al MAS NMR spectra of citrate-derived CA2 gel samples at various stages of the reaction sequence. The spectrum of the as-prepared gel (Fig. 4A) shows a single octahedral resonance at −7 ppm, which on heating the sample to 400°C is replaced by a three-peak spectrum (Fig. 4B) typical of many aluminate gels [12,13]. The resonances at 69 and 8 ppm correspond to tetrahedral and octahedrally coordinated aluminium, respectively, while that at 36–39 ppm is in the region often ascribed to pentacoordinated aluminium, but is also at the lower end of the range of tetrahedral Al shifts such as found in aluminium phosphates (39.7 ppm [18], 41.5 ppm [19]). This three-peak spectrum persists essentially unchanged until 600°C (Fig. 4C) when the 39 ppm peak begins to decrease, becoming a barely resolved shoulder at about 42 ppm at 900°C (Fig. 4E), the temperature at which the crystalline $CaAl_4O_7$ is first detected by XRD. At this temperature, the tetrahedral resonance also shows evidence of splitting into the two singularities of a quadrupolar lineshape arising from a single distorted site. However, by 1000°C (Fig. 4F) the tetrahedral spectrum has developed the complex envelope associated with crystalline $CaAl_4O_7$, which we have analysed in terms of overlapping quadrupolar lineshapes [20]. The peak maximum of this envelope (58 ppm) coincides precisely with the sharper of the
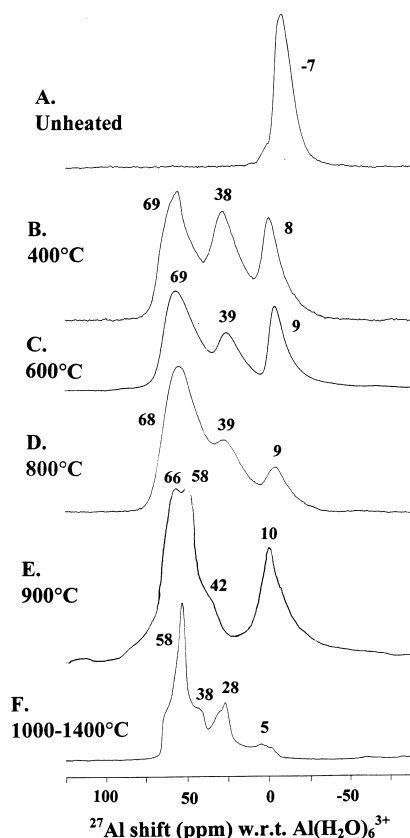

Fig. 4. ^{27}Al MAS NMR spectra of CA2 citrate-derived gel, unheated and heated at the indicated temperatures.

two overlapping peaks seen at 900°C, suggesting that this is part of the spectrum of crystalline $CaAl_4O_7$ detected by XRD in this sample. On this basis, the other tetrahedral feature at 66 ppm and the octahedral peak at 10 ppm must arise from the residual amorphous component present at 900°C; these peak positions also coincide reasonably with the positions of the octahedral and tetrahedral resonances in the amorphous precursor at 800°C. Thus, the spectrum at 900°C can be understood as a composite of the known spectra of crystalline $CaAl_4O_7$ and its amorphous precursor.

A similar pattern of behaviour was found in the ^{27}Al MAS NMR spectra of the gel samples prepared by the glycerol method, but in general the relative proportion of 36 ppm resonance was lower in this gel. Fig. 5 shows a semi-quantitative estimate of the relative proportions of ^{27}Al in the various sites, estimated
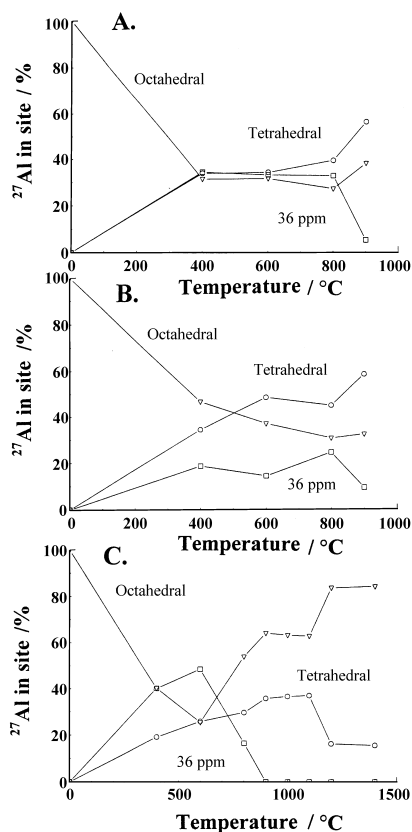
Fig. 5. Changes in the ^{27}Al site occupancies of: (A) citrate-derived CA2 gel; (B) glycerol-derived CA2 gel; (C) citrate-derived CA6 gel as a function of heating temperature. ($\triangledown$) octahedral resonance; ($\bigcirc$) tetrahedral resonance; ($\square$) 36–39 ppm resonance.

by curve-fitting the spectra to a series of Gaussian lineshapes. It is seen that on heating, both the CA2 gels develop tetrahedral and 36 ppm resonances at the expense of the original octahedral sites (Fig. 5). At the crystallisation temperature of $CaAl_4O_7$, the occupancy of the 36 ppm site abruptly decreases, these atoms being relocated in both tetrahedral and octahedral sites.

The site distribution of the final product can be seen from the peak shape to be complex. By using multiple quantum MAS NMR [21] and taking account the magnetic field dependence of the spectrum of extremely crystalline $CaAl_4O_7$ synthesised by high-temperature solid state reaction of the oxides, we have demonstrated that the spectrum contains two overlapping quadrupolar lineshapes corresponding to the

two tetrahedral sites of $CaAl_4O_7$ [20]. Both these tetrahedral Al sites are involved in a tricluster configuration, each of which contains two T2 tetrahedra and one T1 tetrahedron [5]; the average tetrahedral charge is −0.5, and charge balance is achieved in the structure by the presence of one Ca ion for four Al ions. The small intensity component in the octahedral region of the spectrum (Fig. 4E) is probably associated with the XRD impurity peak at 35°2θ or with a trace of an X-ray amorphous impurity phase [20].

3.1.2. $CaAl_{12}O_{19}$

The ^{27}Al MAS NMR spectra of the gel of this composition, both heated and unheated, are shown in Fig. 6. As with the unheated CA2 gels, unheated CA6 shows a single octahedral site (Fig. 6A) which
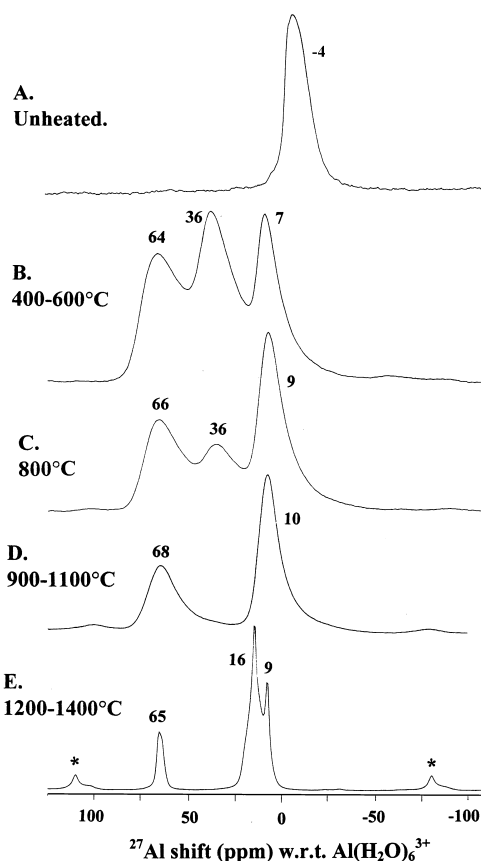

Fig. 6. ^{27}Al MAS NMR spectra of citrate-derived CA6 gel, unheated and heated at the indicated temperatures.

develops into the typical three-line spectrum on heating at 400°C (Fig. 6B). This type of spectrum persists until the crystallisation of the spinel structural blocks at 900°C, when the three-peak amorphous phase signature abruptly changes to that of a structure containing only tetrahedral and octahedral sites (Fig. 6D). The octahedral:tetrahedral ratio remains essentially constant at 1.7–1.8 over the temperature range between the crystallisation of the spinel and its transformation to the magnetoplumbite structure at 1200°C. This ratio is closer to the value of 1.6 determined at the same field strength for γ-alumina spinel than was previously found for the spinel component of lanthanum hexaluminate, which contained more octahedral Al (ratio 2.4) [13,22]. On crystallisation of the magnetoplumbite structure, the ^{27}Al spectrum changes abruptly (Fig. 6E) to a sharp and asymmetric tetrahedral resonance and two sharp peaks in the characteristic octahedral region. The octahedral feature could arise from a single site showing a quadrupolar lineshape due to a significant electric field gradient (EFG), or it could indicate the presence of two different octahedral sites. A multiple quantum MAS NMR study of crystalline CA6 [18] indicates that the latter is the case, and that one of the octahedral sites demonstrates a quadrupolar lineshape.

3.2. ^{43}Ca MAS NMR spectroscopy

The natural abundance ^{43}Ca MAS NMR spectra of crystalline $CaAl_4O_7$ and $CaAl_{12}O_{19}$ derived by thermal treatment of the gels at 1400°C are shown in Fig. 7. The spectrum of CA6 (Fig. 7A) shows a single sharp resonance (80 Hz wide) at −52.6 ppm consistent with a single reasonably symmetrical site. The chemical shift of this site is comparable with the values previously reported for a number of other Ca compounds, being slightly more negative than the shift of the aragonite form of $CaCO_3$ (−34 ppm) in which the Ca atom has a coordination number of 9 with a mean Ca–O distance of 2.528 Å [14]. By comparison, the Ca atom which is located in the mirror plane of CA6 has a coordination number of 12 and a mean Ca–O distance of 2.748 Å [10]. The more negative shift value in CA6 is qualitatively in agreement with the finding that the shifts become more negative as the coordination number increases [14]. Comparison of the actual
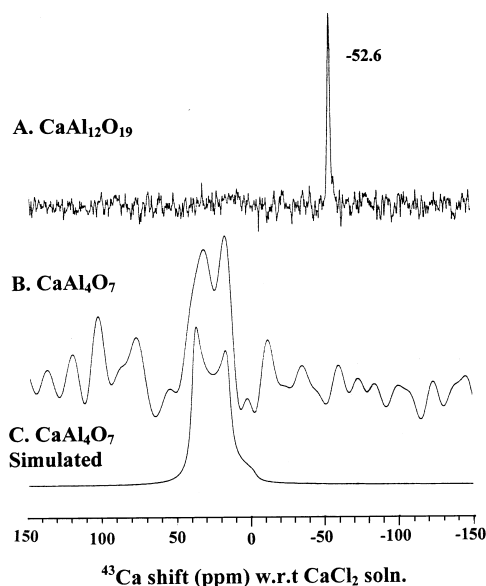

Fig. 7. ^{43}Ca MAS NMR spectra of crystalline calcium aluminates derived from the aluminate gels by heating at 1400°C. (A) CA6; (B) CA2; (C) CA2 spectrum simulated with $C_Q = 3.5$ MHz, $\eta = 0.1$, 100 Hz broadening.

^{43}Ca shift value and mean Ca–O distance of CA6 with the linear relationships which have been established between these parameters for Ca oxides, silicates and carbonates [14] indicates that CA6 fits better on the silicate line than, as would have been expected, on the oxide line.

The ^{43}Ca MAS NMR spectrum of CA2 (Fig. 7B) shows a much broader resonance, with evidence of a quadrupolar lineshape suggesting that the Ca site in this compound is experiencing a comparatively larger EFG. The observed lineshape can be simulated with a nuclear quadrupolar coupling constant $C_Q = 3.5$ MHz and an asymmetry parameter $\eta = 0.1 \pm 0.1$, with broadening of 100 Hz. The resulting isotropic chemical shift δ_{iso} of this site is 45.7 ppm. The Ca atoms in CA2 have a coordination number of 7 and a mean Ca–O distance of 2.525 Å [5]. As for CA6, this isotropic chemical shift and Ca–O distance lies closer to the published relationship for silicates than for oxides, but the fit is not as close as that of CA6. The similarity in the behaviour of these aluminates to documented calcium silicates suggests either that silicon and aluminium exert a similar effect on the isotropic chemical

shift of the calcium, or that the influence of the next-nearest atom species in these compounds is less than other factors such as the structure and geometry of the coordination polyhedron.

4. Conclusions

CaAl$_4$O$_7$ gels prepared by two different methods lose large amounts of solvent and organic by-products when heated at about 600°C. Heating to about 900°C causes the X-ray amorphous gels to crystallise directly to almost phase-pure CaAl$_4$O$_7$ in an exothermic reaction. The solely octahedral Al environment in the as-prepared gel changes on heating at 400°C to that of a more typical aluminate gel, with octahedral and tetrahedral Al and another type of site characterised by a ^{27}Al NMR resonance at 36–39 ppm. The latter disappears when the CaAl$_4$O$_7$ crystallises at about 900°C, leading at 1000°C to the complex spectrum of the crystalline phase which contains two overlapping tetrahedral resonances with quadrupolar lineshapes arising from the EFGs associated with the distorted tricluster Al sites. A small amount of octahedral Al detectable in the ^{27}Al spectrum probably arises from an amorphous aluminate impurity. The ^{43}Ca spectrum is broad and shows a quadrupolar lineshape typical of a distorted site experiencing an EFG, with a nuclear quadrupolar coupling constant estimated by spectral simulation to be about 3.5 MHz.

CaAl$_{12}$O$_{19}$ gels lose large amounts of solvent and organic by-products below about 600°C, remaining X-ray amorphous until the exothermic crystallisation of γ-Al$_2$O$_3$ at 900°C. At this temperature, the three typical Al sites of the aluminate gel change to the tetrahedral and octahedral configuration of the aluminium spinel building blocks of CA6. This phase transforms into the magnetoplumbite structure in an exothermic reaction at about 1160°C in which the large Ca ion migrates into the mirror planes between the spinel blocks. The resulting ^{27}Al NMR spectrum contains resonances corresponding to two octahedral sites and a single tetrahedral site. The ^{43}Ca spectrum of this phase is as expected for a single reasonably symmetrical site of high coordination number.

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