

# The Structure and Decomposition of $\text{Al}_2\text{O}_3\text{-ZrO}_2$ Gels

Wenbang Zhang & F. P. Glasser

Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen, AB9 2UE, UK

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## Abstract

*$\text{Al}_2\text{O}_3\text{-ZrO}_2$  gels were prepared from inorganic reagents. The evolution of structure and crystallinity were investigated by X-ray diffractometry (XRD) and infra-red (IR) spectroscopy, following ageing at 20°C and isothermal heating at temperatures in the range 200–1600°C. The structure of the gels does not change significantly when aged for up to 150 days at 20°C. Upon heating, gels lose water but their nanostructure is partially preserved up to ~300°C. It is suggested that IR spectra are potentially more powerful than XRD for detecting changes in the amorphous structures encountered during low-temperature calcination, but at higher temperatures, such that partial crystallization occurs, XRD is a better indicator of the structural state.*

*Ausgehend von anorganischen Reagenzien wurden  $\text{Al}_2\text{O}_3\text{-ZrO}_2$  Gele hergestellt. Die Entwicklung ihrer Struktur und Kristallinität im Laufe einer Auslagerung bei 20°C und beim isothermen Anlassen im Temperaturbereich zwischen 200 und 1600°C wurden mittels Röntgenbeugung und Infrarot-Spektroskopie untersucht. Bei 150-tägiger Auslagerung bei 20°C tritt keine bezeichnenswerte Strukturänderung der Gele ein. Beim Anlassen verlieren die Gele Wasser, ihre nanokristalline Struktur bleibt jedoch teilweise bis zu etwa 300°C erhalten. Um strukturelle Veränderungen des amorphen Zustandes festzustellen, die bei der Tieftemperatur-Kalziniierung auftreten, erweisen sich Infrarot-Spektren als bedeutend aussagekräftiger als Röntgendiffraktogramme. Bei höheren Temperaturen jedoch, wenn zum Teil bereits Kristallisation eintritt, ist Röntgendiffraktometrie die geeignetere Methode zur Charakterisierung des Strukturzustandes.*

*Des gels  $\text{Al}_2\text{O}_3\text{-ZrO}_2$  ont été préparés à partir de réactifs inorganiques. L'évolution de leur structure et de leur cristallinité a été suivie par diffraction RX et*

*IR, après maturation à 20°C et traitement thermique isotherme à des températures comprises entre 200 et 1600°C. La structure des gels ne varie guère, même après un vieillissement de 150 jours à 20°C. Lors du chauffage, les gels perdent de l'eau, mais leur nanostructure est partiellement préservée jusqu'à 300°C. Les auteurs considèrent que les spectres IR sont potentiellement plus significatifs, par rapport aux spectres de diffraction RX, pour mettre en évidence les modifications de la structure survenant lors d'une calcination à basse température. Cependant, à plus haute température, où des cristallisations partielles se produisent, la diffraction RX est un outil plus performant pour indiquer l'état de la structure.*

## 1 Introduction

Sol-gel processing has been widely used in the synthesis of ceramics because of its ability to produce relatively homogeneous compositions, thereby offering scope for less intense sintering regimes during subsequent pyroprocessing. Most of the published papers on the synthesis of ceramic composites focus on organometallic precursors, such as alkoxides, as is shown by References 1–4. The advantage of organometallic precursors is that it is easy to control hydrolysis and polymerization reactions leading to gel formation. But the precursors are expensive and have a tendency to leave carbonaceous residues after firing.<sup>4</sup>

Gel preparations based on  $\text{ZrO}_2$  offer scope for using relatively inexpensive reagents and permit the introduction of other oxide components, which are essential to stabilize or partially stabilize zirconia by solid solution.  $\text{ZrO}_2$  occurs in three polymorphs; the high-temperature cubic (c) polymorph is the fluorite-structured aristotype, while the two lower temperature polymorphs, tetragonal (t) and monoclinic (m), are distortions of the fluorite structure. However, volume changes associated with the topotactic phase

transitions, especially to the *m* symmetry, may be deleterious to the mechanical properties of dense polycrystalline compacts. Hence it is desirable to stabilize a single polymorphic variant across a broad range of temperatures.

Much work has been done in order to explain the transformation mechanism of *t*-phase to *m*-phase  $\text{ZrO}_2$ <sup>5-8</sup> and to determine conditions under which *t*-phase persists metastably.<sup>9</sup> The sequence and kinetics of phase transformations in gel-derived  $\text{Al}_2\text{O}_3$ - $\text{ZrO}_2$  composites have been investigated.<sup>10-12</sup> Processing by gel routes may introduce surface and strain energy terms which, in turn, affect the inversion sequence which thus differs from that encountered in traditional ceramic reactants.

Investigations on the structural evolution of gel during the low-temperature part of the calcination cycle are uncommon, although it is known that the initial crystalline phase which appears from heated  $\text{ZrO}_2$  or  $\text{Al}_2\text{O}_3$ - $\text{ZrO}_2$  sol-gels may be either *t* or *c*, depending on the nature of the precursors, the preparation process and heating conditions.<sup>13,14</sup> The present work is aimed at determining structural evolution in  $\text{Al}_2\text{O}_3$ - $\text{ZrO}_2$  gels derived from inorganic precursors upon ageing and also during heating. Inorganic gel structures are difficult to characterize and several techniques have been combined, each giving partial structural information, to obtain a picture of the overall process whereby an amorphous gel is converted to crystalline zirconia.

## 2 Experimental

Inorganic precursors used in this investigation were made from basic zirconium nitrate solution (termed  $\text{ZrO}_2$  sol),<sup>15</sup> and basic aluminium chloride solution (termed  $\text{Al}_2\text{O}_3$  sol). The former was found by analysis to be 3.65M in Zr and 3.84M in  $\text{NO}_3^-$ . The main  $\text{Al}_2\text{O}_3$  source was  $\text{Al}_2(\text{OH})_5\text{Cl}$  from Albright & Wilson Ltd; analysis disclosed that it was 6.17M in Al.

To initiate reaction, these two sols were mixed in a predetermined ratio with stirring. Gelation times could be varied by controlling the basicity of *x* in the

general formula  $\text{Al}(\text{OH})_x(\text{Cl}^- \text{ or } \text{NO}_3^-)_{3-x}$ . Once formed, the gel was aged at 20°C and 100% humidity to prevent water loss. All samples intended for thermal treatment and subsequent examination by IR, TEM and XRD were ramped at 15°C min<sup>-1</sup> from room temperature to the selected isotherm with a uniform dwell time of three hours at each isothermal hold.

IR spectra were obtained with a Philips PU9800 FTIR spectrometer with a wavenumber range from 400 to 4000 cm<sup>-1</sup>; its resolution is 4.0, and the number of scans is 10. Solution samples were coated on a KBr disk in a film and examined rapidly. XRD spectra were obtained on a Philips automated powder diffractometer system, PW1710, using  $\text{CuK}_\alpha$  radiation at 40 kV and 40 mA. TEM pictures were taken from a JEOL 2000 EX TEMSCAN with acceleration voltages up to 200 kV and magnification up to 500 000 times.

## 3 Results and Discussion

### 3.1 The starting sols

In the  $\text{Al}_2\text{O}_3$  sol, the general appearance of the spectra (Fig. 1), suggests that  $\text{Al}^{3+}$  ions bonded to  $\text{H}_2\text{O}$  exhibit ionic characteristics, based on similarities with the reported spectra of alkali metal nitrates.<sup>16,17</sup> The metal ion has a high degree of hydration, as evidenced by the strong bands for molecular water. The assignments of the broad peak at around 1070 cm<sup>-1</sup> is attributed to Al-OH absorption<sup>18</sup> while the peak at 2077 cm<sup>-1</sup> is an artifact: it is ascribed to absorption arising from  $\text{CO}_2$  in the air optical path.

The broad absorption peak of  $\text{NO}_3^-$  in  $\text{ZrO}_2$  sol occurs around 1350-1390 cm<sup>-1</sup>, see Fig. 2. It is so wide that it is interpreted as showing that the nitrate group may take a structural role in the sol where it is present as linking or bridging nitro groups.<sup>19-21</sup> Water plays the same role in this sol as in the  $\text{Al}_2\text{O}_3$  sol.

$[\text{Zr}_4(\text{OH})_8 \cdot 16\text{H}_2\text{O}]^{8+}$  is an important species in aqueous acidic solution.<sup>13,22,23</sup> It does not seem likely that nitro groups are bound directly to Zr, although a highly charged polynuclear ion

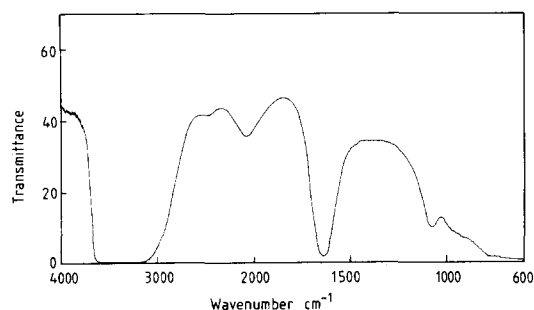


Fig. 1. IR spectrum of  $\text{Al}_2\text{O}_3$  sol ( $\text{Al}_2(\text{OH})_5\text{Cl}$ ).

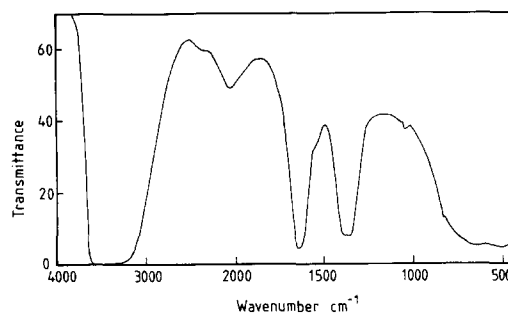


Fig. 2. IR spectrum of  $\text{ZrO}_2$  sol.

$[\text{Zr}_4(\text{OH})_8(16\text{H}_2\text{O})]^{8+}$  would certainly exert a strong attractive force on any negative ions, including  $\text{NO}_3^-$ , and it is suggested that the structural role of nitrate is confined to bridging polynuclear clusters. On the other hand, Zr complex ion aggregates are also enlarged as a result of the formation of olation or oxolation bridges between the primary tetramer units, as a result of which primary units are bound into linear chains. The  $-\text{Zr}-\text{O}-\text{Zr}-\text{O}-\text{Zr}-$  vibration is at frequencies somewhat less than  $900\text{ cm}^{-1}$ , but, unfortunately, it is hardly visible because of the interference of strong water absorption below  $1000\text{ cm}^{-1}$ . Another nitrate group absorption in IR spectra occurs at  $1010\text{--}1050\text{ cm}^{-1}$ ,<sup>24-26</sup> but it is weak.

### 3.2 Fresh Al-Zr gel

There are no significant differences between the IR spectra of fresh gel and those of the superimposed spectra of the two constituent sols,  $\text{ZrO}_2$  and  $\text{Al}_2\text{O}_3$ , used in its formation, except that the absorption peak of  $\text{NO}_3^-$  splits into two peaks which leads to the supposition that the  $\text{NO}_3^-$  ions may play dual roles in the gel structure: structural and non-structural (free ions). The absorption peaks of Al-OH, at  $\sim 1070\text{ cm}^{-1}$ , and  $\text{NO}_3^-$ , at  $\sim 1050\text{ cm}^{-1}$ , overlap, as shown in Fig. 3. The observations could be interpreted as indicating that the resulting gel had a diphasic structure, but a preferred interpretation is that the gel is essentially homogeneous, containing entangled, lightly cross-linked chains. The infrared spectra reflect the presence of two types of chain units, one Zr-rich and the other Al-rich. The constitution of the two chain types, one Al-rich and the other Zr-rich, has been described in the literature.<sup>16,20-23</sup>

Once formed, no further differences in IR spectra occur after prolonged ageing at  $\sim 20^\circ\text{C}$ , see Fig. 3. The gel structure will actually be quite different after ageing—physically it continues to become more rigid—but this and other differences are not reflected in major changes in bonding: any structural changes

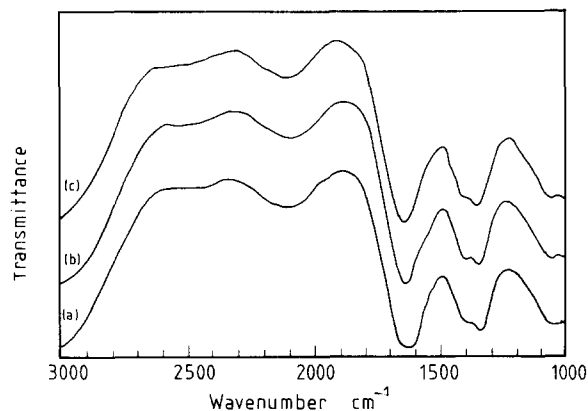


Fig. 3. IR spectra of  $\text{Al}_2\text{O}_3\text{-ZrO}_2$  gel at different ageing time at  $20^\circ\text{C}$ . Composition:  $\text{ZrO}_2$  sol: $\text{Al}_2\text{O}_3$  sol = 3:1 (by volume). (a) 30 mins, (b) 6 days, (c) 2 months.

do not significantly affect the appearance of IR spectra. Thus IR spectroscopy appears to be an insensitive tool with which to study changes occurring during ageing.

The processes which continue during ageing are envisaged as including chain lengthening and changes in chain conformation, with concomitant adjustments to the nature and extent of cross-linking.

There are three 'amorphous' XRD reflections in the spectra of fresh and aged gel. Their positions are similar to the positions of three of the low  $2\theta$  diffraction peak positions of cubic  $\text{ZrO}_2$  (see Fig. 4). The gel is therefore believed to have some rudimentary structure with respect to the location of the heavier zirconium atoms. The size of ordered structure has been approximately calculated using the relation:<sup>27,28</sup>

$$L = k\lambda / \sqrt{(B^2 - b^2)} \cos \theta$$

where  $L$ , the crystallite size, is related to the differences in half width of a reflection at diffracting angle  $\theta$ ;  $B$  is its width at half maximum intensity and  $b$  is the characteristic width for a well-crystallized material;  $k$  is a constant, taken as 1, and  $\lambda$  the wavelength, which in this case is  $1.5418\text{ \AA}$ . Strain is assumed to make a negligible contribution to line broadening. Two reflections are believed to occur in the range between  $18.5^\circ$  and  $36.5^\circ$   $2\theta$  (Cu). They were deconvoluted, assuming that both were symmetrical. The calculation, based on the strongest reflection, centred at  $\sim 20\text{--}27^\circ$ , was used to estimate a value for  $L \approx 15\text{ \AA}$ . This equation is approximate, but its solution gives an order-of-magnitude indication of the size of the ordered domains, which must be very small.

### 3.3 Firing at different temperatures

The XRD and IR spectra of  $\text{Al}_2\text{O}_3\text{-ZrO}_2$  gel ramped to high temperature are shown in Figs 4 and 5, respectively.

From room temperature to  $200^\circ\text{C}$ , the gel remains nearly amorphous. By XRD, it gives three reflections with a large shoulder on the left side (high  $2\theta$  side) at  $25.6^\circ$ ,  $41.5^\circ$ ,  $57.5^\circ$  ( $2\theta$ ,  $\text{CuK}_\alpha$  radiation), which are considered to arise from the rudimentary structure of the gel. The IR spectra also remain almost identical from room temperature to  $200^\circ\text{C}$ . At  $300^\circ\text{C}$ , the two peaks at  $41.5^\circ$  and  $57.5^\circ$  in the XRD spectra merge, while in the IR spectra all features below  $1000\text{ cm}^{-1}$  disappear. These changes indicate that a loss of structure occurs, accompanied by loss of structural water: in other words, the gel transforms to a hydrous glass which, in turn, gradually becomes anhydrous. XRD spectra show that the glassy state persists upon continued heating to  $800^\circ\text{C}$ , although some changes in XRD peak

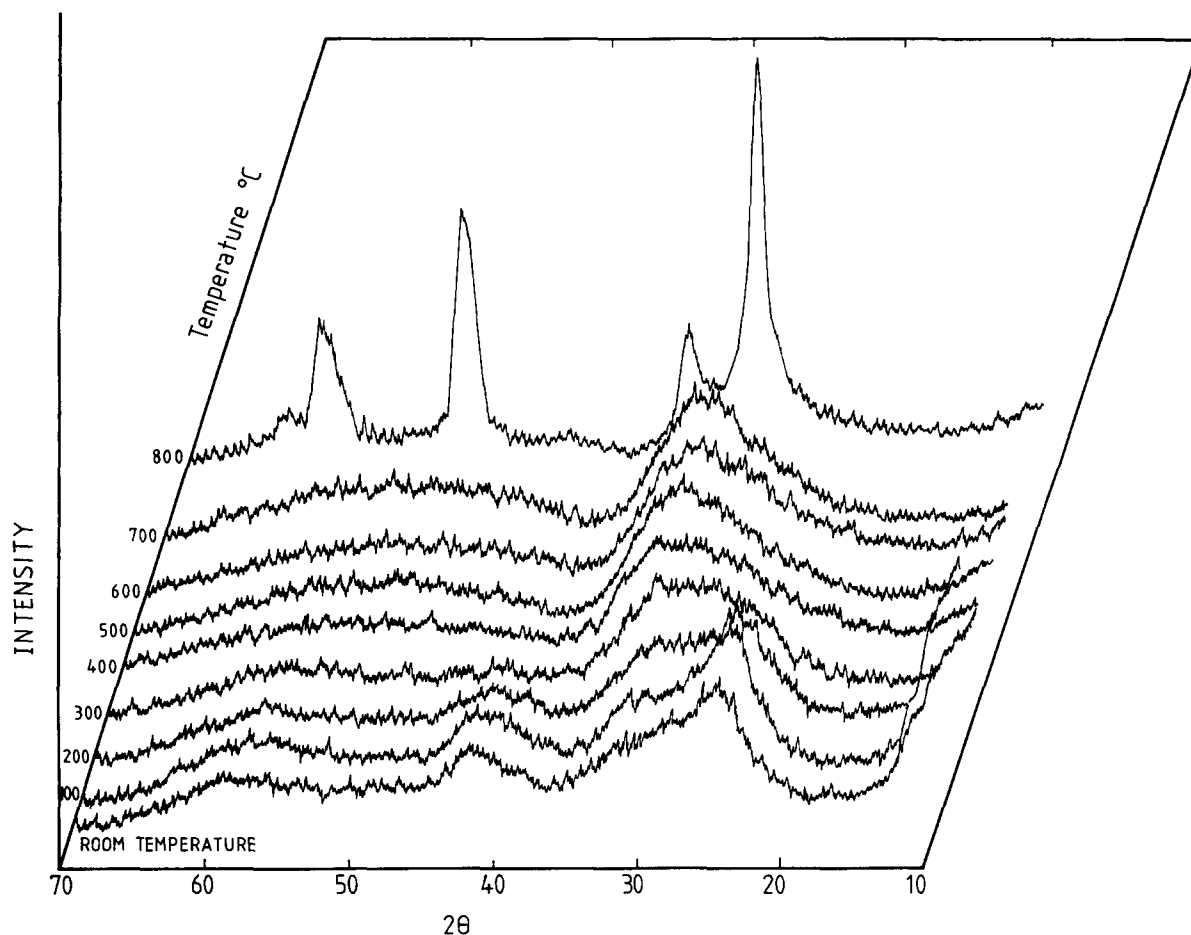


Fig. 4. XRD spectra of  $\text{Al}_2\text{O}_3$ - $\text{ZrO}_2$  gel heated at different temperatures (same composition as the sample in Fig. 3).

intensities occur. Initially the glass contains much water, together with some nitrate, but by  $400^\circ\text{C}$ , the IR spectra shows that all  $\text{NO}_3^-$ , together with almost all structural water, are lost. Between  $400$  and  $1000^\circ\text{C}$  no change occurs in the IR spectra.

However, by X-ray diffraction, crystalline  $\text{ZrO}_2$  appears at  $800^\circ\text{C}$ ; initially the crystallite diffractions are very broad because the crystals are very small. Their nucleation must be inhomogeneous because while X-ray diffraction shows that crystallization is occurring, amorphous material still persists. The symmetry of the first-formed crystals is apparently cubic, based on the similarity in structure between cubic  $\text{ZrO}_2$  and the gel. This similarity, supported by X-ray diffraction and high-resolution electron microscopy<sup>22,29</sup> has been widely used as an indicator of apparent *c* symmetry. Upon continued heating to  $1000^\circ\text{C}$ , the crystalline component transforms to tetragonal symmetry. This does not appear to be a sharp phase transition, but by  $1100^\circ\text{C}$ , the IR spectra also began to show the characteristic absorption of

crystalline *t*- $\text{ZrO}_2$ ; IR is clearly much less sensitive than XRD to the beginnings of crystallization.

### 3.4 Effect of $\text{Al}_2\text{O}_3$ on crystallization of $\text{ZrO}_2$

The mechanisms of transformation-toughening zirconia are based on controlling the  $\text{ZrO}_2(\text{t})$ - $\text{ZrO}_2(\text{m})$  polymorphic transition. Pure  $\text{ZrO}_2(\text{t})$  transforms to  $\text{ZrO}_2(\text{m})$  at  $1170^\circ\text{C}$ , but phase assemblages including  $\text{ZrO}_2(\text{t})$  can be made to persist to ambient temperatures by incorporation of other metal oxides, such as  $\text{Y}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,<sup>9,30-32</sup> etc., in solid solution. However, other stabilization mechanisms may operate; it is found that  $\text{Al}_2\text{O}_3$  stabilizes  $\text{ZrO}_2(\text{t})$  to ambient temperatures in sol-gel preparations.

Quantitative phase analysis in polymorphic mixtures of zirconia was carried out by integrated X-ray intensity measurements in (*c* + *m*), (*t* + *m*) and (*c* + *t*)  $\text{ZrO}_2$  systems, using a method outlined in the literature.<sup>32-34</sup> Table 1 shows data for the phase content of two representative compositions pre-

Table 1. Fraction, in wt%, of the total  $\text{ZrO}_2$  present as the tetragonal polymorph

$\text{ZrO}_2$ gel composition (%)	Temperature ( $^\circ\text{C}$ )						
	1000	1100	1200	1300	1400	1500	1600
$\text{ZrO}_2$ 81.10, $\text{Al}_2\text{O}_3$ 18.9	96.3	78.4	6.32	2.16	0	0	0
$\text{ZrO}_2$ 32.41, $\text{Al}_2\text{O}_3$ 67.59	100	100	56.4	59.6	49.2	38.1	38.2

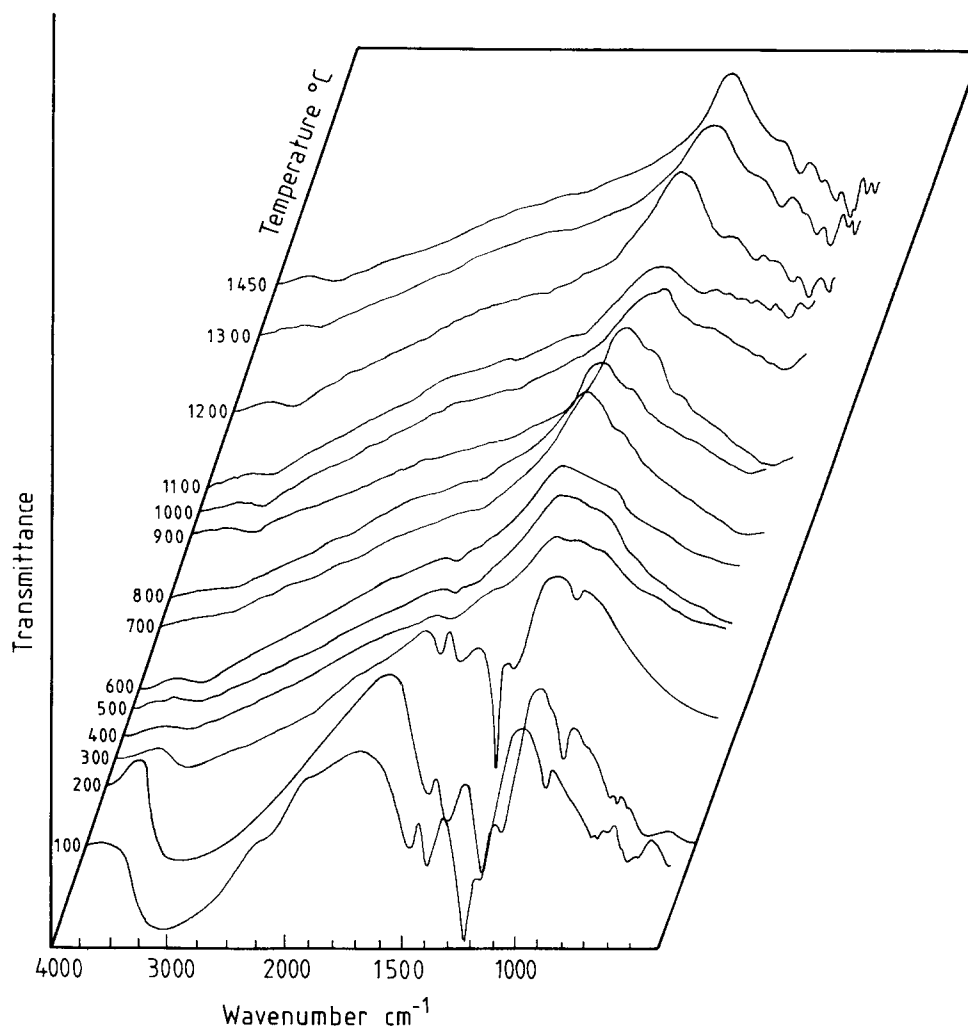


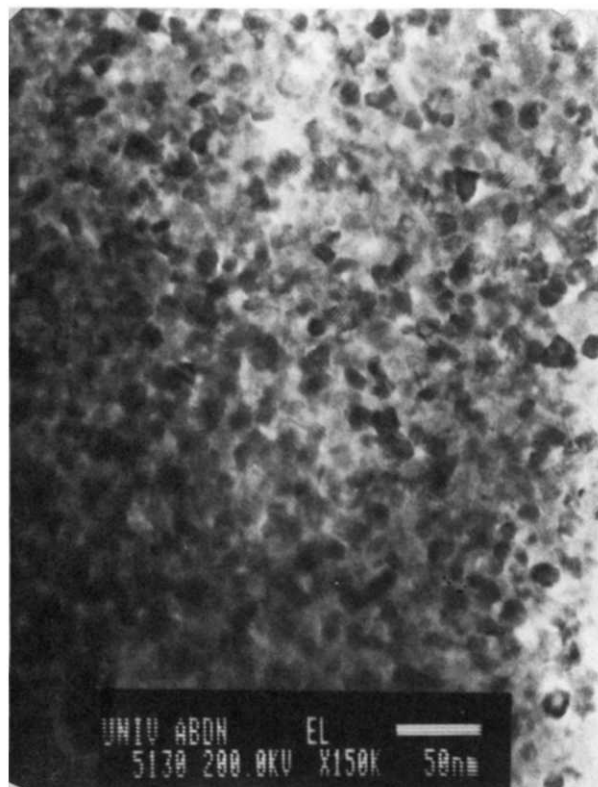
Fig. 5. IR spectra of  $\text{Al}_2\text{O}_3$ - $\text{ZrO}_2$  gel heated at different temperatures (same composition as the sample in Fig. 3).

pared by sol-gel methods. Both contain  $\text{Al}_2\text{O}_3$  substantially in excess of that which can be incorporated in zirconia solid solution; nevertheless, the effect of increasing the proportion of excess free alumina is to secure increasing stabilization of the t-polymorph. For example, after ramping to  $1300^\circ\text{C}$ , the composition with 18.9%  $\text{Al}_2\text{O}_3$  had little remaining tetragonal zirconia (2.2%), whereas in the higher alumina composition, 60% of the zirconia remained tetragonal. Much of the excess alumina persists as an amorphous phase:  $\text{Al}_2\text{O}_3$  needs a higher temperature to crystallize than  $\text{ZrO}_2$ ; thus, by XRD, the first weak alpha-alumina reflections appear around  $1000^\circ\text{C}$ . The mechanism whereby a physical excess of  $\text{Al}_2\text{O}_3$  stabilizes tetragonal  $\text{ZrO}_2$  is unclear: it may simply act as a grain growth inhibitor for the zirconia phase. Whatever the reason, the unique microstructure developed from gel precursors persists even upon prolonged sintering in air at  $1600^\circ\text{C}$ ; the powder X-ray diffraction patterns exhibit line-broadened profiles and the grain size remains near the practical lower limits of SEM resolution. Thus particle size, rather than chemical effects, may be primarily responsible for stabilizing the t-polymorph.

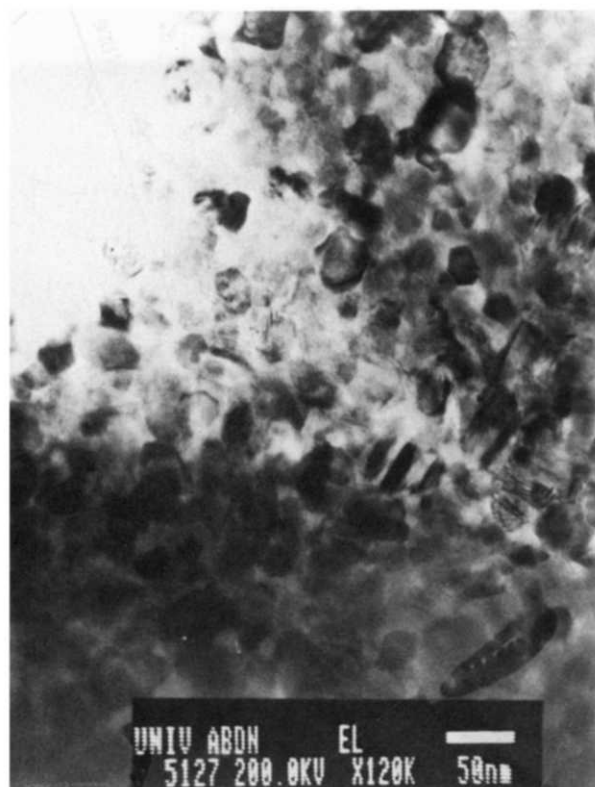
Several TEM pictures show that the size of gel particles gradually increases from low temperature to high temperature, as shown in Fig. 6. At  $1000^\circ\text{C}$ , the size is about  $200 \text{ \AA}$  at  $1100^\circ\text{C}$ ,  $0.1 \mu\text{m}$  at  $1200^\circ\text{C}$ , then to  $0.3\text{--}0.4 \mu\text{m}$  at  $1300^\circ\text{C}$ .

#### 4 Conclusions

$\text{Al}^{3+}$  and  $\text{Zr}^{4+}$  ions readily undergo hydrolysis and polymerize in solution. By controlling solution compositions and pH, satisfactory gel-based ceramics can be obtained using entirely inorganic precursors. The rudimentary structure of gel resembles an overlap of both precursors:  $\text{ZrO}_2$  sol and  $\text{Al}_2\text{O}_3$  sol. Gelatinization occurs primarily because  $\text{Al}_2\text{O}_3$  sol, which has a higher pH, accelerates polymerization of  $\text{Zr}^{4+}$  ions. The natural structure of the mixed gel does not change upon prolonged ageing at  $25^\circ\text{C}$  and constant water content. Upon heating to  $300^\circ\text{C}$ , the structure of gel still does not change significantly, although much water and nitrate are lost, but at  $400^\circ\text{C}$ , it becomes nearly amorphous and glass-like. Both XRD and FTIR can be used to trace the structural evolution of the gel



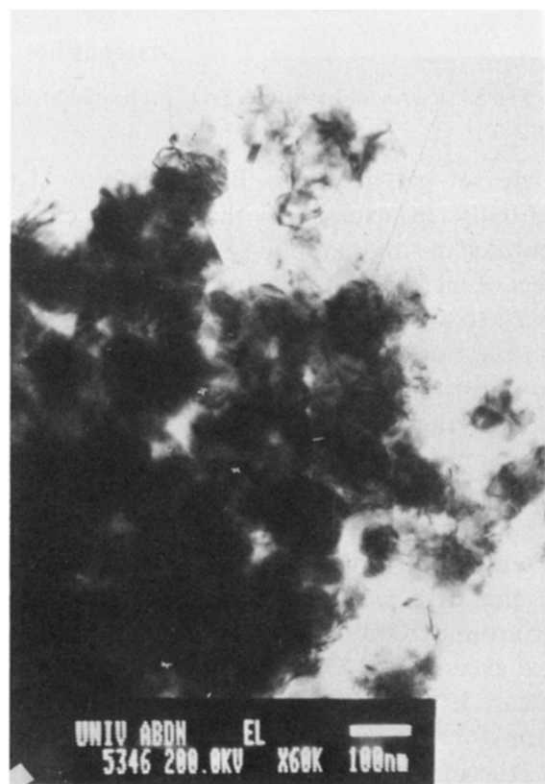
(a)



(b)



(c)



(d)

**Fig. 6.** Transmission electron micrographs of a  $\text{ZrO}_2:\text{Al}_2\text{O}_3$  sol (3:1 ratio by volume) after isothermal heat treatment at (a) 1000°C, (b) 1100°C, (c) 1200°C and (d) 1300°C. Incipient crystallite formation (note lattice fringing) is visible at 1000°C. More complex fringing and with crystallites to *c.* 40 nm is visible at 1100°C. Formation of polygonal grains begins at 1200°C but is only complete at 1300°C, where an equant microstructure develops. The grains still retain a complex internal structure.

during isothermal heating, but the FTIR spectrum is more structure-sensitive than XRD at low temperature: the reverse is true at higher temperature, at 800°C or above. The presence of free  $\text{Al}_2\text{O}_3$ , in excess of that which can be incorporated in solid solution in  $\text{ZrO}_2$ , stabilizes the latter as the tetragonal phase, thereby ensuring better volumetric stability of fired ceramics.

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