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Crystallization of fibre-coating compounds of potential use in fibre-reinforced oxide ceramics

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Abstract

Mixed oxide compounds of potential usefulness for fibre coatings (hexagonal celsian, $BaAl_2Si_2O_8$ and lanthanum hexaluminate, $LaAl_{11}O_{18}$) were prepared by hybrid sol–gel synthesis and their thermal crystallisation was monitored by thermal analysis, X-ray diffraction and multinuclear solid state MAS NMR. Both the gels convert to the crystalline phase below about 1200°C, via amorphous intermediates in which the Al shows an NMR resonance at 36–38 ppm sometimes ascribed to Al in five-fold coordination. Additional information about the structural changes during thermal treatment was provided by ^{29}Si and ^{137}Ba MAS NMR spectroscopy, showing that the feldspar framework of celsian begins to be established by about 500°C but the Ba is still moving into its polyhedral lattice sites about 400°C after the sluggish onset of crystallization. Lanthanum hexaluminate crystallises sharply at 1230°C via γ-Al_2O_3. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Fibre-reinforced ceramic composites consist of a matrix material, the fibres, and possibly one or more layers of fibre-coating material whose purpose is to permit only weak bonding of the fibre to the matrix, allowing efficient crack deflection and fibre pullout. In composites for use in high-temperature oxidising conditions, the use of oxides as the matrix and fibres has advantages, but introduces the need for compatible oxide-based interface phases.

A number of simple and complex oxides have been suggested[1] as candidates for the interface layer in oxide–oxide composites. The desirable properties of the fibre/matrix interface material for oxide–oxide composites are that it should have long-term stability in high-temperature oxidising environments, it should bond only weakly with either the fibre or the matrix material, *or* that it should itself be weak, either because of the presence of crystallographic cleavage planes which can be oriented parallel to the fibre-matrix interface, or because it undergoes phase changes which are associated with small volume changes.

Hexagonal celsian, $BaAl_2Si_2O_8$, is a potentially useful example of the latter type of interface phase, since this crystalline modification undergoes a polymorphic phase transformation at 300°C, with an associated volume change which can lead to mechanical instability. Hexacelsian is a feldspar with a structure consisting of tetrahedral Al, Si double-layers with the larger Ba ion in the polyhedral sites between the double layers [Fig. 1(A)].

Lanthanum hexaluminate is an example of an interface candidate containing cleavage planes, since it has the magnetoplumbite structure[2] related to β-alumina, consisting of alumina spinel blocks separated by mirror planes containing the La^{3+} [Fig. 1(B)]. The aim of the present work was to study the sol–gel preparation and properties of hexacelsian and lanthanum hexaluminate fibre coatings, with particular reference to the thermal

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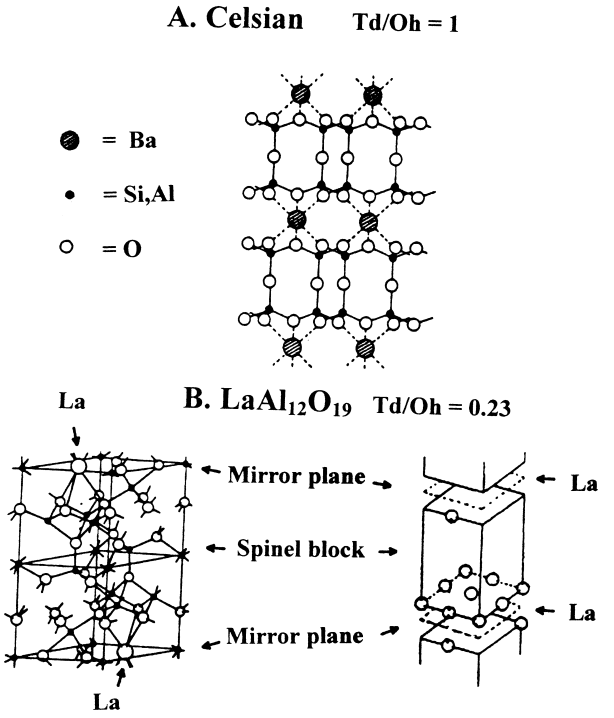

Fig. 1. Structures of: (A) hexagonal celsian; (B) lanthanum hexaluminate.

crystallisation of these materials. The ultimate goal was to develop fibre-reinforced composites based on mullite ($Al_6Si_2O_{13}$).

The soft chemical approach of sol–gel synthesis has considerable advantages as a method for producing interface phases which can be applied by dip-coating or drawing the fibres through a gel bath. The thermal evolution of crystalline products from these gel-derived precursors involves several steps, including the removal of solvent and volatile by-products and the atomic rearrangements necessary to establish the crystal structure. Solid state nuclear magnetic resonance spectroscopy with magic-angle spinning (MAS NMR) has proved to be a useful technique for studying the atomic arrangements in gel-derived ceramic precursors prior to their crystallization. The present work uses a combination of MAS NMR, thermal analysis and X-ray powder diffraction to study the thermal evolution of crystalline hexacelsian and lanthanum hexaluminate from hybrid (organic/inorganic) gels of the appropriate compositions.

2. Experimental

The gels were prepared from reagent grade Al-sec-butoxide, tetraethylorthosilicate (TEOS), and the acetates of Ba and La as appropriate. The celsian gel was prepared by the method of Tredway and Risbud[3] involving the slow addition of a dilute solution of Al-sec-butoxide in isopropanol to partially-hydrolysed TEOS in ethanol followed by the addition of an aqueous solution of Ba acetate acidified with acetic acid. After gelation, the product was dried slowly to allow the volatilization of the alcohol by-products. A similar preparation method was used by Liu et al.[4] in the synthesis of one of their gels for a study of the use of seeding to encourage the preferential crystallization of monoclinic celsian.

Several different methods for the preparation of lanthanum hexaluminate were tried; the results reported here are for a gel prepared from a solution of Al-sec-butoxide in 2-propanol, stabilised by adding 38 mol% acetylacetonate (AcAc). La acetate was dissolved in this solution under an Ar atmosphere with stirring and the mixture peptized with HNO_3. Gelation was carried out in air at 60(C, followed by vacuum drying at 40–60°C.

Thermal analysis was carried out on the gels in flowing air (50 ml min^{-1}) at a heating rate of 10°C min^{-1} using a Rheometrics STA 1500 thermoanalyser. Powdered samples of the gels were heated separately to various temperatures in platinum crucibles for 15 min (celsian) or for 60 min (lanthanum hexaluminate) in a pre-heated electric muffle furnace, then examined by XRD (Philips PW1700 computer-controlled goniometer with a graphite monochromator and Co K_α (radiation) and by multinuclear MAS NMR spectroscopy at 11.7 T (Varian Unity 500 spectrometer with 5 mm Doty MAS probe spun at 10–12 kHz). The NMR acquisition conditions were:

> ^{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 and a refocussing interval of 20 μs, the spectra referenced to 1 M aqueous BaCl solution. Approximately 500,000 transients were acquired for each spectrum, which was processed by left-shifting by two points to minimise the effects of probe ringdown, pulse breakthrough, etc.

3. Results and discussion

The differential scanning calorimetric (DSC) and thermogravimetric (TG) curves of the three gels are shown in Fig. 2.

All the gels lose volatile constituents (solvents and alcohol by-products) in more than one stage below about 450°C. The total mass losses associated with the $<450°C$ exotherms in celsian and lanthanum hexaluminate are 40.9 and 60%, respectively. After the exothermic loss of the volatiles, both gels remain X-ray

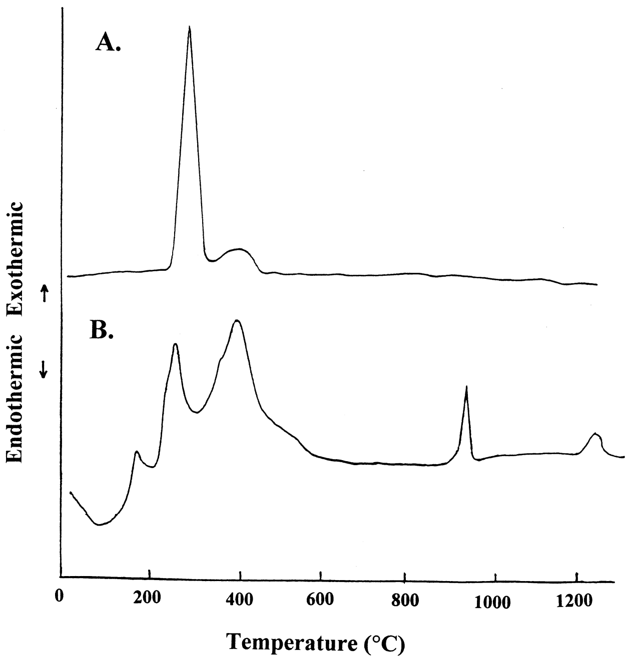

Fig. 2. DSC and TG traces of: (A) celsian gel; (B) lanthanum hexaluminate gel. Heating rate 10°C min^{-1} in air (50 ml min^{-1}).

amorphous. The DSC of celsian gel [Fig. 2(A)] shows no further thermal events up to 1300°C, but the lanthanum hexaluminate gel shows a sharp exotherm at 936°C and a broader exotherm at 1237°C [Fig. 2(B)]. These higher-temperature events have no associated mass change, and are related to the crystallisation process.

XRD shows that, despite the lack of a crystallisation exotherm in the celsian gel, crystallisation occurs sluggishly over the temperature range 900–1100°C (Fig. 3); at 900°C, the major reflection of celsian has begun to develop on the side of the major broad amorphous gel XRD hump. At the same temperature, peaks corresponding to the major reflections of mullite ($Al_6Si_2O_{13}$) and BaO appear, suggesting the presence of inhomogeneous aluminosilicate and Ba-rich regions in the gel. By 1100°C, these have given way to well-crystallised celsian, with very small traces of Ba_2SiO_4 and $BaAl_2O_4$, the latter disappearing only slowly on heating to 1250°C. The XRD patterns of lanthanum hexaluminate (Fig. 4) show the development of diffuse lines above the temperature of the 936°C exotherm, corresponding to γ-Al_2O_3 [PDF pattern no. 10-425, indicated by asterisks in Fig. 4(D)]. At about the temperature of the second exotherm, the diffuse pattern changes abruptly to that of hexagonal $LaAl_{11}O_{18}$ [PDF no. 33-699, shown in Fig. 4(G)], but some of these peaks, notably the major 017 reflection at $d = 2.64$ Å, are broad and poorly developed [Fig. 4(E)]. Heating at 1350°C produces a sharper pattern [Fig. 4(F)], but a small trace of crystalline α-Al_2O_3 is also detectable at this temperature, resulting from the transformation of a slight excess of γ-Al_2O_3.

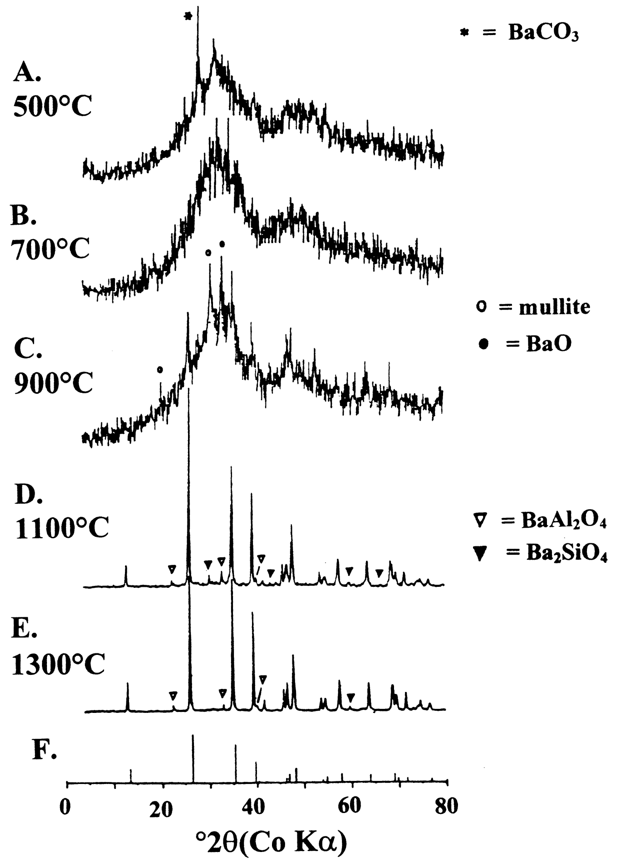

Fig. 3. XRD traces of celsian gel heated at the indicated temperatures for 15 min.

3.1. ^{27}Al MAS NMR spectroscopy

The ^{27}Al MAS NMR spectra of celsian gels show a predominance of octahedral Al in the unheated gel (Fig. 5), in which the two peaks in the octahedral region (at −11 and −32 ppm) arise from a single site acted on by an electric field gradient (EFG) which gives rise to a typical quadrupolar lineshape. This lineshape can be simulated by allowing the nuclear quadrupole coupling constant and the asymmetry parameter to take the values of 7.8 MHz and 0.2, respectively [Fig. 5(A), insert]. The resulting calculation indicates that the isotropic chemical shift (the chemical shift in the absence of the EFG) is −0.5 ppm, close to the value of the hydrated Al ion used as the reference for these spectra.

Heating the gel produces a progressive increase in the proportion of the tetrahedral Al resonance at about 60 ppm, as the tetrahedral Al(Si)–O feldspar framework is slowly established. Between about 500–800°C, a broad shoulder at about 36 ppm appears, in the position often attributed to Al in five-fold coordination. An alternative explanation which appears to be valid for aluminosilicate gels of mullite composition,[5] ascribes this resonance to a relaxed form of a characteristic tetrahedral oxygen tricluster defect. In the present gels, this shoulder

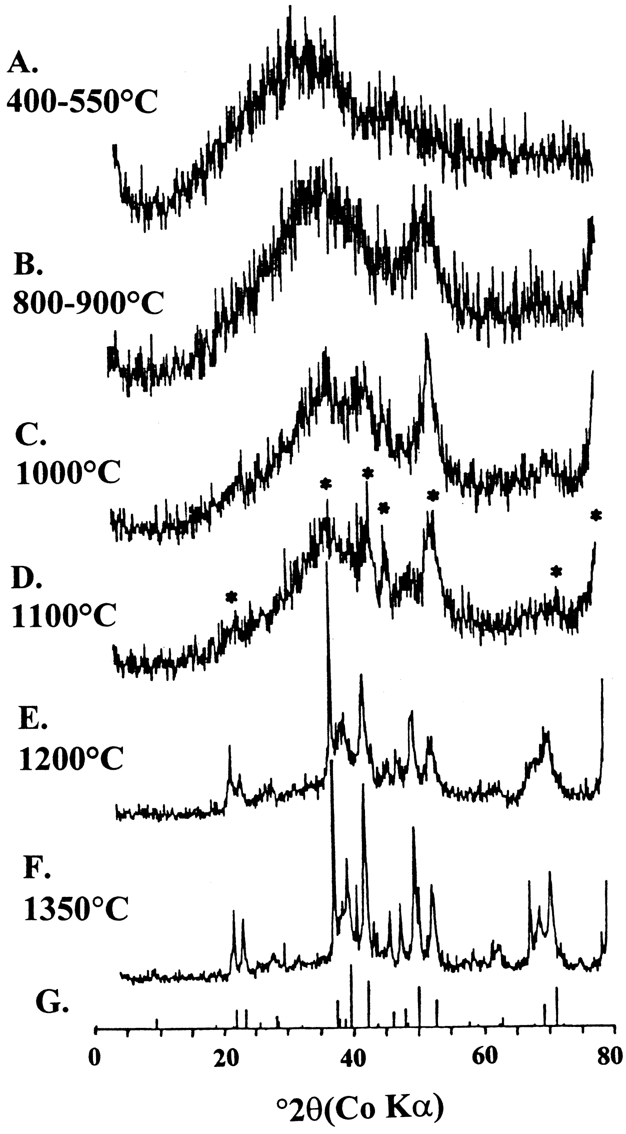

Fig. 4. XRD traces of lanthanum hexaluminate gel heated at the indicated temperatures for 60 min. Asterisks indicate the reflections of γ-Al_2O_3 (PDF no. 10-425). The powder pattern of $LaAl_{11}O_{18}$ (PDF no. 33-699) is shown in (F).

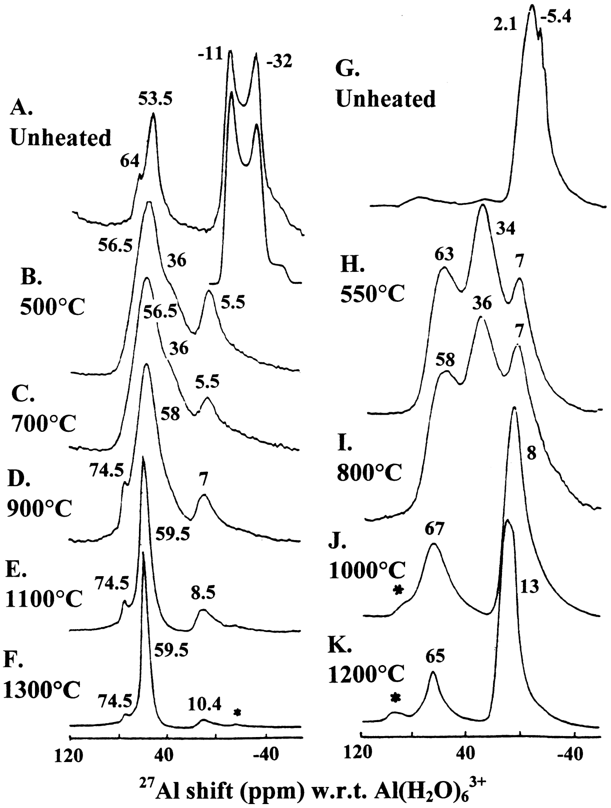

Fig. 5. 11.7 T ^{27}Al MAS NMR spectra of: (A)–(F) celsian gel; (G)–(K) lanthanum hexaluminate gel, heated at the indicated temperatures for 15 min. Asterisk indicates spinning side bands.

may be accounted for by the formation of some mullite-like units, as revealed at higher temperatures by XRD. The smaller tetrahedral and octahedral peaks, at 74.5 and about 8 ppm, respectively, decrease with heating temperature, suggesting that they arise from intermediate phases (the 74.5 ppm peak coincides with that of $BaAl_2O_4$ which is known from XRD to persist in small amounts). The changes in the relative population of the Al sites during heating, as deduced by curve-fitting the ^{27}Al NMR spectra, are shown in Fig. 6(A).

The ^{27}Al MAS NMR spectrum of the unheated lanthanum hexaluminate gel indicates that the Al is present predominantly in octahedral sites [Fig. 5(G)]. Despite the broadness of this resonance, partial resolution of at least two peaks can be observed, the lineshapes of which suggest multiple sites rather than a quadrupole profile. Heating to 550°C converts a significant proportion of the octahedral sites to tetrahedral and the 34 ppm site which may represent either pentacoordinate Al or tricluster defect sites. The mechanism for tricluster formation as a charge-compensation mechanism can readily be understood in aluminosilicate tetrahedra[5] but is less easily envisaged in Si-free systems especially where the other cation (La) is too large to enter into the tetrahedral network. The gel may therefore consist of an amorphous aluminate network containing irregularly cross-linked tetrahedral/octahedral clusters. Tricluster formation may be necessary to provide a localised charge compensation mechanism in the regions where the relatively large and immobile rare earth ion is too remotely located to carry out this function. As was found for celsian, the intensity of the 36 ppm resonance decreases abruptly and disappears altogether at 1000°C [Fig. 5(J)]; by contrast with celsian, however, this corresponds to the formation of γ-Al_2O_3 spinel, and is well below the temperature at which crystalline $LaAl_{11}O_{18}$ appears. Most of the Al from the 36 ppm sites finds its way into the octahedral sites [Fig. 6(B)] such that at the appearance of crystalline $LaAl_{11}O_{18}$ [Fig. 5(K)] the measured tetrahedral/octahedral ratio is 0.24, in excellent agreement with the value of 0.23 expected from the crystal structure.

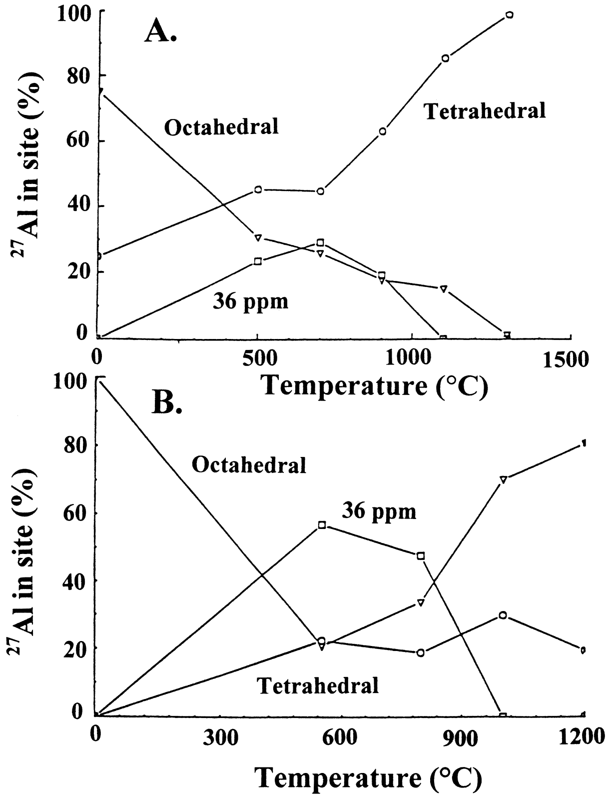

Fig. 6. Changes in the ^{27}Al site occupancies as a function of heating temperature: (A) celsian gel; (B) lanthanum hexaluminate gel.

3.2. ^{29}Si and ^{137}Ba MAS NMR spectroscopy

Since the celsian samples contain other elements whose nuclei are suitable for NMR study, their NMR spectra were also obtained in order provide additional information about the gel transformations in these compounds.

The NMR spectra of both ^{29}Si and ^{137}Ba acquired for the unheated and heated celsian gels (Fig. 7) are broad and somewhat featureless. Soon after expulsion of the volatiles <500°C, the ^{29}Si spectrum acquires the essential features of the tetrahedral feldspar framework (the poorly resolved group of resonances at about -86 ppm to -113 ppm). The development of crystalline celsian is characterised principally by the increasing importance of the resonance at -88 ppm associated with $Q^4(4Al)$ sites (tetrahedral Si with four Al nearest neighbours). The spectral intensity in the region of -113 ppm is associated with the $Q^4(0Al)$ sites of uncombined SiO_2 and is sometimes found in natural feldspars in which it is attributed to XRD-undetectable silica impurities in the grain boundaries. Another ^{29}Si resonance at -62 to -66 ppm which appears at 500°C and remains throughout the heating process arises from the presence of incipient Ba_2SiO_4. This phase appears in small amounts in the XRD trace and is still present at 1300°C.

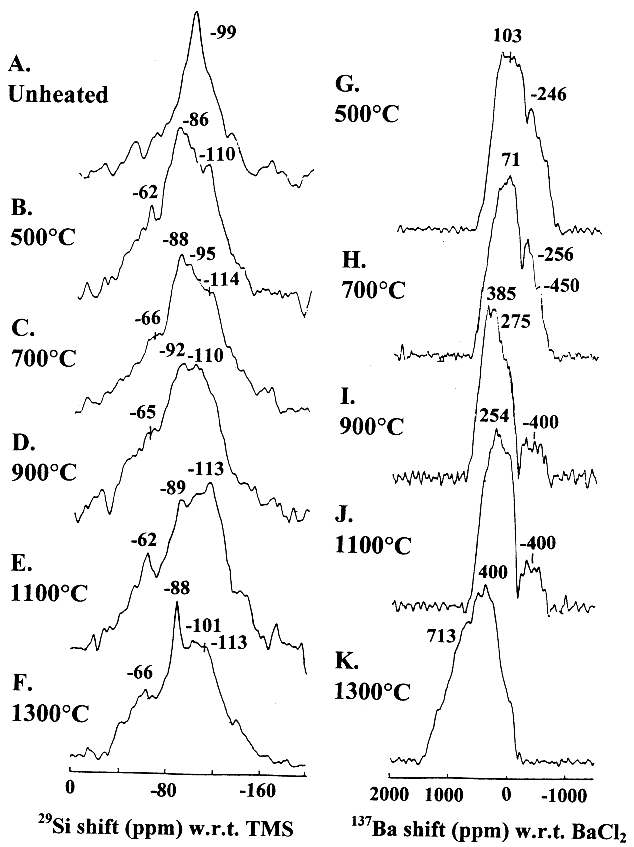

Fig. 7. 11.7 T MAS NMR spectra of celsian gel heated at the indicated temperatures for 15 min: (A)–(F) ^{29}Si spectra; (G)–(K) ^{137}Ba spectra.

The ^{137}Ba spectra of the gels (Fig. 7) show a progressive shift in the centre-of-gravity (COG) of the broad resonance envelope from about 70 to 250 ppm at 900°C. The broad envelope contains the unresolved resonances of the Ba species known by XRD to be present at various stages of the thermal reaction sequence, namely $BaCO_3$ (386 and -406 ppm),[6] Ba_2SiO_4 (COG -270 ppm)[6] and $BaAl_2O_4$ (COG -191 ppm).[6] The major shift of the gel COG towards the less shielded position of celsian (COG $\approx$600 ppm) occurs late in the thermal sequence (1300°C), indicating that the large Ba ion moves into its final coordination polyhedron of nine oxygen nearest neighbours well after the establishment of the feldspar aluminosilicate framework.

4. Conclusions

1. Multinuclear solid-state MAS NMR results are useful in complementing thermal analysis and XRD studies of gel crystallisation reactions, by providing information about changes in the atomic environments in the gels prior to crystallisation.
2. The combined data for hexacelsian gels indicates that the Si atoms assume the essential features of a

typical feldspar framework soon after the expulsion of the volatiles at about 500°C. Al occupies the tetrahedral feldspar sites more gradually, and Ba migrates into its final nine-fold coordinated polyhedra well after the establishment of the long-range ordering of feldspar is indicated by XRD.

3. The present lanthanum hexaluminate gel remains X-ray amorphous until an exothermic event at 936°C which accompanies the formation of the cubic γ-Al_2O_3 spinel component. The associated conversion of octahedral Al to tetrahedral involves an intermediate coordination state characterised by a ^{27}Al NMR resonance at 36 ppm. By 1200°C, when the characteristic XRD pattern of $LaAl_{11}O_{18}$ abruptly appears, the tetrahedral/octahedral Al ratio has assumed the value demanded by the crystal structure.

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