

Synthesis and Characterization of Precursors for Group II Metal Aluminates

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Precursors to Group II metal aluminates (MAI_2O_4 , M=Mg, Ca, Ba, Sr) are synthesized from inexpensive starting materials including Group II metal oxides/hydroxides, $Al(OH)_3$, triethanolamine (TEA) and ethylene glycol, in a one-pot synthesis process. The precursors are soluble in common organic solvents and can be handled in moist air for a reasonable period of time. On pyrolysis in air to 1200 °C, all three precursors transform to the corresponding Group II metal aluminates. A termetallic double alkoxide, 'ionomer-like' structure is proposed, wherein the alkaline-earth metal is encapsulated by a TEA molecule bridging two alumatrane units. The precursors were characterized using TGA, NMR, mass spectroscopy and elemental analyses, and the pyrolysed precursors were briefly characterized using x-ray diffraction analysis. © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

Chemical synthesis has become an indispensable tool in processing mixed-cation oxide ceramics, especially as newer applications typically require

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greater purity and better control over product properties. The Group II metal aluminates (MAI_2O_4 , M=Mg, Ca, Ba, Sr) are one important class of mixed-cation oxide ceramics with widespread applications. For example, $CaAl_2O_4$ is used as a hydraulic material in the cement industry¹ and also in high-strength, high-toughness ceramic/polymer composite materials.² Spinel ($MgAl_2O_4$) is used as a refractory and insulating material.^{3,4} Strontium and barium aluminates are used as catalyst supports⁵ and they make good luminophores when doped with appropriate transition-metal ions.⁶ The availability of homogeneous, chemically and phase-pure, high surface area materials is crucial for most if not all of these applications.

Conventional synthesis of ceramic materials by solid-state reactions which involve reaction of individual oxides or carbonates at high temperatures (>1400 °C)⁷ are inefficient, especially in the case of mixed-cation oxide ceramics, as they often lead to inhomogeneous products with imprecise control over product stoichiometry and phase purity. Although chemical synthesis routes overcome these problems and offer access to processable precursors and homogeneous ceramic materials, they are still plagued by certain problems. For example, sol-gel processing, the most widely used chemical processing route, requires hydrolytically unstable and expensive metal alkoxides.⁸ Other chemical approaches, such as freeze-drying, co-precipitation etc., involve cumbersome processing techniques.⁹

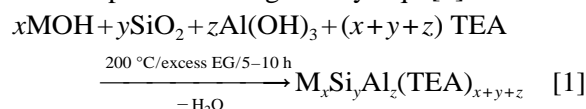
To date, the Pechini process, which involves polyesterification of citric acid metal chelates with ethylene glycol (EG) and subsequent pyrolysis of the resultant resinous intermediate, offers the most efficient, economical and general method for the synthesis of multimetallic oxides.¹⁰ A variety of mixed-metal oxides, including calcium aluminate, can be prepared by the Pechini process and its modifications, e.g. the 'liquid-mix' process.¹¹ However, the final mor-

phology of the ceramic material depends on a number of factors, including: the order of addition of reagents; the H₂O/citric acid/EG ratio; the heating schedule during gelation and calcination; and the mass ratio of polymeric resin to the metal.^{10,12} The chemistry of the starting precursor solution and that of intermediate species in Pechini processes have been studied in a few systems,¹²⁻¹⁴ but not for aluminate precursors.

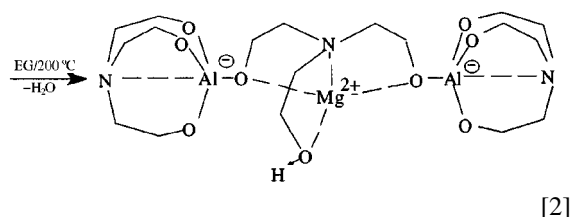
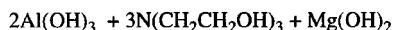
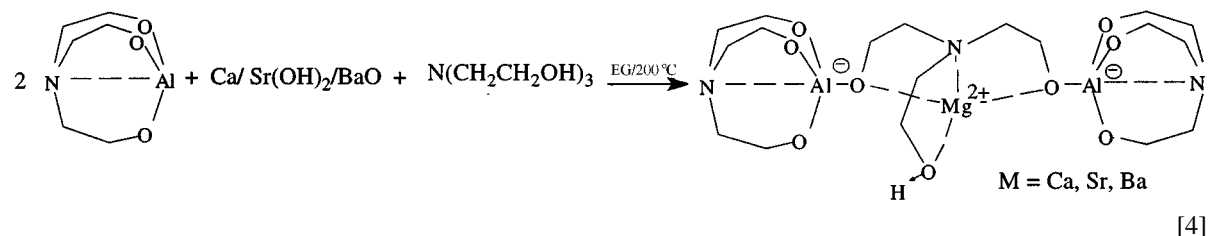
A few alternative chemical routes to Group II metal aluminates have been reported, but the precursor chemistry is not discussed to any extent.¹⁵⁻¹⁷ The rational synthesis of materials via chemical routes requires an understanding of the structure and chemistry of the precursors, so that the process can be generalized.

We recently reported a general, low-cost route to alkoxide precursors to mixed-cation oxide ceramics (spinel, mullite and cordierite), by direct reaction of any stoichiometric mixture of SiO₂, Al(OH)₃ and Group I/II metal hydroxides with EG and triethanolamine (TEA).¹⁸ This route, termed the 'oxide one-pot synthesis' (OOPS) process, provides stable processable precursors to a wide variety of phase-pure and selectively doped ceramics. It uses simple, inexpensive starting materials that make it more economical than the Pechini process, where metal nitrates can account for 60–80% of the total cost.¹⁰ Of the various OOPS precursors synthesized to date, molecular structures have been described only for the spinel (MgAl₂O₄) and potassium aluminosilicate (K₂O · Al₂O₃ · 2SiO₂) precursors.^{19,20} Herein we extend the efforts to other Group II metal aluminates.

A general reaction for the synthesis of OOPS-derived precursors is given by Eqn [1].



The OOPS synthesis of the magnesium aluminate (spinel) precursor is shown in Eqn [2]. The

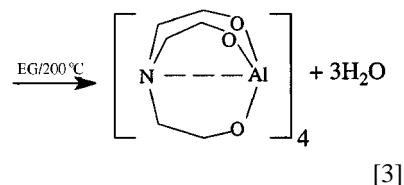


spinel precursor can also be made stepwise via an alumatrane [(TEAAl)₄] intermediate.¹⁹ In the present study the precursors are made stepwise, via a variation on the OOPS process according to the reactions represented by Eqns [3] and [4], so that the intermediates and precursors can be characterized. It is shown that the OOPS process leads to similar precursors.

EXPERIMENTAL

General synthesis procedures

All operations were carried out with careful exclusion of extraneous moisture. Air- and moisture-sensitive materials were handled using standard Schlenk techniques in a nitrogen atmosphere in a Vacuum Atmospheres MO40-2-Dri-Lab glovebox (Vacuum Atmospheres Co., Hawthorne, CA, USA). All chemicals were reagent-grade, purchased from standard vendors and used as received unless otherwise specified. Ethylene glycol (EG) (AR,



Baker) was used as received. Recovered EG was distilled twice and recycled.

Stepwise syntheses

Syntheses of alumatrane from $\text{Al}(\text{OH})_3$, and from it the spinel precursor, are described elsewhere.¹⁹ Syntheses of other Group II metal aluminate precursors from alumatrane are described below. NMR, mass spectroscopy and elemental analyses data for the precursors are tabulated in the Results and discussion section.

Calcium aluminate precursor

($\text{CaAl}_2\text{C}_{18}\text{H}_{37}\text{O}_9\text{N}_3$)

Calcium (0.92 g, 23.0 mmol) was dissolved in approx. 100 mL of EG by refluxing for about 10 h. A solution of $(\text{TEAAl})_4$ (ceramic yield=28.8%, 7.98 g, 23.0 mmol) and triethanolamine (TEA) (3.43 g, 23.0 mmol) in 100 ml of EG was added to the calcium solution. The reaction mixture was stirred and heated to distill off EG. The reaction mixture cleared on heating and after about an hour the solution was concentrated to 100 ml. The remaining solvent was removed by heating under vacuum at 170 °C for 12 h. The resultant light-brown solid was crushed under nitrogen and vacuum-dried at 200 °C for 6 h. Yield: 11.3 g (91.9%). The TGA ceramic yield of the solid is 28.9% (1000 °C in air). Theoretical ceramic yield calculated for the formation of CaAl_2O_4 from the proposed precursor: 29.6%. Elemental analysis (%): Found (calculated): C, 40.5 (40.5); H, 7.1 (6.9); N, 7.6 (7.9).

Strontium aluminate precursor

($\text{SrAl}_2\text{C}_{18}\text{H}_{37}\text{O}_9\text{N}_3$)

$\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (10.0 g, 37.7 mmol) was dissolved in 200 ml of EG by heating in a 500 ml Schlenk flask. $(\text{TEAAl})_4$ (ceramic yield=28.8%, 14.0 g, 79.2 mmol) along with TEA (5.62 g, 37.7 mmol), dissolved in 60 ml of EG, was then added. The resultant solution was heated to 200 °C to distil off EG. The reaction mixture cleared on heating and after about two hours the solution was concentrated to 100 ml. The resultant viscous solution was vacuum-dried at 180 °C for 12 h to yield a light-brown solid. Yield: 21.3 g (97.2%). The solid was dissolved in THF, reprecipitated in hexane, vacuum-dried at 100 °C for 6 h and then subjected to analyses.

The TGA ceramic yield of the resultant solid was 35.2% (1000 °C in air). Theoretical ceramic yield calculated for the formation of SrAl_2O_4 from the proposed precursor: 35.4%. Elemental analysis (%): Found (calculated): C-, 36.1 (37.2); H, 6.5 (6.4); N, 6.6 (7.2).

Barium aluminate precursor

($\text{BaAl}_2\text{C}_{18}\text{H}_{37}\text{O}_9\text{N}_3$)

BaO (8.0 g, 52.3 mmol) was weighed and mixed with 150 ml of degassed EG in a 250 ml Schlenk flask, in the drybox. The mixture was taken out of the drybox and heated under nitrogen to obtain a cloudy viscous solution. A solution of $(\text{TEAAl})_4$ (ceramic yield=28.8%, 18.6 g, 105 mmol of Al_2O_3) in approx. 60 ml of EG and TEA (7.80 g, 52.3 mmol) were then added to the BaO solution. The reaction mixture was stirred and heated to distil off EG. The reaction mixture did not become clear, and a solid precipitated out within 10 min after the two solutions were mixed. The reaction mixture was vacuum-dried at 180 °C for 6 h. The solid that formed was crushed under nitrogen and further vacuum-dried at 180 °C for 12 h. Yield: 30.8 g (92.5%). The TGA ceramic yield of the solid is 40.1% (1000 °C in air). Theoretical ceramic yield calculated for the formation of BaAl_2O_4 from the proposed precursor: 40.5%. Elemental analysis (%): Found (calculated): C, 33.3 (34.2); H, 5.7 (5.9); N, 5.6 (6.6). The results of the elemental analysis are outside the acceptable range, probably due to the precipitation that occurred during the synthesis as a result of the low solubility of the barium aluminate precursor, as discussed in the Results and discussion section.

OOPS syntheses

Calcium aluminate precursor

($\text{CaAl}_2\text{C}_{18}\text{H}_{37}\text{O}_9\text{N}_3$)

Aluminium hydroxide hydrate (6.61 g, 35.8 mmol of Al_2O_3), and CaO (2.01 g, 35.9 mmol) were mixed with TEA (16.1 g, 108 mmol, 1 nitrogen per metal atom) in 200 ml of EG in a 250 ml flask. The solution was heated and EG was distilled off along with the H_2O formed. The solution cleared in about 30 min during heating. The solution was concentrated to 50 ml and the remaining solvent was vacuum-dried at 150 °C for 12 h. The resultant light-yellow solid weighed 17.7 g (92.9%) and had a TGA ceramic yield of 26.5% (950 °C in

air). Theoretical ceramic yield calculated for CaAl_2O_4 : 29.6%.

Strontium aluminate precursor

($\text{SrAl}_2\text{C}_{18}\text{H}_{37}\text{O}_9\text{N}_3$)

Aluminium hydroxide hydrate (3.52 g, 19.1 mmol of Al_2O_3), $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (5.01 g, 18.9 mmol), and TEA (8.61 g, 57.7 mmol) were mixed and heated with 200 ml of EG in a 250 ml flask. The reaction cleared in about 30 min and EG was distilled out along with by-product water until the solution had been concentrated to about 50 ml. Then the solvent was vacuum-dried at 150 °C for 12 h, to yield a white solid. Yield: 9.15 g (98.2%). The solid was dissolved in THF, and rapidly reprecipitated in hexane, vacuum-dried at 100 °C for 6 h and then subjected to analyses. TGA ceramic yield 33.2% (950 °C in air). Theoretical ceramic yield calculated for SrAl_2O_4 : 35.4%. Elemental analysis (%): Found (calculated): C, 37.0 (37.2); H, 6.7 (6.4); N, 6.9 (7.2).

Thermogravimetric analysis (TGA)

TGAs were performed using a 2950 Thermal Analysis Instrument (TA Instruments, Inc., New Castle, DE, USA). Samples (10–20 mg) were placed in a platinum pan and heated in flowing, dry air ($60 \text{ cm}^3 \text{ min}^{-1}$), in 'Hi-Res 4.0 mode' at 50 °C min^{-1} to 1000 °C.

NMR spectroscopy

NMR spectra were recorded using a Bruker Aspect 3000, AM-360 MHz spectrometer (Bruker Instruments Inc., Manning Park, Billerica, MA, USA). $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra were obtained with the spectrometer operating at 59.6 MHz and using a 32 000 Hz spectral width, a relaxation delay of 15 s, a pulse width of 58°, and 32 000 data points. The samples were dissolved in distilled EG. C_6D_6 and tetramethylsilane, in a sealed inner tube, served as lock and reference materials, respectively. ^{27}Al NMR spectra were obtained with the spectrometer operating at 93.8 MHz and using a 41 000 Hz spectral width, a relaxation delay of 0.2 s and a pulse width of 13°. The samples were dissolved in distilled EG. D_2O in a sealed inner tube served as the lock solvent and a 1 M solution of AlCl_3 in $\text{D}_2\text{O}/\text{H}_2\text{O}$ (1:1) served as the external reference. ^1H and ^{13}C spectra were taken with the samples dissolved in CDCl_3 .

Mass spectroscopy

Mass spectra of the samples were recorded at the University of Michigan, Department of Chemistry. FAB studies were conducted using a VG 70-70-E, a magnetic-sector, double-focusing mass spectrometer made by VG Analytical; the spectrometer is operated using the 11-250-J data collection software system supplied with it.

The spectrometer was scanned from m/z 2800 to m/z 75, using an exponential-down magnet scan and an external calibration against CsI clusters. The sample was dissolved in 3-nitrobenzyl alcohol and deposited on the target, on the probe tip. Prominent matrix (3-nitrobenzyl alcohol) peaks were subtracted out. Low-intensity peaks were the average of 10 or more scans, averaged as continuum data. The continuum data were then smoothed and centroided by the data system. The FAB gun used xenon gas, and was run at 1 mA current and 10 kV.

Pyrolysis studies

Samples (approx. 1 g) of all three aluminate precursors were placed in separate alumina boats and heated in dry air at 10 °C min^{-1} to 300 °C; this was followed by a 2 h hold in a Thermolyne Type 6000 Furnace in flowing air (100 ml min^{-1}), equipped with a Eurotherm programmable temperature controller (Model No. 818P, Northing, UK). Then the samples were transferred to a 51314 Lindberg furnace equipped with a Lindberg 59246-P Com controller, and heated in flowing air to 1200 °C at 40 °C min^{-1} , with 1 and 2 h holds at 300 °C and 500 °C respectively.

X-ray diffraction (XRD) studies of precursor pyrolysis products

Samples (40–80 mg) were loaded in sample holders (glass plates) and a Rigaku rotating anode goniometer (Regaku Denki Co. Ltd, Tokyo, Japan) was used for data collection. The working voltage and current were 40 kV and 100 mA respectively. $\text{Cu K}\alpha$ ($\lambda = 1.54 \text{ \AA}$) radiation with a nickel filter was used. Scans were continuous in the range $2\theta = 5\text{--}80^\circ$ with a step scan of $2\theta = 10^\circ \text{ min}^{-1}$ and increments of $2\theta = 0.05^\circ$. Products (peak positions and relative intensities) were characterized by comparison with standard JCPDS files.

RESULTS AND DISCUSSION

The precursors were made from inexpensive starting materials in high yields. Both routes (stepwise and one-pot) provide the same precursors, as was proved by thermogravimetric and mass spectral analyses. Only the stepwise route product is analysed in detail here to establish the molecular structure of the precursor. The precursors are soluble in common organic solvents and in EG, except for the barium aluminate precursor, which precipitates out during the synthesis (see the Experimental section) and is insoluble in any solvent. However, it is soluble enough in CDCl_3 and EG to obtain satisfactory ^1H and ^{13}C , and ^{27}Al , NMR spectra respectively. The decreased solubility of the barium aluminate precursor is not unexpected, based on the proposed structure, as the solubility of these precursors is believed to be due to the encapsulation of the metal ion by bridging TEA. The larger Ba^{2+} ion may not fit into the TEA cavity. Efforts to synthesize related double alkoxide complexes with a bridging glycolato ligand, instead of bridging TEA, always lead to EG insoluble precipitates (R. Narayanan and R. M. Laine, unpublished results). This supports the idea that the TEA encapsulation (see Eqn [4]) is required for solubility.

Analyses of the precursors and characterization of precursor structure by various techniques are discussed below.

TGA

The TGA profiles can be used to develop a pyrolysis protocol to transform precursors to carbon-free inorganic materials in minimum times and at minimum temperatures, and to confirm the composition of the proposed precursor. The TGA decomposition profiles (Figs 1–3) of all three precursors are similar and have three major mass-loss regions. The first major mass loss occurs below $400\text{ }^\circ\text{C}$ and corresponds to ligand decomposition, the second from 400 to $600\text{ }^\circ\text{C}$ to oxidation of organic char produced by ligand decomposition, and the third one between 800 and $950\text{ }^\circ\text{C}$ to carbonate decomposition. The proposed mechanisms for the decomposition processes are discussed elsewhere.²¹ No excess solvent or solvent of recrystallization is seen in any case and the ceramic yields observed in TGA match (within 0.4 – 0.8%) those calculated from the proposed precursor structure in all three

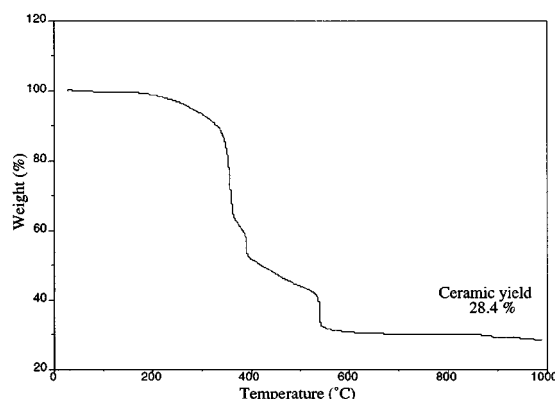


Figure 1 TGA of $\text{CaAl}_2\text{C}_{18}\text{H}_{37}\text{O}_9\text{N}_3$ precursor in air.

‘stepwise synthesis’ precursors. The ceramic yields of the precursors made by one-pot synthesis are lower by 2.5 – 3% , because a slight excess of TEA is used and it is difficult to remove by vacuum evaporation.¹⁹ The ceramic yields, along with the elemental analyses, confirm the compo-

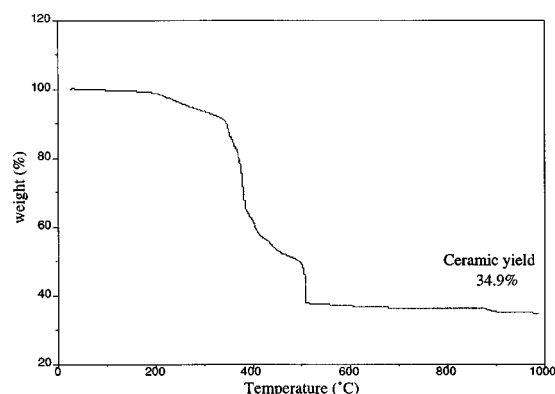


Figure 2 TGA of $\text{SrAl}_2\text{C}_{18}\text{H}_{37}\text{O}_9\text{N}_3$ precursor in air.

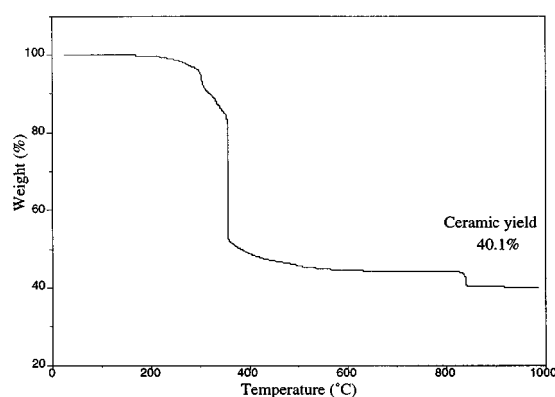


Figure 3 TGA of $\text{BaAl}_2\text{C}_{18}\text{H}_{37}\text{O}_9\text{N}_3$ precursor in air.

sition of the structure proposed for the precursors in the reaction of Eqn [4] above.

NMR

The ^1H and ^{13}C NMR values for the precursors, along with their tentative assignments, are listed in Table 1. The presence of quadrupolar nuclei (Al and N) broaden the peaks, thus obscuring their multiplicity in ^1H NMR and making the ^{13}C NMR less informative. Furthermore, the three ethyleneoxy 'arms' in the central bridging TEA may exchange on the NMR timescale, which could also lead to peak broadening. The free ethyleneoxy group among the three 'arms' of the bridging TEA is not discernible by either ^1H or ^{13}C NMR. However, the chemical shift values are in agreement with standard, predicted values and also similar to those reported for the spinel precursor.¹⁹

The ^{27}Al NMR spectrum has only one broad peak, indicative of a tetracoordinated Al,²²⁻²⁴ in all three precursors (Table 1). In contrast, alumatrane exhibits two broader (than the aluminates) peaks, corresponding to hexa- and tetra-coordinate Al, as expected from the asymmetric tetrameric structure reported.²⁵ The tetramer results from the dative bonds between the aluminium of one alumatrane and oxygens on three other alumatranes.²⁵ The quadrupole moment then of ^{27}Al nucleus causes considerable dependence of the signal width on the gradient of the electric field around the Al nucleus, i.e. on the geometrical arrangement of the substituents around the Al atom.²² In the Group II dialuminate precursors, the ^{27}Al NMR peak is sharper than alumatrane, indicating a more symmetrical envi-

ronment, as in the trimetallic double alkoxide structure proposed in reaction [4]. The chemical shift values (around 62 ppm) are typical of tetracoordinate Al,²²⁻²⁴ suggesting that the dative bonds seen in alumatrane no longer exist.

Mass spectroscopy

Fast atom bombardment (FAB) mass spectral analysis is the only technique that can be used for complexes such as the aluminate precursors. FAB analysis requires that the samples be dispersed on a matrix. All three possible matrix solvents, i.e. TEA, glycerol and *p*-nitrobenzyl alcohol (NBA), interact with the precursors, as was found for the spinel and potassium aluminosilicate precursors.^{19,20} However, with NBA the peaks due to fragmentation of precursors can still be seen amidst matrix interaction peaks (Table 2). Both positive- and negative-ion FAB analyses were done and only the latter was found to be informative. The fragmentation patterns can be explained on the basis of the proposed precursor structure. Intensities of molecular peaks and matrix interaction peaks differ from sample to sample, but the fragmentation patterns for all three precursors are quite similar. A deprotonated molecular ion peak is seen as a significant peak in all three cases. The isotope distributions for the molecular ion peak in all three precursors agree reasonably with those calculated using an 'Isotope pattern calculator' (see Table 3). No evidence is found for higher molecular weight species that might arise by disproportionation or exchange reactions that are common in aluminium alkoxides.²⁶ However, low-intensity

Table 1 NMR data for TEA–Al–TEA–Al–TEA M precursors

$\text{MAl}_2\text{C}_{18}\text{H}_{37}\text{O}_9\text{N}_3$ precursor	^1H NMR	^{13}C NMR	^{27}Al NMR
M=Ca	2.7(b), (NCH_2), 3.7(b), (AlOCH_2); equal intensities, shoulder peaks (free ethyleneoxy?)	53.2 ($\text{NCH}_2\text{CH}_2\text{OAl}$), 56.3 ($\text{NCH}_2\text{CH}_2\text{OH}$), 57.5 (AlOCH_2), 58.0 ($\text{NCH}_2\text{CH}_2\text{OH}$)	62.9 (tetracoordinate)
M=Sr	2.7 (b), (NCH_2), 3.7 (b), (AlOCH_2); equal intensities, shoulder peaks (free ethyleneoxy?)	53.1 ($\text{NCH}_2\text{CH}_2\text{OAl}$), 54.1 ($\text{NCH}_2\text{CH}_2\text{OH}$), 57.5 (AlOCH_2), 59.7 ($\text{NCH}_2\text{CH}_2\text{OH}$)	62.7 (tetracoordinate)
M=Ba	2.7 (b), (NCH_2), 3.7 (b), (AlOCH_2); equal intensities, shoulder peaks (free ethyleneoxy?)	53.0 ($\text{NCH}_2\text{CH}_2\text{OAl}$), 56.2 ($\text{NCH}_2\text{CH}_2\text{OH}$), 57.6 (AlOCH_2), 58.9 ($\text{NCH}_2\text{CH}_2\text{OH}$)	62.6 (tetracoordinate)

Table 2 Mass spectral analyses^a of TEA–Al–TEA–Al–TEA M

Fragment assigned	M=Ca		M=Sr		M=Ba	
	<i>m/z</i>	Intensity	<i>m/z</i>	Intensity	<i>m/z</i>	Intensity
(TEA–Al) ₂ TEA–M–H ⁺	532	97.6	580	72.4	630	20.5
TEA–Al–O–CH ₂ –C ₆ H ₄ –NO ₂	325	85.2	325	100.0	325	100.0
(TEA–Al) ₂ TEA–M+O–CH ₂ –C ₆ H ₄ –NO ₂	686	42.5	734	76.0	784	76.0
(TEA–Al) ₂ TEA–M–H ⁺ +TEA–Al	705	100.0	753	5.6	—	—
[(TEA–Al) ₂ TEA–M+2(HO–CH ₂ –C ₆ H ₄ –NO ₂)]–H ⁺	839	3.2	887	5.2	937	2.4
[(TEA–Al) ₂ TEA–M] ₂	1066	2.2	1162	2.3	—	—

^a Matrix, *p*-nitrobenzyl alcohol. Method, negative-ion FAB.

(approx. 2%) dimer peaks were seen, which might arise by hydrogen bonding.

Pyrolysis studies

A two-stage bulk pyrolysis process, developed for the spinel precursor based on the TGA profile,¹⁹ was used to pyrolyse these precursors. The precursors were pyrolysed to 1200 °C, where crystallization is complete in the spinel precursor.¹⁹ Strontium and barium aluminate precursors transform to the corresponding phase-pure aluminates (Fig. 4). Pyrolysis of calcium aluminate precursor results in a mixture of CaAl₂O₄, CaAl₄O₇ and CaO phases. However, it is known that variations in the pyrolysis time and temperature greatly affect the phase distribution in calcium aluminates.¹⁶ Thus the formation of mixed phases as seen here is not uncommon.

Table 3 Isotope pattern analyses of the molecular ion peaks of MA₂O₄ precursors

Element	Intensity ^a					
	<i>M</i> +1		<i>M</i> +2		<i>M</i> –1	
	Obs.	Calcd	Obs.	Calcd	Obs.	Calcd
Ca	21.2	22.1	5.66	4.8	—	—
Sr	20.0	22.1	5.60	4.1	—	—
Ba	24.9	22.1	—	—	20.9	17.8

^a Molecular ion peak intensity was taken as 100% in each case, for calculations.

CONCLUSIONS

Low-cost Group II metal aluminate precursors are efficiently synthesized using a simple, general process starting from Al(OH)₃, metal oxides/hydroxides, EG and TEA. As the precursors are soluble in common organic solvents, the processability of these precursors into different shapes and forms (films, fibres, coatings etc.) should be possible. The analyses of the precursors suggest an ‘ionomer-like’ structure, in which two alumatrane units are bridged by a TEA moiety and the bridging TEA encapsulates the Group II metal ion (see reaction [4]). Only determination of crystal structure will constitute a direct proof for the ‘metal-encapsulating TEA’ proposed in the structure. To date, efforts to grow crystals have been unsuccessful. However, other analyses prove the composition of the precursor beyond doubt and the decreasing solubility with increasing metal ion size, as seen in the case of Ba, suggests the proposed metal-encapsulated structure for the given composition.

In any molecular ceramic precursor, homogeneous cation distribution and stoichiometry at the molecular level are necessary conditions to produce a homogeneous ceramic material.¹³ In our precursors, stoichiometric control at the molecular level has been achieved as seen in the precursor structure. Understanding the chemistry of the precursors enables us to appreciate and utilize the generality of the technique. This aspect of the OOPS process sets it apart from any existent solution processing techniques and it is expected to be widely used for the production of a variety of mixed-cation oxide materials.

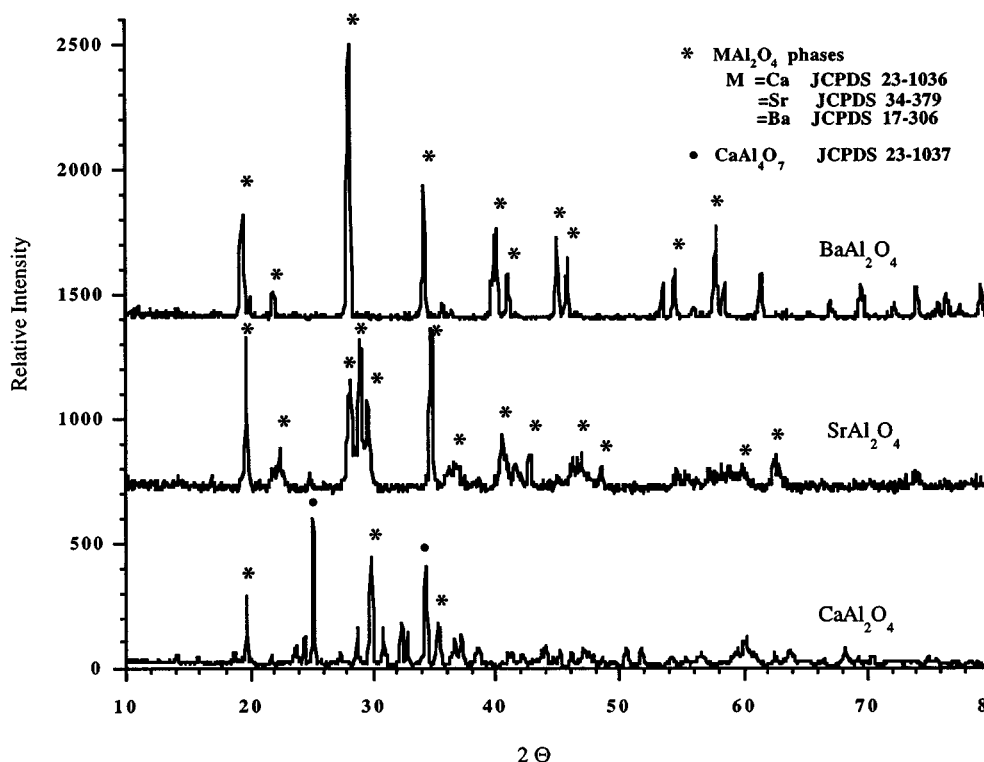


Figure 4 XRD of $\text{MAI}_2\text{C}_{18}\text{H}_{37}\text{O}_9\text{N}_3$ precursors pyrolysed to 1200 °C.

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