

# An X-ray diffraction and NMR study into the mechanism of zircon formation from aqueous sols

A. K. BHATTACHARYA, A. HARTRIDGE, K. K. MALLICK

*Centre for Catalytic Systems and Materials Engineering, Department of Engineering, University of Warwick, Coventry CV4 7AL, UK*

Solid solutions of the formula  $Zr_{1-x}Si_xO_2$  ( $x=0-0.5$ ) were produced by an aqueous inorganic sol-gel route. X-ray diffraction and solid state magic-angle spinning-nuclear magnetic resonance (MAS-NMR) were used to characterize the products at various calcination temperatures. The solubility limit of silica in zirconia at  $<950^\circ\text{C}$  was found to be  $\sim x=0.15$  and that this amount stabilized the tetragonal zirconia phase to higher temperatures and inhibited the formation of zircon. With  $x=0.5$ , zircon formation was 70% at only  $1100^\circ\text{C}$ .

## 1. Introduction

Zircon,  $ZrSiO_4$ , is a high temperature ceramic oxide renowned for its low thermal expansion coefficient and low thermal conductivity [1]. Doped with suitable inorganic oxides such as praseodymium, vanadium, iron and nickel, it has also been extensively used as an inorganic pigment [2]. Sintered forms are used as refractory components with high thermal shock resistance and good mechanical properties [1, 3, 4]. However, achieving a high purity single phase powder with small grain size is extremely difficult. Recent research has been directed towards improving homogeneity of the powder precursor by use of the solution-sol-gel route. Here, organometallic reagents and/or salts are dissolved in a suitable solvent and hydrolysed under strict conditions to obtain a homogeneous gel. Even then, firing to temperatures in excess of  $1350^\circ\text{C}$  is necessary to obtain a high purity product in the absence of mineralizers or seeding [3–8]. Previous research has shown that the rate of zircon formation can depend on the heating rate of the powder precursor [7, 8] and it is suggested that it also depends on the saturation of the tetragonal zirconia phase with silica [9], since it seems likely that it is in this form that the zirconia reacts with amorphous silica to form zircon. The presence of monoclinic zirconia as an unreacted product has been attributed to the quenching of unreacted tetragonal zirconia [9]. The purpose of this present paper therefore, is to clarify these observations by producing a series of  $ZrO_2-SiO_2$  solid solutions with the general formula  $Zr_{1-x}Si_xO_2$  and characterizing product formation with calcination conditions. These solid solutions are prepared using an inorganic sol-gel route, since a series of zirconia containing high temperature ceramics have already been successfully prepared at low temperature using a specific inorganic zirconia sol [10–12].

## 2. Experimental procedure

### 2.1. Sample preparation

Samples of the general formula  $Zr_{1-x}Si_xO_2$  ( $x=0-0.5$ ), were prepared in the following manner. An inorganic polymeric zirconia sol was prepared by adding a salt of zirconium (basic carbonate or hydroxide) to a requisite quantity of concentrated mineral acid, followed by dilution and boiling to produce a transparent sol. The sol had a density of  $1.35\text{ g cm}^{-3}$ , a concentration of  $280\text{ g l}^{-1}$   $ZrO_2$ , and a counter ion/ $Zr^{IV}$  ratio of 1.0. To portions of this sol, the requisite amount of silica sol was added (syton D30). The silica sol was first acidified using 1–2 drops of concentrated mineral acid to prevent gellation. The sol mixture was then dispersed in an organic solvent-surfactant mixture with stirring to produce spherical sol droplets which were then gelled using an organic anion extracting agent. The gel spheres were then washed and dried in an air oven at  $105^\circ\text{C}$  before heat treatment in a muffle furnace at various temperatures.

### 2.2. Sample characterization

#### 2.2.1. X-ray powder diffraction measurement (XRD)

X-ray powder diffraction (XRD) patterns for samples treated at various temperatures were recorded in the region of  $2\theta = 5-120^\circ$  with a step scan of  $0.1^\circ\text{ min}^{-1}$  on a Philips diffractometer (Model PW1710) using  $\text{CuK}_\alpha$  radiation. Cell parameters were calculated and further refined using linear regression procedures (Philips APD 1700 software) applied to the measured peak positions of all major reflections up to  $2\theta = 90^\circ$ .

The percentile volume fractions of tetragonal zirconia, monoclinic zirconia and zircon were calculated from the normalized ratios of relative intensities corresponding to the (200) peak of  $ZrSiO_4$ , the (111)

and (11 $\bar{1}$ ) peak of monoclinic zirconia and the (101) peak of tetragonal zirconia. For example,  $V_{\text{zircon}} = I_{\text{zircon}(220)}/[I_{\text{mono}(111)+(11\bar{1})} + I_{\text{tetra}(101)} + I_{\text{zircon}(200)}]$  and vice versa.

### 2.2.2. Magic-angle spinning–nuclear magnetic resonance spectroscopy (MAS–NMR)

MAS–NMR was performed on solid samples using a Bruker MSL 360 spectrometer using an 8.45 tesla superconducting magnet. Spectra were taken using a probe tuned to the  $^{29}\text{Si}$  isotope at 59.584 MHz, with a spin rate of 3500–4500 Hz.

## 3. Results and discussion

X-ray diffraction patterns (XRD) of the gel spheres [ $\text{Zr}_{1-x}\text{Si}_x\text{O}_2$  ( $x = 0-0.5$ )] calcined to 600 °C are shown in Fig. 1. For  $x = 0.1$  and 0.2, this shows a single phase solid solution of tetragonal zirconia with silica, but as substitution increases, so does the amount of amorphous silica in the background, merging the tetragonal splitting into a cubic looking spectrum. Lattice parameter measurements of unsubstituted zirconia made in a similar manner, indexes as a tetragonal phase with  $a = 0.3597$  nm and  $c = 0.5180$  nm. For a silica substitution of  $x = 0.1$ , the unit cell becomes pseudo-tetragonal with  $a = 0.5094$  nm and  $c = 0.5179$  nm. This is repeated in all other substitutions to  $x = 0.5$ , with no further change in the lattice parameters. This would indicate that the solid solution limit of silica in zirconia is between 0.1 and 0.2 at this temperature.

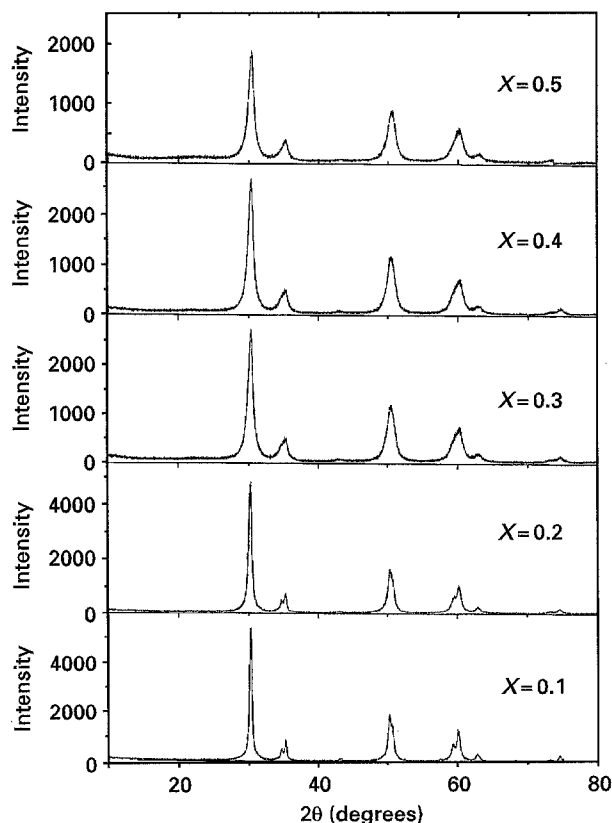


Figure 1 XRD patterns of  $\text{Zr}_{1-x}\text{Si}_x\text{O}_2$  ( $x = 0.1-0.5$ ) calcined to 600 °C.

Solid state  $^{29}\text{Si}$  MAS–NMR of the gel spheres and 600 °C calcined samples shows a single peak at  $-111$  p.p.m. A typical spectrum is shown in Fig. 2. This indicates that the silica is in  $\text{q4 SiO}_4^{4-}$  units with no direct Zr–O–Si bonding, and that the environment of lattice incorporated silica remains the same from  $x = 0.1$  to 0.5.

Further calcination of the samples to 950 °C, the tetragonal to monoclinic transition temperature, shows stabilization of the tetragonal phase by silica. This can be seen in Fig. 3. Unstabilized zirconia is almost entirely monoclinic at this temperature, but inclusion of silica into the lattice  $\geq x = 0.2$  produces almost entirely tetragonal zirconia. The effect is consistent with both NMR and XRD observations in that no greater stabilization is achieved above  $x = 0.15-0.2$ . It is also interesting to note that 10–15% of the zirconia remains unstabilized, i.e. monoclinic, regardless of silica content above  $x = 0.2$ .  $^{29}\text{Si}$  NMR of the

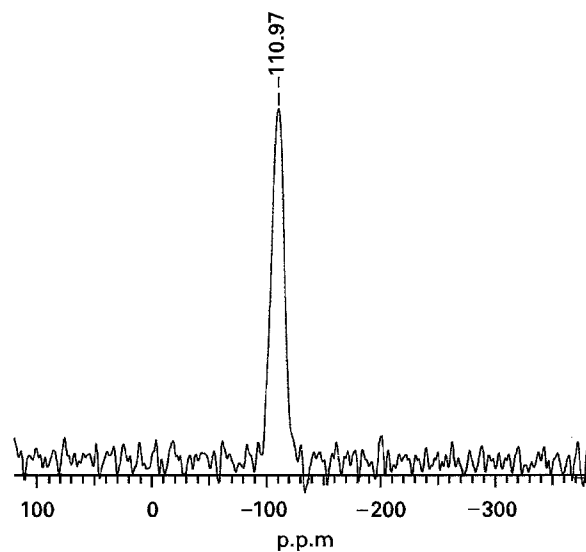


Figure 2 MAS–NMR spectrum of  $^{29}\text{Si}$  in  $\text{Zr}_{0.9}\text{Si}_{0.1}\text{O}_2$  calcined to 600 °C.

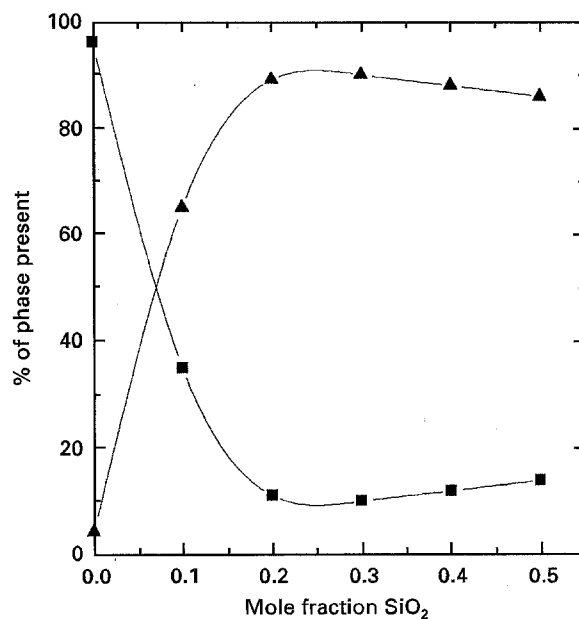


Figure 3 Volume fraction of products on calcining  $\text{Zr}_{1-x}\text{Si}_x\text{O}_2$  ( $x = 0.1-0.5$ ) to 950 °C. (▲) tetragonal; (■) monoclinic.

950 °C samples were identical to the 600 °C calcined ones.

The volume fraction of phases produced on calcination of the samples to 1100 °C is shown in Fig. 4. Here it can be seen that inclusion of silica in the lattice up to  $x = 0.2$ , produces an unreactive phase which merely transforms from a stabilized tetragonal phase to a stable monoclinic solid solution, with the absence of any significant zircon formation. As the substitution increases above this, the amorphous silica, which is not lattice stabilized, readily reacts with the tetragonal zirconia forming zircon. Any unreacted zirconia that is not stabilized, transforms to the monoclinic phase and remains inert. Thus, at  $x = 0.5$ , stoichiometric for zircon, we would expect  $\sim 15\%$  monoclinic zirconia which was unstabilized and therefore inert since 950 °C,  $\sim 70\%$  zircon where the 35% reactive amorphous silica has reacted with 35% tetragonal zirconia, and 15% remaining tetragonal zirconia. These expectations are confirmed in the experimental observations in Fig. 4. Heating for prolonged periods at 1100 °C, (Table I), produces no increase in zircon formation to that above, or changes the proportions of monoclinic and tetragonal zirconia. This shows that monoclinic zirconia is unreactive with silica to form zircon, and that lattice stabilized silica is also unreactive at these temperatures.

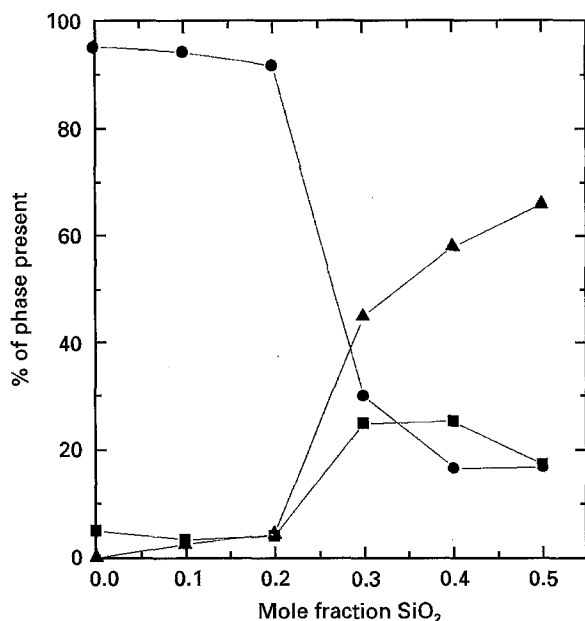


Figure 4 Volume fraction of products on calcining  $Zr_{1-x}Si_xO_2$  ( $x = 0.1-0.5$ ) to 1100 °C. (■) tetragonal; (●) monoclinic; (▲) zircon.

TABLE I Volume fractions of the products on calcination of  $Zr_{1-x}Si_xO_2$  ( $x = 0.5$ )

Calcination temperature (°C)	Volume fraction of phase present (%)		
	ZrSiO <sub>4</sub>	ZrO <sub>2</sub> monoclinic	ZrO <sub>2</sub> tetragonal
1100/12 h	20.4	21.1	58.5
1100/16 h	65.9	16.8	17.3
1100/32 h	69.3	16.7	14.1
1200/12 h	71.5	14.5	14.1

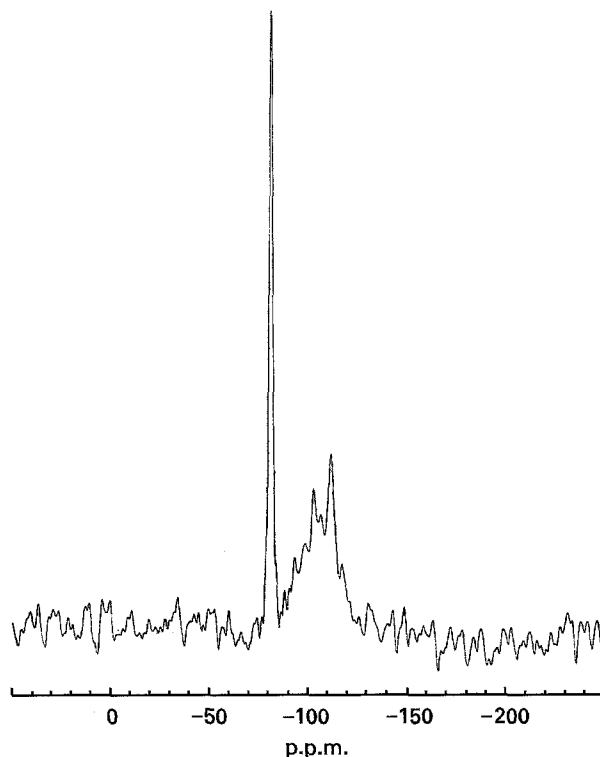


Figure 5 MAS-NMR spectrum of  $^{29}Si$  in  $Zr_{0.5}Si_{0.5}O_2$  calcined to 1100 °C.

TABLE II Volume fraction of the products on calcination of  $Zr_{1-x}Si_xO_2$  ( $x = 0.5$ )

Treatment at 1200 °C/12 h	Volume fraction of phase present (%)		
	ZrSiO <sub>4</sub>	ZrO <sub>2</sub> monoclinic	ZrO <sub>2</sub> tetragonal
A	71.5	14.5	14.0
B	71.4	17.2	11.4
C	69.0	17.0	14.0

- A. Heating of  $5^\circ C \text{ min}^{-1}$  and normal air cooling.  
 B. Heating rate of  $60^\circ C \text{ min}^{-1}$  and normal air cooling.  
 C. Heating rate of  $5^\circ C \text{ min}^{-1}$  and quenched in liquid nitrogen.

$^{29}Si$  NMR data of the  $x = 0.5$  composition heated to 1100 °C is shown in Fig. 5. This clearly shows the presence of the remaining silica in solid solution, at  $-111$  p.p.m., together with the zircon type silica at  $-82$  p.p.m. caused by Zr-O-Si bonds.

Finally, differing heat treatments and quenching of the  $x = 0.5$  composition was tried, to see if these parameters were responsible for different amounts of zircon formation, and/or differing monoclinic/tetragonal zirconia ratios. The results are shown in Table II. This shows that in our experiments, this treatment had little or no effect on the volume fractions of the products expected.

#### 4. Conclusions

Analysing these results, it is clear that amorphous silica reacts with tetragonal zirconia to form zircon, and that any secondary phase of unreacted zirconia is due to transformation of the tetragonal zirconia to monoclinic before zircon formation. In homogeneous

systems such as this, stabilization of some of the silica within the tetragonal zirconia phase is also responsible for secondary phases.

In order therefore to obtain high purity zircon by this method, high temperatures in excess of 1300 °C are needed to remove the unreacted or stabilized zirconia.

## References

1. T. MORI, H. YAMAMURA, H. KOBAYASHI and T. MITAMURA, *J. Ceram. Soc. Japan*, **98** (1990) 1017.
2. G. R. OHEIM, H. PAULUS and C. RUSSEL, *J. Mater. Sci. Lett.* **10** (1991) 1171.
3. T. MORI, H. YAMAMURA, H. KOBAYASHI and T. MITAMURA, *J. Ceram. Soc. Japan* **99** (1991) 1098.
4. *Idem.*, *ibid.* **99** (1991) 1058.
5. *Idem.*, *ibid.* **98** (1990) 1109.
6. *Idem.*, *ibid.* **99** (1991) 42.
7. T. MORI, H. HOSHINO, Y. ISHIKAWA, T. YAMAGUCHI, H. YAMAMURA, H. KOBAYASHI and T. MITAMURA, *idem.* **99** (1991) 227.
8. T. MORI, H. YAMAMURA, H. KOBAYASHI, T. MITAMURA, *idem.* **98** (1990) 567.
9. I. TAKAO, *J. Cryst. Growth*, **125** (1992) 223.
10. A. K. BHATTACHARYA, A. HARTRIDGE and K. K. MALLICK, *Mater. Lett.* **18** (1994) 247.
11. *Idem.* *J. Mater. Sci.* **29** (1994) 6076.
12. *Idem.*, *ibid.* **31** (1996) 267.

*Received 19 April  
and accepted 13 June 1996*