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

I. Celsian, $BaAl_2Si_2O_8$

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Abstract

Hybrid gels of celsian composition were prepared from Al alkoxide, tetrathylorthosilicate (TEOS) and Ba acetate and their structure evolution was studied up to 1300°C by thermal analysis and X-ray diffraction. Information on their pre-crystallization behaviour was also provided by ^{27}Al, ^{29}Si and ^{137}Ba MAS NMR spectroscopy. Apart from some excess Ba acetate which decomposed to traces of $BaCO_3$ and BaO by ca. 500°C, the gels are X-ray amorphous and relatively homogeneous, and begin to crystallize to hexagonal celsian at 900°C. From ≈500°C onwards, an Al-substituted tetrahedral SiO_4 framework begins to be established, evidenced by a progressive increase in the tetrahedral ^{27}Al sites and the $Q^4(4Al)$ ^{29}Si resonance. Migration of Ba into the polyhedral celsian sites occurs much more slowly. A small amount of mullite and Ba_2SiO_4 which crystallize from Al-rich and Ba-rich regions, respectively, also form crystalline celsian in secondary reactions at ca. 1100°C. The observation of a ^{27}Al shoulder at ca. 36 ppm at 500–900°C may arise from Ba-poor mullite-like regions. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Sol–gel synthesis is a versatile method for producing a wide range of inorganic materials and precursors which can be converted into ceramics by heat treatment. While still in the gel state, the precursor may be cast into a monolithic body which retains its integrity with careful drying techniques, or it can be used as a medium for dip-coating on to a substrate. Aluminates and aluminosilicates are commonly prepared by co-condensation and hydrolysis of the metal alkoxides (e.g. Al-sec-butoxide and tetraethylorthosilicate (TEOS)). To prepare a phase such as celsian, $BaAl_2Si_2O_8$, the Ba may be introduced into the system either as the Ba alkoxide (prepared by refluxing Ba metal in isopropanol [1]) or as an aqueous solution of Ba acetate with the pH adjusted to ca. 3–4 with acetic acid [2]. Since the latter method involves a combination of inorganic and organic reagents, it is sometimes termed a hybrid synthesis, and is commonly used to prepare multi-component gels containing elements such as Ba, Y or La. A recent study of the solubility of Ba acetate in mixed alcoholic solutions [3] has improved the understanding of the Ba–Si–Al system and systematized the hybrid synthesis of these gels.

Celsian is of technical interest as a highly refractory glass–ceramic with attractive electrical and thermal

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properties. It occurs in four crystalline forms; two naturally occurring minerals of celsian composition (celsian and paracelsian) are monoclinic, while an orthorhombic (low temperature) and a hexagonal (high temperature) forms are the usual products of synthesis. Monoclinic celsian is the most desirable form for many ceramic applications, since it is stable to 1590°C, whereas hexagonal celsian undergoes a polymorphic phase transformation at 300°C with an associated volume change which leads to mechanical instability. Since hexagonal celsian is the normal synthesis product, considerable effort has been directed at producing the monoclinic form, by seeding [6] and the use of additives such as Li_2O [4]. The volume change in hexacelsian may, however, prove useful in applications such as fibre coatings for long-fibre reinforced composite ceramics to prevent undesirable bonding between the fibre and the matrix.

The evolution of crystalline phases during heat treatment of mixed aluminate gels of celsian composition has also been well studied, principally by thermal analysis and X-ray diffraction of the crystalline products [1,4–6]. These techniques provide information about the crystalline phases, but not about changes in the gel while it is still amorphous; such information has been obtained for other aluminate gel precursors (e.g. those forming mullite) by solid-state nuclear magnetic resonance with magic angle spinning (MAS NMR) [7]. An MAS NMR result of particular interest is the appearance in monophasic mullite precursor gels during heat treatment of a ^{27}Al resonance at ca. 30 ppm which has been attributed either to 5-coordinated Al [8], or to a relaxed form of the defect tetrahedral oxygen tricluster structure which occurs in crystalline mullite [9]. Similar studies of other aluminate gels such as celsian precursors should provide interesting structural information, but have not been previously reported.

The aim of the present study was to monitor by multinuclear MAS NMR (^{27}Al, ^{29}Si and ^{137}Ba) the structural changes occurring during the thermal treatment of an aluminate gel of celsian composition, augmenting these results by XRD and thermal analysis.

2. Experimental

The celsian composition gel was prepared from Al-sec-butoxide, TEOS and Ba acetate by the hybrid synthesis of Tredway and Risbud [2], taking into account the further data of Winter and Phalippou [3]. After drying in the ambient atmosphere, the gel was lightly crushed and subjected to thermal analysis in flowing air (50 ml/min) at a heating rate of 10°C/min, using a Rheometrics STA 1500 thermoanalyzer. Aliquot samples of the unheated gel were fired in air in platinum crucibles in a pre-heated electric muffle furnace for 15 min at several different temperatures dictated by the thermal analysis results. These samples were then characterized by powder X-ray diffraction (Philips PW1700 computer-controlled goniometer with graphite monochromator and CoK_α radiation). Their ^{27}Al, ^{29}Si and ^{137}Ba MAS NMR spectra were recorded at 11.7T using a Varian Unity 500 spectrometer and 5-mm Doty high-speed MAS probe spun at 10–12 kHz under the following conditions:

^{27}Al: spectra acquired at 130.245 MHz using a 15° pulse of 1 μs and a recycle time of 1 s, the spectra referenced to $Al(H_2O)_6^{3+}$.

^{29}Si: spectra acquired at 99.297 MHz using a 90° pulse of 6 μs and a recycle time of 60 s, the spectra referenced to tetramethylsilane (TMS).

^{137}Ba: spectra acquired at 55.541 MHz using a Hahn spin echo pulse sequence with 16-step phase recycling with a refocusing interval of 20 μs, the spectra referenced to 1 M aqueous $BaCl_2$ solution. Typically 500 000 transients were collected for each spectrum, but the spectral processing was complicated by their broadness and the need to left-shift the spectra to minimize the effects of probe ringdown, pulse breakthrough, etc. [10]. This was accomplished by left-shifting all the spectra by two points and a baseline correction was also applied. The ^{137}Ba spectra of some samples were also acquired using a Bloch decay pulse sequence which confirmed the general features of the spin echo spectra.

3. Results and discussion

The thermal analysis traces of the celsian gel precursor (Fig. 1) show an initial mass loss of 7.6 mass% below 200°C, corresponding to the removal of adsorbed species, most probably solvent and water. This is followed by a two-stage exothermic mass loss (22.1 mass% and 11.2 mass%) at 250–300°C and 300–
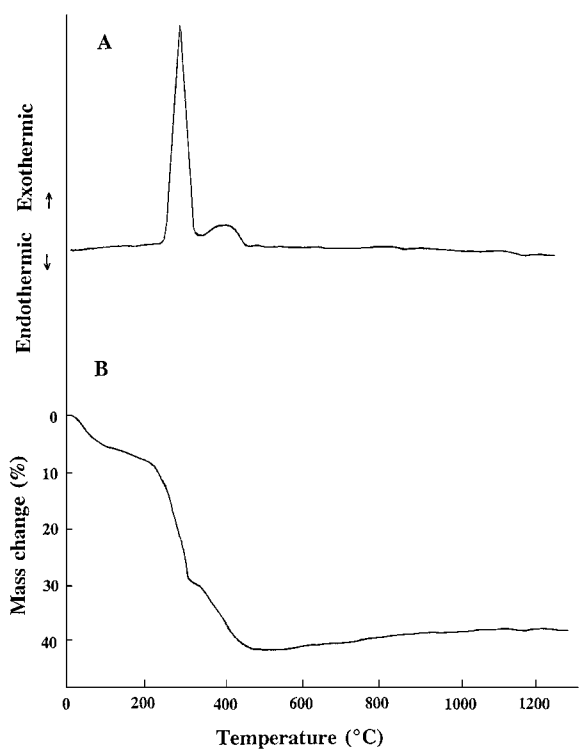
Fig. 1. Thermal analysis curves for hybrid celsian gel in flowing air (50 ml min^{-1}), heating rate 10°C min^{-1}. (A) DSC curve, (B) TG curve.
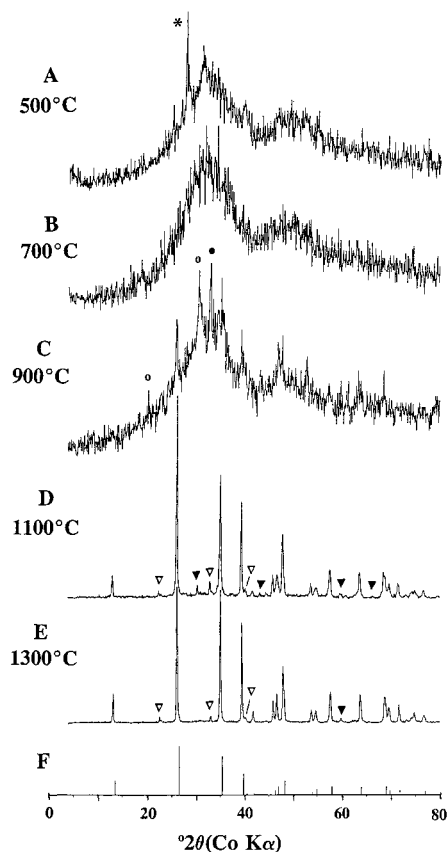

Fig. 2. XRD traces of hybrid celsian gel heated in air at the indicated temperatures for 15 min. F. PDF powder pattern 28–124, hexagonal celsian. Key: (*), $BaCO_3$; (○), mullite; (●), BaO; (▽), $BaAl_2O_4$; and (▼), Ba_2SiO_4, unmarked reflections are hexagonal celsian.

450°C, respectively, similar to exothermic events at 380–490°C reported by Tredway and Risbud [2] and Du et al. [5], who ascribed them, respectively, to pyrolysis of residual organic groups in the gel, and to the oxidation of residual carbon. In contrast to the present results, Du et al. found the higher-temperature exotherm to be the sharper and more intense, possibly reflecting the removal of their chelating agent, which was not present in our gels. The higher-temperature exotherm observed at 1080–1090°C by Liu et al. [6] and Debsikdar [11], and attributed to the crystallization of hexacelsian, was not found in the present samples in which the crystallization was shown by XRD (below) to extend over a wider temperature range.

The XRD trace of the as-prepared gel indicated the presence of crystalline barium acetate superimposed on a baseline characteristic of the amorphous gel phase; this has also been reported by other authors using the acetate hybrid synthesis route [2,6]. Heating

to 500°C decomposes the barium acetate, leaving the broad amorphous trace and one sharp peak at 3.1 Å (Fig. 2(A)), indicating the presence of a small amount of $BaCO_3$. The latter has been reported by other authors [6,11], who ascribed its formation either to absorption of CO_2 during powder handling, or (more likely) as a reaction product of organic residue oxidation. The carbonate disappears on heating to 700°C (Fig. 2(B)), and by 900°C, the XRD trace (Fig. 2(C)) indicates the appearance of new poorly crystalline phases including hexagonal celsian (PDF no. 28-124), mullite (PDF 15-776) and barium oxide (PDF 26-177), still superimposed on an amorphous baseline. Complete transformation to crystalline hexagonal celsian has occurred by 1100°C (Fig. 2(D)), with only
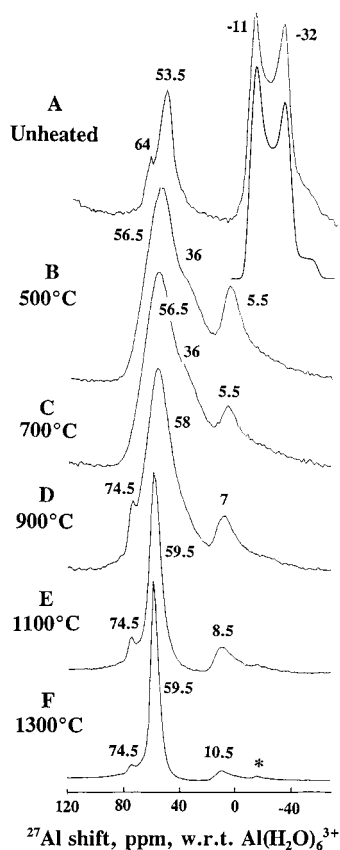
Fig. 3. $11.7T$ ^{27}Al MAS NMR spectra of hybrid celsian gels heated in air at the indicated temperatures for 15 min. Asterisk denotes spinning side band. Insert beneath spectrum (A) is the octahedral simulated with $\chi=7.8$ MHz, $\eta=0.2$, Gaussian linebroadening of 5 ppm.

slight improvement in the crystallinity on heating to 1300°C (Fig. 2(E)). Small traces of crystalline Ba_2SiO_4 (PDF 26-1403) and $BaAl_2O_4$ (PDF 17-306) were detected in the sample fired at 1100°C (Fig. 2(D)); by 1300°C, the orthosilicate had virtually disappeared and the intensity of the aluminate reflections decreased (Fig. 2(E)). In contrast to the findings of Du et al. [5] β-$BaSi_2O_5$ (sanbornite) was not detected as either a major or minor product of gel crystallization.

The $11.7T$ ^{27}Al MAS NMR spectra of the unheated and heated gel samples are shown in Fig. 3.

The unheated gel (Fig. 3(A)) shows tetrahedral resonances at 64 and 53 ppm, and an octahedral feature showing a typical quadrupolar lineshape. This portion of the spectrum can be simulated as a single site with a nuclear quadrupole coupling constant (χ) of 7.8 MHz, an asymmetry parameter (η) of 0.2 and a Gaussian broadening of 5 ppm; the resulting simulated spectrum is shown as an insert below Fig. 3(A). The isotropic chemical shift of this site is deduced from the simulation to be −0.5 ppm, close to the value of 0 ppm for the hydrated Al-ion used as the reference for these spectra.

Heating to a temperature which removes the hydration water (Fig. 3(B)) destroys the quadrupolar line shape and shifts the octahedral peak to 5.5 ppm, at the same time broadening and merging the tetrahedral resonances of the previous spectrum. A new shoulder at ca. 36 ppm also develops, persisting to 900°C, where it may still be present as a slight asymmetry on the high-field side of the major tetrahedral peak (Fig. 3(D)). A broad peak in this general position is often reported in non-crystalline aluminum-containing compounds such as gels, glasses, dehydroxylated clay minerals and aluminates which have been amorphized by grinding. Since the position of this peak coincides with the isotropic chemical shift of five-fold coordinated Al in crystalline compounds, it is often ascribed to Al[5], but it does not show the characteristic quadrupolar peak shape and magnetic field dependence which would result from the presence of the significant electric field gradients associated with the Al[5] sites in well-characterized crystalline compounds. Alternative interpretations associate this resonance with highly distorted tetrahedral sites [12] which may be characteristic of specific structural units such as the tetrahedral oxygen-deficient aluminum tricluster occurring in mullite [9]. In aluminosilicate gels, such triclusters provide a charge-balancing mechanism for Al substitution in the tetrahedral framework, but their function can be replaced by other charge-balancing ions such as Na^+, which reduce the intensity of the 30 ppm resonance to zero when present in sufficient concentrations [13]. Although charge balance in the celsian system does not require the formation of triclusters, the possible transient formation of poorly crystalline mullite has been noted by XRD at 900°C (Fig. 2(C)). It is therefore possible that the shoulder at ca. 36 ppm is associated with Ba-poor regions which temporarily form a mullite-like phase before further reaction converts them to celsian. Fig. 4 shows the changes in the partitioning of Al over the
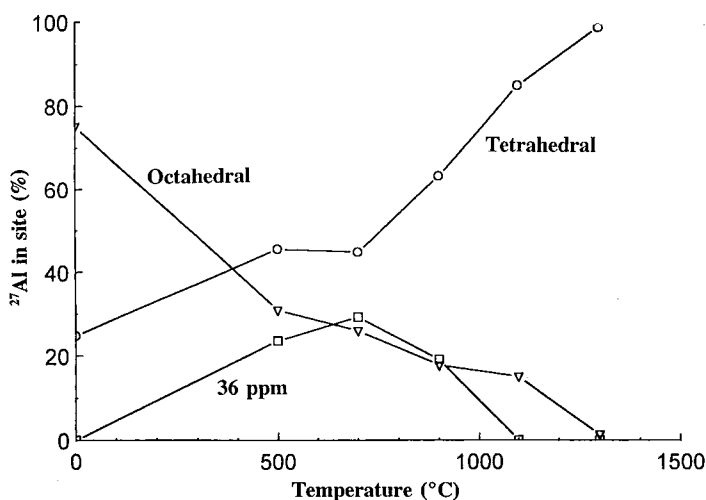
Fig. 4. Distribution of [27]Al over the sites in hybrid celsian gels as a function of heating temperature.

various sites during thermal treatment, estimated semi-quantitatively by curve-fitting the [27]Al spectra.

The thermal evolution of celsian from the present gel is seen from Fig. 4 to involve a progressive decrease in the amount of Al in octahedral sites, with a corresponding increase in the tetrahedral sites, which also replace the transient 30 ppm sites as the reaction proceeds. The [27]Al spectrum of the gel heated at 1300°C, containing predominantly hexacelsian (Fig. 3(F)), essentially shows a single tetrahedral Al site; although the ^{27}Al and ^{29}Si NMR spectra of celsian have not previously been reported, the chemical shift of the Al tetrahedral is very similar to those of the related alkali feldspars albite (59 ppm) [14], microcline (54, 57 ppm) [14] and sanidine (58 ppm) [14]. The intensities of the small additional tetrahedral and octahedral features at 74.5 and 7–10 ppm, respectively, decrease with the heating temperature; the tetrahedral peak at 74.5 ppm probably arises from the small amount of $BaAl_2O_4$ observed by XRD at 1100° and 1300°C, which has a single characteristic resonance at 75 ppm (our unpublished 11.7T results, which are in poor agreement with a much earlier reported 6.7T value of 69 ppm for this compound [20]).

The ^{29}Si MAS NMR spectra of the unheated and heated gel samples are shown in Fig. 5. The [29]Si spectrum of the unheated gel (Fig. 5(A)) shows a rather featureless, broad resonance centred at −99 ppm, typical of a silicate glass or an amorphous
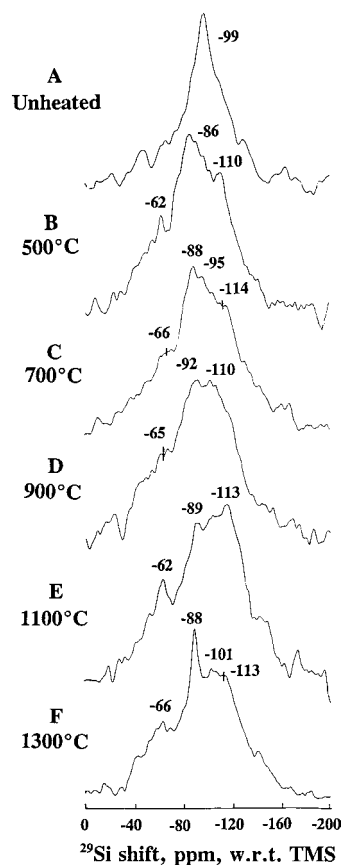

Fig. 5. 11.7T ^{29}Si MAS NMR spectra of hybrid celsian gels heated in air at the indicted temperatures for 15 min.

aluminosilicate such as dehydroxylated kaolinite ($\delta=101$ ppm [15]). Heating to 500°C produces a new broad resonance at -86 ppm (Fig. 5(B)), in the position of the Si(Al)O$_4$ peak found in aluminosilicates such as mullite; although crystalline mullite is not identifiable in the XRD trace until 900°C, this result suggests the establishment of an Al-substituted tetrahedral silicate framework at a much lower temperature. Two smaller resonances appear at this temperature and remain in the spectra up to the highest temperature; the peak at -110 ppm is typical of the (Q^4(0Al) unit of unsubstituted SiO$_2$, while that at ca. -62 to -66 ppm is in the diagnostic region of orthosilicates such as Mg$_2$SiO$_4$ [16], and may arise from the presence of incipient orthorhombic Ba$_2$SiO$_4$ which appears in small amounts in the XRD trace at 1100°C and is still present as a trace at 1300°C. The crystalline form of this compound has its diagnostic resonance at -69 ppm (our unpublished 11.7T results, which are in good agreement with a previously reported value of -70.3 ppm [21]).

On heating above 500°C, the main spectral feature at ca. -85 to -110 ppm remains broad and poorly resolved, typical of alkali feldspars, such as albite and microcline (-93, -97, -100 to -105 ppm [16]), nepheline (-85, -88 ppm [16]) and disordered anorthite (-84 to -89, -95, -101 ppm [14]), in which the latter two resonances correspond to Q^4(2Al) and Q^4(1Al) units resulting from a increased degree of Al/Si disorder [14]. The broadness and poor resolution of feldspar peaks is also a function of tetrahedral disorder giving rise to Al–Si spin–spin coupling through the electrons [17]. Although the ^{29}Si MAS NMR spectrum of celsian has not been reported previously, it should show similarities to the reported spectra of the potassium feldspars and anorthite, which have related structures but different distributions of Al over the four tetrahedral sites [18]. During heating to progressively higher temperatures, the Q^4(4Al) resonance at -88 ppm becomes dominant, suggesting the establishment of celsian-type ordering, in which two of the four distinguishable tetrahedra are about three times more Al-rich than the other two tetrahedra [18]. At 1300°C, the ^{29}Si spectrum retains the Q^4(0Al) SiO$_2$ resonance at -113 ppm and a small contribution from the Ba$_2$SiO$_4$ resonance at -66 ppm (Fig. 5(F)). The Q^4(0Al) peaks sometimes found in natural feldspars are attributed to XRD-undetectable
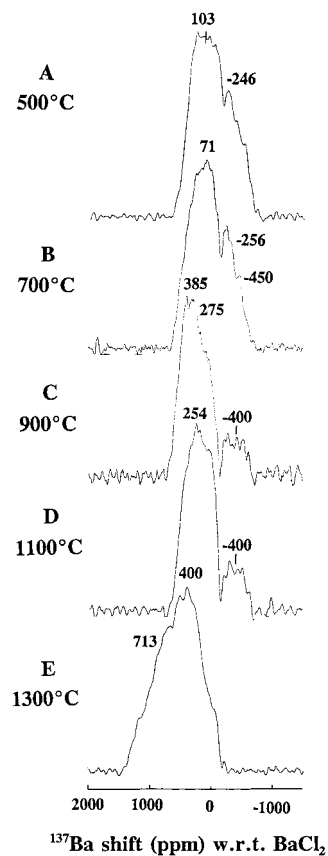

Fig. 6. 11.7T ^{137}Ba NMR spectra of hybrid celsian gels heated in air at the indicated temperatures for 15 min.

quartz impurities in the grain boundaries [14], and the present resonance might be similarly explained.

Fig. 6 shows a selection of ^{137}Ba MAS NMR spectra of the celsian gel at various stages of heating. As has previously been shown, the ^{137}Ba spectra of all but very symmetrical environments are rather broad and featureless, as is the case with the present samples. However, despite this drawback, some insight into the behaviour of the Ba during heating of the celsian gel is provided by the present spectra.

After decomposition of the adhering barium acetate at 500°C, two broad resonances can be seen in the ^{137}Ba spectrum (Fig. 6(A)). The major feature is centred at ca. 60 ppm but extends from ca. 600 to -800 ppm and is characteristic of the gel; one of the resonances of the BaCO$_3$ known by XRD to be present in this sample occurs at 386 ppm [10] and is, therefore, incorporated in this envelope. The other BaCO$_3$ reso-

nance at −406 ppm is incorporated in the shoulder of the smaller broad resonance at −250 ppm (Fig. 6(A)). The maximum of this peak is in the vicinity of Ba_2SiO_4 (centre of gravity of this phase is −270 ppm [10]), but it is also sufficiently broad to encompass a $BaAl_2O_4$ resonance (centre of gravity −191 ppm [10]). Both these phases are known to crystallize in small amounts at 1100°C; the [137]Ba spectra may suggest that the necessary atomic associations are being formed much earlier in the reaction.

Heating to 700°C yields a narrower but otherwise unchanged [137]Ba spectrum (Fig. 6(B)). Although $BaCO_3$ is not detectable by XRD in this sample, the shoulders on the major resonances of this spectra suggest that this phase may still be present.

By 900°C, the centre of gravity (COG) of the major resonance has shifted from ca. 70 to 250 ppm, i.e. in the direction of celsian (COG ≈600 ppm [10]) (Fig. 6(C)). The small amount of BaO known by XRD to be present in this sample should appear as a narrow peak at ca. 750 ppm [10], and may account for a smaller shoulder at this position on the main envelope. The weaker broad feature at ca. −100 to −700 ppm in this spectrum is in the region of Ba_2SiO_4 and $BaAl_2O_4$.

At 1100°C, the COG of the major resonance has shifted further towards the celsian position, and the amounts of Ba_2SiO_4 and $BaAl_2O_4$ have decreased (Fig. 6(D)). The product at 1300°C is predominantly celsian, in which the Ba is placed in an irregular site located in the (Al, Si) tetrahedral network, with nine oxygen neighbors in the Ba coordination polyhedron and another oxygen outside the bonding range [18]. The broad [137]Ba spectrum of this phase (Fig. 6(D)) appears to be composed of at least three component resonances between 400 and 700 ppm, but the spectra are broad and not enough is presently known about the effect of atomic environments, including next-nearest neighbour effects, to interpret these results in terms of the celsian structure.
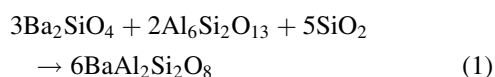
4. Gel transformation reactions

These results suggest that the original gel consists of an intimate association of Al, Si and Ba, with additional crystalline Ba acetate attached to the gel surface. After heating to 500°C, the gel remains amorphous but the surface acetate is decomposed to $BaCO_3$. The gel displays the NMR characteristics of a homogeneous aluminosilicate gel, (the [27]Al shoulder at ca. 36 ppm and the prominent [29]Si feature at −86 ppm). The [137]Ba spectrum suggests that the Ba occurs predominantly in this gel, which is not totally homogeneous; some Ba may also be present in Si-rich regions (the [29]Si peak at −62 ppm) which later form Ba_2SiO_4, and uncombined amorphous SiO_2 is also evidenced by a [29]Si resonance at −110 ppm.
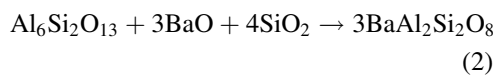
Further heating to 700°C produces a disordered feldspar-like aluminosilicate framework in which the Ba has not achieved its final sites and which remains X-ray amorphous. By 900°C, crystallization of hexacelsian has begun, together with a small amount of BaO and mullite, the latter formed in the Ba-poor regions. This temperature also marks the first appearance of some $BaAl_2O_4$, evidenced by a small ^{27}Al NMR peak at 74.5 ppm. The crystallinity of the celsian improves on heating to higher temperatures, during which the Ba increasingly occupies the polyhedral feldspar sites.

The present results suggest that the bulk of the celsian forms directly from the more homogeneous region of the gel, but secondary celsian-forming reactions may also occur:
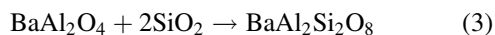
(i) Reaction of Ba_2SiO_4 from the Si-rich regions with mullite from the Al-rich regions

$$3Ba_2SiO_4 + 2Al_6Si_2O_{13} + 5SiO_2 \rightarrow 6BaAl_2Si_2O_8 \tag{1}$$

(ii) Reaction of mullite with the surface BaO

$$Al_6Si_2O_{13} + 3BaO + 4SiO_2 \rightarrow 3BaAl_2Si_2O_8 \tag{2}$$

(iii) Reaction of $BaAl_2O_4$ with SiO_2

$$BaAl_2O_4 + 2SiO_2 \rightarrow BaAl_2Si_2O_8 \tag{3}$$

On the basis of previous studies of celsian formation from oxide mixtures reviewed by Allameh and Sandhage [19], reaction (3) occurs only slowly, consistent with the small amount of $BaAl_2O_3$ remaining at 1300°C.

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