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Sol–Gel Synthesis and NMR Characterization of Ceramics

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Abstract: Sol–gel chemistry allows the low temperature synthesis of ceramic powders. The molecular engineering of alkoxide precursors leads to the crystallization of ceramic powders of controlled morphology and structure. Stable sols of tetragonal zirconia have been synthesized via the hydrolysis of chemically modified zirconium alkoxides. Complexing acetylacetone ligands slow down condensation processes and prevent the aggregation of nanosized zirconia particles. The hydrolysis rates of the different molecular precursors have to be matched when multicomponent ceramics such as cordierite are prepared via the sol–gel route. Otherwise phase separation occurs leading to the undesired spinel phase $MgAl_2O_4$. The complexation of aluminium alkoxides decreases their reactivity toward hydrolysis and condensation. Al–O–Si bonds can be formed in solution and the tetrahedral coordination of Al^{III} is preserved allowing the crystallization of cordierite at lower temperatures. Multinuclear NMR appears to be a valuable technique for the characterization of all the species formed during the sol–gel synthesis, from the molecular precursor to the ceramic powder. © 1996 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Ceramics are traditionally made from powders, via solid state reactions. This requires high temperatures and rather long reaction times. In the so-called sol–gel process, a solution of molecular precursors is converted by a chemical reaction into a sol or a gel which on drying and densification gives a solid material.[1] This allows the production of single or multicomponent ceramics with high purity, novel compositions and tailored microstructures. Moreover, films or fibres can be obtained directly from sols or gels by such techniques as dip-coating, spin-coating, spray or drawing.[2]

Sol–gel syntheses are based on inorganic polymerization reactions, refocussing attention on the importance of chemistry in the field of ceramics.[3] The hydrolysis and condensation of metal alkoxides lead to the formation of oxopolymers which transform into an oxide network upon calcination. The structure and morphology of the resulting oxide powders depend strongly on the chemical procedure. They can be conveniently controlled via the chemical modification of alkoxide precursors allowing the production of fine powders.[4] Moreover, metal-organic chemistry leads to the formation of heterometallic species in which M–O–M′ bonds are formed already, in the solution.[5] Such precursors could be used as building blocks for the sol–gel synthesis of multicomponent ceramics.[6] This article first reports on the synthesis of tetragonal zirconia from chemically modified zirconium alkoxides, showing how organic ligands can prevent the growth and aggregation of colloidal particles. The sol–gel synthesis of multicomponent ceramics such as cordierite is then described. The main problem comes from the different hydrolysis rates of the various molecular precursors and the challenge would be to form a homogeneous gel in order to avoid phase separation during the thermal treatment. All these reactions, from the molecular precursors in solution to the solid phases in the ceramics, can be conveniently followed by liquid and solid state multinuclear NMR.

2 SOL–GEL SYNTHESIS OF FINE ZIRCONIA POWDERS

Zirconia based ceramics are used in a wide range of applications. Nanocrystalline zirconia particles would be specially adapted for the processing of homogeneous microstructures and to decrease sintering temperatures. However, the stability of colloidal oxide particles, with a high surface/volume ratio, is difficult to achieve. Such particles usually aggregate unless they are kept apart via electrostatic repulsion or steric hindrance.

Zirconia powders can be easily obtained via the hydrolysis and condensation of zirconium alkoxide precursors as follows:

hydrolysis $Zr(OR)_4 + 2H_2O \Rightarrow Zr(OH)_4 + 4ROH$
condensation $Zr(OH)_4 \Rightarrow ZrO_2 + 2H_2O$

However, zirconium alkoxides are highly reactive toward such reactions.[5] This arises from the electrophilicity of Zr^{IV} and its tendency to increase its coordination number up to $N=7$ or 8 as in crystalline zirconia.[7] Precipitation readily occurs as soon as water is added to the alkoxide solution and intermediate molecular compounds corresponding to the early stages of hydrolysis are very difficult to observe. Only very unstable crystals of $Zr_{13}O_8(OCH_3)_{36}$ have been reported in literature.[8] Therefore, complexing ligands such as β-diketones are currently used in order to decrease the reactivity of zirconium alkoxides, allowing a better control over the formation of the oxide.[9,10]

2.1 Chemically controlled condensation of zirconium alkoxides

A solution of zirconium *n*-propoxide in *n*-propanol (0.8 M) was first reacted with a given amount of acetylacetone ($x=[\text{acac}]/[\text{Zr}]$). A slightly exothermic reaction occurs when acetylacetone ($\text{acacH} = CH_3–CO–CH_2–CO–CH_3$) is added to the alkoxide precursor. The solution turns yellow, suggesting that acetylacetone becomes bonded to zirconium (charge transfer coloration). The reaction can be described as a nucleophilic substitution as follows:

$$Zr(OPr^n)_4 + x\,\text{acacH} \Rightarrow Zr(OPr^n)_{3-x}(\text{acac})_x + x\,Pr^nOH$$

Acetylacetone behaves as a chelating bidentate ligand.[11] It leads to the formation of a new molecular precursor which exhibits a different molecular structure. These complexing ligands are much more difficult to hydrolyse than alkoxy groups. They decrease the reactivity and functionality of the new molecular precursor, prevent condensation and lead to the formation of smaller species.[7]

The modified precursor, $Zr(OPr^n)_{3-x}(\text{acac})_x$, is then hydrolysed by adding a given amount of water, $h=[H_2O]/[\text{Zr}]$, to the clear solution. The resulting mixture is left at room temperature, in a closed vessel, for several days. The hydrolysis of alkoxy groups gives reactive Zr–OH groups allowing condensation to proceed and larger species to be formed. The size and composition of the resulting solid particles can then be controlled with two chemical parameters, the complexation ratio $x=[\text{acac}]/[\text{Zr}]$ and the hydrolysis ratio $h=[H_2O]/[\text{Zr}]$. A gelatinous precipitate of amorphous hydrous zirconia ZrO_2, nH_2O is formed for low complexation ratio ($x \leq 0{\cdot}1$), whereas crystalline $Zr(\text{acac})_4$ precipitates beyond $x \geq 4$.

Only a few alkoxy groups are hydrolysed when a small amount of water ($h<1$) is added. Molecular oligomeric species such as $[Zr_4O(OPr^n)_{10}(\text{acac})_4]$ or $[Zr_{10}O_6(OH)_4(OPr^n)_{18}$ $(\text{allylacetoacetate})_6]$ are then obtained.[12,13] In these molecular clusters several propoxy groups have been hydrolysed giving rise to μ-oxo or μ-OH bridges, while complexing ligands remain bonded to zirconium. β-diketonates are much more difficult to hydrolyse than alkoxy groups. The Zr–acac bond is stabilized by chelation and complexing ligands remain located outside the oxo core of the cluster. They prevent further condensation and lead to the formation of zirconium-oxo clusters.[12]

Clear sols of nanometric colloidal particles are obtained when more water is added to the modified precursor solution. The mean diameter of these particles, measured by dynamic quasi elastic light scattering (QELS) experiments, increases when h increases and x decreases. For low complexation ratio ($x=0{\cdot}5$) the mean diameter increases from 2 nm to 10 nm as h increases from 2 to 10. For large hydrolysis ratio ($h=10$), the mean diameter decreases from 15 nm down to 2 nm as x increases from 0·1 to 1. The size of colloidal particles does not increase any longer beyond $h=10$ but aggregation occurs when a large excess of water is added ($h>100$). The hydrodynamic diameter measured by QELS then increases up to 150 nm. All these sols are made of rather polydisperse and amorphous particles. They result from a competitive growth/termination mechanism of zirconium oxo-species in the presence of organic surface complexing species.

2.2 Formation of crystalline zirconia colloids

Crystalline zirconia cannot be obtained when hydrolysis is performed at room temperature. Two conditions are required for crystallization to occur.

1. The solution must be heated in order to favour ion diffusion and increase crystallization rates.[14]

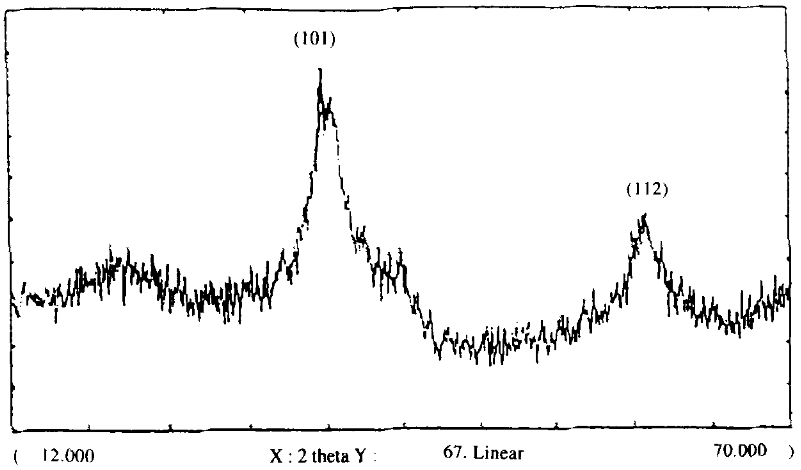

Fig. 1. X-ray diffraction of the zirconia powder showing broad lines corresponding to tetragonal zirconia.

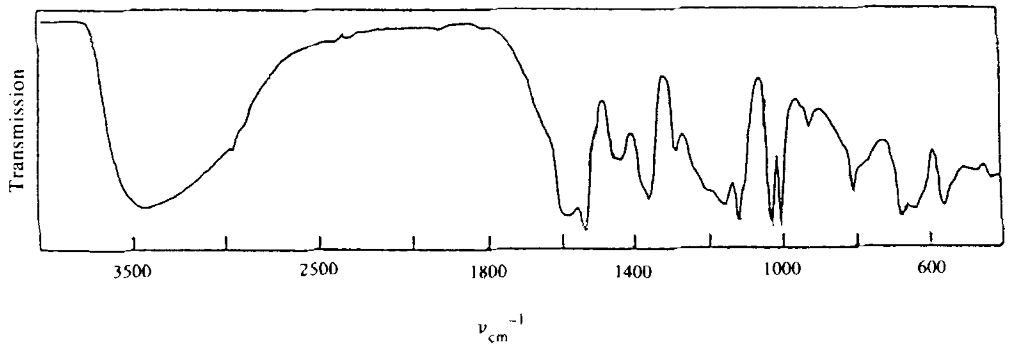

Fig. 2. Infra-red spectrum of colloidal particles evidencing the presence of zirconium bonded acetylacetone.

2. Complexing acac ligands have to be removed in order to allow more Zr–O–Zr bonds to be formed.

These conditions can be obtained by heating hydrolysed precursors under reflux in the presence of an organic acid such as paratoluene sulfonic acid (PTSA). It is well known that β-diketonate ligands lose their complexing ability in an acidic medium and can then be released in the solution.[11] The reversible dissociation of Zr–acac bonds then occurs, followed by preferential recoordination at the surface of the growing cluster. Therefore, another series of experiments ($x = 1 \cdot 1$, $h = 11$) were performed using 4 M aqueous solutions of PTSA for hydrolysis instead of pure water. Hydrolysed solutions were then heated for 24 h at $T = 60°C$, giving rise to transparent sols which remain stable for several months. These sols are made of monodisperse colloidal particles with a mean hydrodynamic diameter of 2–3 nm as measured by QELS. X-ray diffraction performed on the powder obtained upon drying at room temperature gives very broad peaks corresponding to crystalline tetragonal zirconia (Fig. 1). Infra-red spectroscopy shows several bands [1525 cm^{-1} ($\gamma_{C=O}$), 1425 cm^{-1} ($\nu_{C=C}$), 1280 cm^{-1} ($\nu_{C\text{-}CH_3}$), 1000 cm^{-1} ($\nu_{C\text{-}C}$) and 800 cm^{-1} ($\gamma_{C\text{-}H}$)] which can be assigned to acac groups bonded to zirconium at the surface of the colloidal particles (Fig. 2). ^{1}H and ^{13}C NMR spectra show that organic ligands, at the surface of zirconia particles, are in fast exchange equilibrium with free acetylacetone in the solution. They slow down the growth process of the colloidal particles. Moreover, the surface of the colloidal particles is covered by organic groups which prevent aggregation via steric hindrance effects. Kinetically stable non-aggregated zirconia nano-particles are then obtained. Such an assumption is supported by the fact that aggregation occurs when the acac concentration in the solution decreases via dilution or through dialysis. The equilibrium between surface bonded acac and free acacH is then displaced toward dissociation and colloidal particles are no longer protected toward aggregation.

3 SOL–GEL SYNTHESIS OF MULTICOMPONENT CERAMICS

Most advanced ceramics are multicomponent materials having two or more cations in the oxide network. The main advantage of the sol–gel route is then to allow the homogeneous mixing of precursors

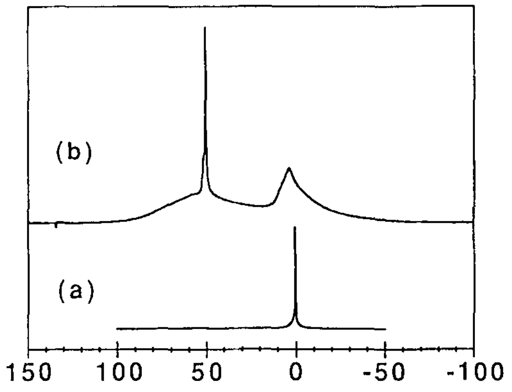

Fig. 3. ^{27}Al NMR spectra of two precursor solutions for cordierite. (a) TEOS hydrolysed by an aqueous solution of aluminium and magnesium nitrates. (b) TEOS and $Al(OBu^s)_2(etac)$ hydrolysed by an aqueous solution of magnesium acetate.

at a molecular level. This leads to faster crystallization rates and lower reaction temperatures. However, a major problem in forming homogeneous multicomponent gels is the unequal hydrolysis and condensation rates of the metal alkoxides. This may result in chemical inhomogeneities leading to higher crystallization temperatures, increased reaction times and even undesired crystalline phases. These drawbacks become especially important with silica based ceramics. Silicon is a small and rather electronegative element ($\chi_{Si} = 1{\cdot}74$) which always remains four-fold coordinated. Silicon alkoxides are not very reactive toward hydrolysis and condensation. Gelation typically occurs within days unless acid or base catalysts are used.

Other alkoxides such as $Al(OR)_3$ are much more reactive. Hydrolysis and condensation rates are very different preventing the formation of Si–O–Al bonds even when $Si(OR)_4$ is prehydrolysed before mixing with $Al(OR)_3$. Commercially available double alkoxides such as $(Bu^sO)_2$–Al–O–$Si(OEt)_3$ have then been used for the sol–gel synthesis of SiO_2–Al_2O_3 ceramics.[15] Si–O–Al bonds are already formed in the molecular precursor and it could be expected that they would remain in the gel. However, ^{29}Si and ^{27}Al NMR experiments show that Al–OBu^s groups are hydrolysed much faster than Si–OEt groups. Condensation then occurs with Al–OBu^s rather than with Si–OEt, leading to the formation of Al–O–Al bonds instead of Al–O–Si bonds.[16]

Many sol–gel preparations have been proposed for cordierite $Mg_2Al_4Si_5O_{18}$ which corresponds to a $2MgO$–$2Al_2O_3$–$5SiO_2$ composition. However, magnesium alkoxides cannot be used as molecular precursors. The large difference between the coordination number ($N = 6$) of Mg^{2+} in the oxide and its oxidation state ($z = 2$) leads to the formation of polymeric species which remain non-soluble in most usual solvents. Other water-soluble precursors such as $Mg(NO_3)_2$ or $Mg(OAc)_2$ have then to be used.

Therefore the easiest way to produce cordierite would be to hydrolyse $Si(OEt)_4$ with an aqueous solution of aluminium and magnesium nitrates.[17,18] Six-fold coordinated aqueous $[Al(OH_2)_6]^{3+}$ species are characterized by a ^{27}Al NMR peak at $\delta = 0$ ppm (Fig. 3(a)). This coordination state remains in the gel as evidenced by the ^{27}Al MAS-NMR spectrum (Fig. 4(a)). The ^{29}Si MAS-NMR spectrum presents features caused by a silica network with Q_4 ($\delta \approx -110$ ppm) and Q_3 ($\delta \approx -90$ ppm) units (Fig. 4(c)). This gel can thus be described as a silica gel in which Al^{III} and Mg^{II} ions are dispersed. Si–O–Al or Si–O–Mg bonds are not formed at this stage. During a thermal treatment, Al^{III} reacts first with Mg^{II} leading to the crystallization, around 800°C, of the stable spinel phase $MgAl_2O_4$ in which Al is six-fold coordinated. Cordierite cannot be formed until the crystalline spinel reacts, via solid state reactions, with the amorphous silica matrix. The μ-cordierite is then formed around 1000°C and the α-cordierite phase is obtained above 1200°C.[17]

Cordierite can also be synthesized from aluminium alkoxide precursors such as $Al(OBu^s)_3$.[17–20] These alkoxides are always oligomeric species in which Al^{III} is four-fold or six-fold coordinated. They are highly reactive toward hydrolysis leading to the precipitation of aluminium oxo-species in which Al^{III} becomes six-fold coordinated as soon as water is added. But, as in cordierite, aluminium atoms are four-fold coordinated, it would be very important to favour such a coordination state in solution and avoid coordination expansion when water is added. This can be obtained via the complexation of aluminium alkoxide precursors by acetylacetone or ethylacetoacetate (etac) ligands.[17] The resulting modified alkoxide $Al(OBu^s)_2(etac)$ is less viscous and less reactive than $Al(OBu^s)_3$. Complexation slows down hydrolysis reactions and partially prevents coordination expansion.

In our experiments, $[Al(OBu^s)_2(etac)]_n$ was mixed with TEOS and hydrolysed by aqueous solution of magnesium acetate.[17] The hydrolysis–condensation process was followed by ^{27}Al and ^{29}Si solution NMR. ^{27}Al NMR spectra show the formation of transient species characterized by a sharp peak around $\delta \approx 51$ ppm caused by tetracoordinated Al atoms in a highly symmetric environment (Fig. 3(b)). Such a chemical shift can be assigned to Al–O–Si bonds and the corresponding sharp peak could correspond to $Al\{O[Si(OR)_3]\}_4$ species.[21]

These results are in agreement with the ^{29}Si NMR spectra showing a peak caused by $Si(OAl)(OR)_3$.

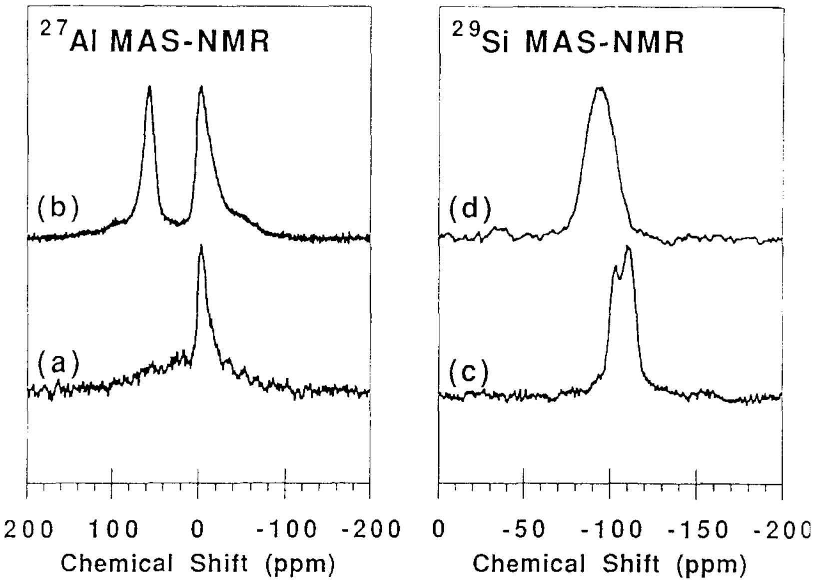

Fig. 4. ^{27}Al and ^{29}Si MAS-NMR spectra of gel precursors for cordierite obtained from: (a), (c) TEOS hydrolysed by an aqueous solution of aluminium and magnesium nitrates. (b), (d) TEOS and $Al(OBu^s)_2(etac)$ hydrolysed by an aqueous solution of magnesium acetate.

Such species should give rise to the alumino-silicate network. The sharp NMR peak disappears when the gel forms, while a broad component around $\delta \approx 55$ ppm increases in intensity. This peak is clearly visible in the ^{27}Al MAS-NMR spectrum of the dried gel (Fig. 4(b)). Its chemical shift is close to that found for crystalline α-cordierite, in which all $[AlO_4]$ tetrahedra are surrounded by four $[SiO_4]$ tetrahedra.[22] The ^{29}Si MAS-NMR spectrum confirms the formation of an alumino-silicate network (Fig. 4(d)) with a broad signal around $\delta \approx -92$ ppm, caused by some distribution of Si sites. The chemical shift value suggests that Si should be bonded to two or three Al. Upon heating, these gels do not lead to the formation of the spinel $MgAl_2O_4$, Al^{III} remains four-fold coordinated and the pure α-cordierite phase is obtained at 1000°C.[17]

These sol–gel preparations of cordierite clearly demonstrate the importance of the formation of Si–O–Al bonds in the solution. Such bonds are not formed when an aqueous solution of aluminium nitrate, in which Al^{III} is solvated by six water molecules, is used as a precursor. They can be formed with aluminium alkoxides which provide reactive species containing Al–OH groups which can react with Si–OEt groups to build an alumino-silicate network. Moreover, the four-fold coordination of Al^{III} seems to be favoured when Al is bonded to Si atoms. The ability for Al^{III} to be four-fold coordinated is certainly related to the large amount of Si–O–Al bonds formed in the gel. All SiO_4 tetrahedra seem to be bonded to at least one, but more probably two or three, AlO_4 tetrahedra.

4 CONCLUSION

The sol–gel synthesis of ceramic powders offers many advantages over more conventional methods based on solid state reactions: lower processing temperature, better control of the morphology and microstructure, powderless processing of ceramics. However, a better knowledge of sol–gel chemistry has to be developed before a real mastery of the process can be reached. This requires the careful characterization of all the chemical species formed during the course of the sol–gel process. Multinuclear liquid and solid state NMR then provides an efficient tool which could be used together with other techniques such as X-ray absorption (EXAFS). The chemical modification of alkoxide precursors opens new opportunities for the molecular design of advanced ceramics. However, many problems remain to be solved. The main one could be: How to make possible heterometallic M–O–M′ bonds in solution and keep them till the formation of the oxide network? This is a major key point for the sol–gel synthesis of multicomponent ceramics.

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