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Preparation and characterization of precursors of Y_2O_3 stabilized ZrO_2 by metal-organic compounds

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8 mol % Y_2O_3-stabilized ZrO_2 has been prepared by four routes which involve yttrium and zirconium metal organic compounds as starting materials. The thermal decomposition of the precursors has been investigated by means of thermal analysis, X-ray diffraction and SEM technique with regard to their chemical homogeneity and phase composition. The possible reactions during precursor preparations are discussed.

1. Introduction

For long time it has been interesting for ceramists to acquire ultra-fine and high purity powders for the preparation of high density ceramics at lower temperatures and for making of thin films, catalysts, absorbents and so on. In the conventional techniques for preparing fine particle oxide powders, a number of methods, such as thermal decomposition of salts and hydroxides have commonly been used. Recently, several relatively novel techniques such as the plasma arc with induction coupling and Vicro electric process have been used. However, these methods do not achieve higher purity than thermal decomposition and precipitation techniques, although particle size lower than 100 nm may be produced. The use of metal-organic compounds is another method to prepare high-purity and ultra-fine ceramic powders with homogeneous chemical composition.

Fully and partially stabilized ZrO_2 are widely used as solid electrolytes and structural ceramics. Although it has been reported by a number of papers that pure ZrO_2 can be prepared from zirconium alkoxide [1, 2], it also appears interesting for precursors of stabilized ZrO_2 with Y_2O_3, CaO or MgO from metal-organic compounds to be obtained. In the present work, either zirconium and yttrium both from organic compounds, or an organic compound of Y (Zr) with an inorganic salt of Zr (Y) have been investigated as starting materials to prepare the precursor of Y_2O_3 stabilized ZrO_2 (YSZ). The morphology and element distributions as well as the phase composition of the powders produced by the precursors have been identified by means of SEM combined with X-ray diffraction analysis. The phase stability after calcination for various precursors has also been estimated and compared.

2. Experimental procedures

Four routes have been investigated for the elaboration of 8 mol % Y_2O_3 doped ZrO_2 precursors.

2.1. Route A

An yttrium propionate solution is dropped according to the stoichiometry into a zirconium propoxide solution in isopropanol (50 wt % concentration). About ten minutes after the end of mixing a precipitate is formed in the mixed solution. Both precipitate and solution are dried together at 100 °C. The resulting powder is designated as precursor A. The similar designation is made in the following text.

The yttrium propionate solution was made by means of refluxing an excess propionic acid with Y_2O_3 at 75 °C. A few cubic centimetres of water were added during refluxing. It took about 80 h to obtain a perfect clear solution with a concentration of about 2 wt %.

2.2. Route B

An yttrium propionate solution is mixed with a $Zr(OC_3H_7)_4$ solution in propionic acid (50 wt % concentration) according to the stoichiometry of 8 mol % Y_2O_3–92 mol % ZrO_2, yielding a stable clear solution. After drying at 200 °C, the resultant precursor was designated as B.

2.3. Route C

An yttrium propionate solution is added into a $ZrOCl_2$-propionic acid solution according to the previous stoichiometry. A precipitate is formed during addition. Further water addition into the suspension

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heated at 75 °C allows the former precipitate to be dissolved, giving rise to a clear solution. The water quantity able to dissolve the precipitate nearly corresponds to the suspension volume. The solution is then evaporated in a heating dessicator at 100 °C. The resulting powder is designated as C.

$ZrOCl_2$-propionic acid solution was prepared by dissolving $ZrOCl_2 \cdot 8H_2O$ in propionic acid at 75 °C. It took around 30 h by adding a small amount of water to obtain complete dissolution.

2.4. Route D

$Zr(OC_3H_7)_4$ is added to a $Y(NO_3)_3 \cdot 6H_2O$-isopropanol (1:4) solution, allowing a clear solution to be obtained at room temperature. Solvent evaporation at 100 °C yields precursor D.

The thermal evolution of the precursors has been followed by differential thermal analysis, DTA. The phase composition of precursors calcined at various temperatures has been studied by X-ray diffraction measurements. The grain sizes and morphologies have been observed by scanning electron microscopy, SEM, combined with element analysis.

3. Results

3.1. DTA results

Fig. 1a–d are DTA curves up to about 950 °C for precursors A, B, C and D, respectively. On these curves, three kinds of thermal effects are observed:

(i) endothermic and appearing below 200 °C, can be related to the evaporation of residual solvents (propionic acid, water,...).
(ii) strongly exothermic, may be caused by the burning of the organic molecules bounded to zirconium. The temperature of this kind of thermal effect varies according to the nature of the precursor and appears at the lowest temperature for the D precursor (230 °C).
(iii) exothermic and which can be broad and diffuse, could be related to the crystallization of yttria doped zirconia.

No thermal effects appear during cooling down to room temperature.

Thermogravimetric analyses show that all samples do not exhibit any weight loss above 500 °C, except for the C precursor. In this case, the presence of chlorides seems to be responsible for the higher temperature (900 °C) final weight loss.

3.2. X-ray diffractometry

The four precursors were calcined for 4 h at temperatures ranging from 400 to 800 °C and the resulting products were examined by means of X-ray (CoK_α) diffraction analysis. From Fig. 2a and b, it can be seen that A and B begin to transform at 400 °C from amorphous to YSZ with the cubic crystalline structure, though the diffraction patterns are rather wide and spreading. For this reason some other phases could not be identified. Furthermore, 400 °C calcination is not high enough to eliminate all organic compounds, as revealed from the DTA and TGA measurements, and by the black or grey colour of the resulting powders. Powders C and D calcined at 400 °C reveal sharper X-ray diffraction patterns (Fig. 2c and d) than A and B. D exhibits a pure cubic YSZ X-ray diffraction pattern. For C, in addition to the cubic phase, a peak with an interreticular d value equal to 0.2765 nm appears and may be attributed to the existence of YOCl.

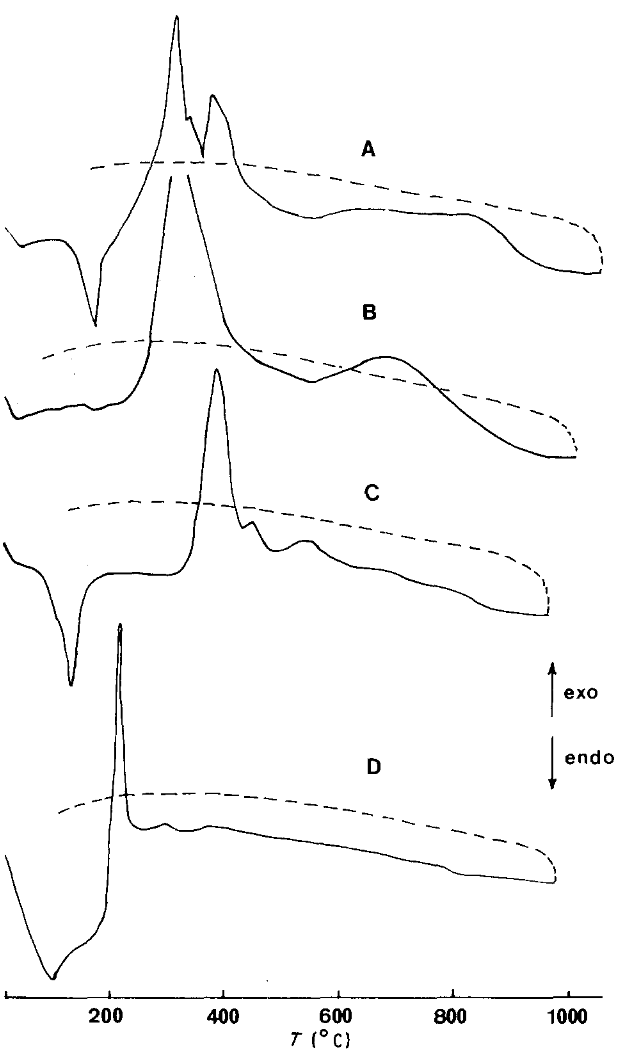

Figure 1 DTA curves of precursors A, B, C and D.

The diffraction patterns obtained for the precursors calcined above 700 °C show much sharper diffraction peaks (Fig. 3a–d), indicating that the crystallites are much more developed. However, the phase compositions of the four samples exhibit strong differences. Y_2O_3 and monoclinic ZrO_2 phase (m-ZrO_2) occur in the A, B and C powders. According to the Garvie's calculation formula [3], the volume percentage of cubic phase relative to the coexisting monoclinic one are 75.6%, 78.4% and 71.7% for A, B and C, respectively. As the calcination temperature increases, both m-ZrO_2 and Y_2O_3 concentrations enhance significantly while the cubic phase one decreases. Only sample D retains a pure cubic phase through the temperatures from 400 °C to above 1000 °C. The X-ray diffraction results are summarized in Table I.

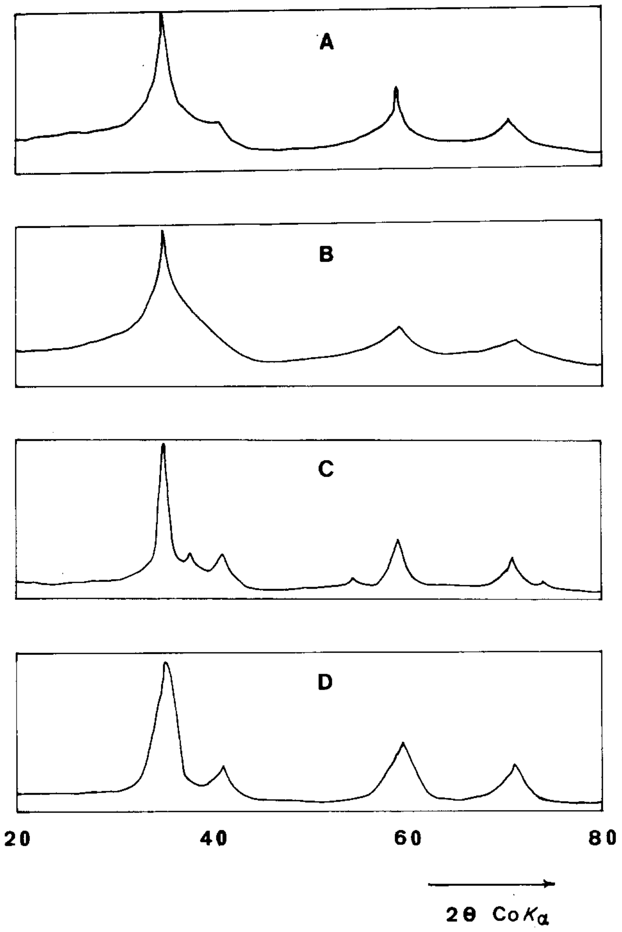

Figure 2 X-ray diffraction patterns of precursors calcined at 400 °C.

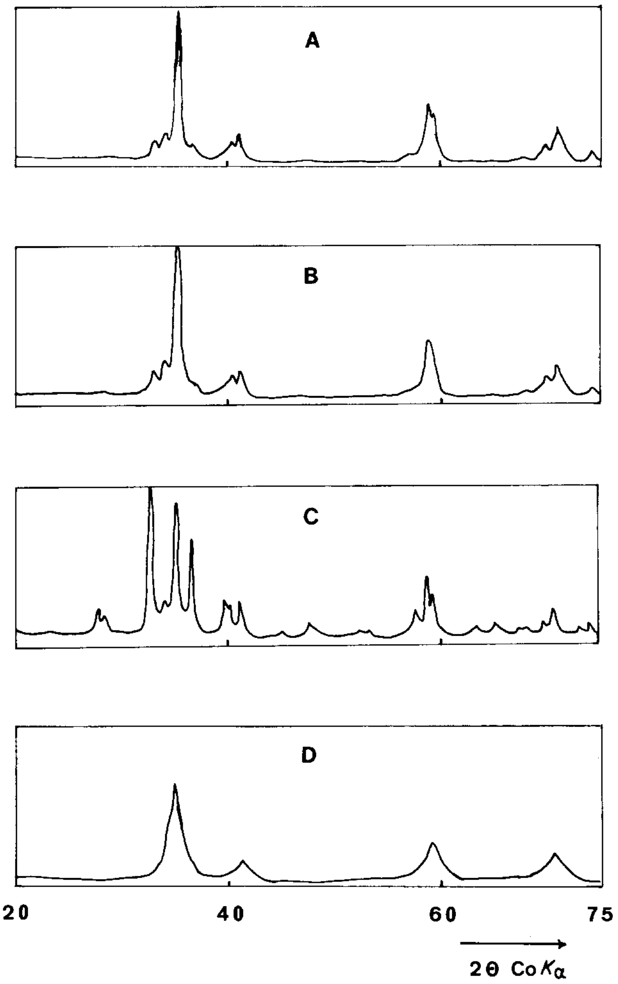

Figure 3 X-ray diffraction patterns of precursors calcined at 700 °C.

TABLE I Phase compositions of calcined precursors

Calc. temp. (°C)	A		B		C		D	
	C%	Y_2O_3	C%	Y_2O_3	C%	Y_2O_3	C%	Y_2O_3
400	100	ND	100	ND	100[a]	ND	100	ND
450					71.7	Tr		
650					70.0	Tr		
700	75.6	Ex	78.4	Tr	35.4	Ex	100	ND
750					20.0	Ex		
800	52.1	Ex	57.0	Ex	17.5	Ex	100	ND

C: cubic phase; [a]: YOCl probably existed; ND: not detected; Ex: existed; Tr: trace.

3.3. SEM observation

The morphology of the calcined powders has been observed by SEM, meanwhile element concentration analysis was done at some characteristic morphological locations by the fluorescence X-ray spectrum.

The typical morphologies of the four samples calcined at 700 °C are shown in Fig. 4. The crystallites of sample A appear well developed. Agglomerates with a size that can reach 40 μm are built up from smaller particles with a size of roughly a few micrometres. Sample B (Fig. 4b) exhibits a feature of aggregates which consist of smaller grains with size 0.5–2 μm. Sample C particles can obviously be distinguished into two kinds of morphologies: one is bigger and corresponds to well developed crystals with a mean size around 6 μm, the other one appears as aggregates of smaller grains with submicrometre size.

Sample D (Fig. 4d) exhibits somewhat uniform particles, the mean size of which ranges from 2 to 4 μm.

The results of grain size estimation and element analysis by SEM combined with fluorescence X-ray spectrum for the four samples are listed in Table II.

It is apparent from Table II that Sample D exhibits the most homogeneous element distribution, while A and C show the worst ones. This is particularly evident by considering the element distribution inside the biggest particles that reveals strong discrepancies

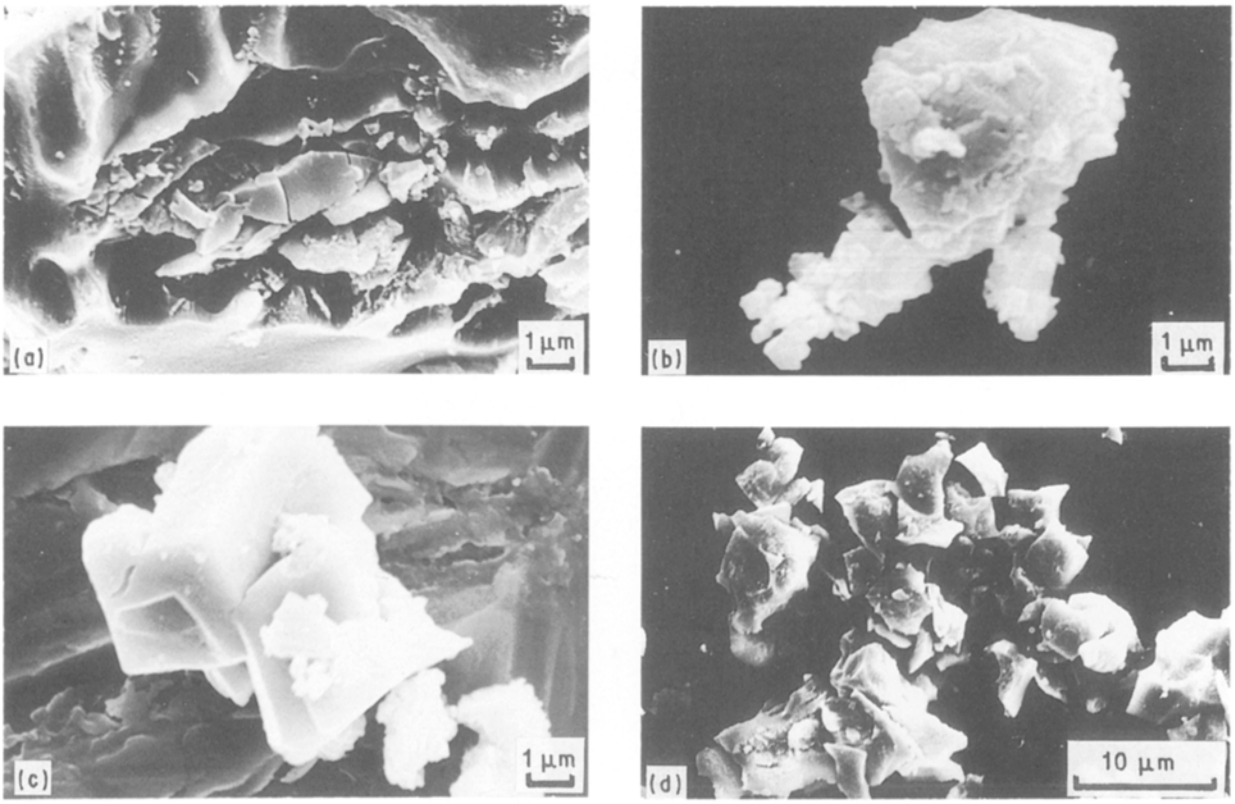

Figure 4 SEM micrographs of powders calcined at 700 °C.

TABLE II Grain sizes and element analyses of powders calcined at 700 °C by SEM combined with fluorescence X-ray spectrum

	Y_2O_3 (wt %) Mean	BG	ZrO_2 (wt %) Mean	BG	MGS (µm)
A	17.12	5.32	82.88	94.77	40
B	16.30	22.65	83.70	77.35	0.5–2
C	14.33	8.53	85.76	91.47	1 and 6
D	16.47	16.11	83.53	83.89	2–4

BG: biggest grains; MGS: mean grain size.

compared to the overall composition. B, C and D samples have a similar particle size of a few microns, whereas sample A has a mean size of roughly 40 µm.

4. Discussion

As revealed by X-ray diffraction measurements, a single cubic phase is observed in sample D after calcination above 400 °C, indicating that Y_2O_3 has completely entered into ZrO_2 lattice to form a stabilized cubic solid solution, in agreement with the phase diagram reported in the literature. The results of the fluorescence X-ray element analysis (Table II) also prove the inexistence of free Y_2O_3 and/or m-ZrO_2, which should have different concentrations of Zr and Y from cubic stabilized zirconia.

According to above experimental conditions, the starting D solution has the following composition:

$$0.92\,Zr(OC_3H_7)_4 + 0.16\,Y(NO_3)_3 \cdot 6H_2O + 9\,C_3H_7OH$$

Because zirconium isopropoxide can very easily be hydrolysed [5–7], hydrolysis can be performed from crystalline water available from yttrium nitrate with a H_2O/Zr ratio close to 1. According to Bradley *et al.* [8], in such conditions, species like $(Zr_2O_3(OPr)_2(PrOH)_2)_x$ or $(Zr_3O_6(PrOH)_6)$ can be formed. Yttrium can be either dispersed within the zirconium compound or forming a mixed Zr–Y oxo-alcoolate. At the moment, it is not possible to give a definite answer concerning the composition of the D precursor. Even if the starting solution appears to be quite simple, its evolution probably yields the formation of complex species that are not easy to characterize. However, it appears that the homogeneity of the starting solution can be retained after solvent elimination in the D precursor. The cubic solid solution appears to be formed after 400 °C calcination and further thermal treatment does not modify this observation, apart from subsequent grain growth.

The three other routes, A, B and C, can be considered as metalloorganic decomposition (M.O.D.) routes. The choice of propionic acid, C_2H_5COOH, as a solvent comes from previous works on titanates and cuprates using the same M.O.D. process [9, 10].

In both cases, it has been shown that polymer-like compounds can be obtained by heating a propionic acid solution containing the corresponding metallic cations. The final pyrolysis yields fine powders exhibiting high reactivity.

For A and B precursors, the starting constituents are in the following proportions:

$$\text{A route: } 0.92\,\mathrm{Zr(OC_3H_7)_4} + 0.08\,\mathrm{Y_2O_3} + 5\,\mathrm{C_3H_7OH} + 12\,\mathrm{C_2H_5COOH} + x\,\mathrm{H_2O}$$

$$\text{B route: } 0.92\,\mathrm{Zr(OC_3H_7)_4} + 0.08\,\mathrm{Y_2O_3} + 16\,\mathrm{C_2H_5COOH} + x\,\mathrm{H_2O}$$

In both cases, there is a strong excess of propionic acid, that will react with zirconium isopropoxide yielding the formation of the corresponding propionate. Such a reaction has already been observed with other alkoxides (Mg, Ti, Al,...). Whereas for titanates and cuprates solvent elimination allows a polymer like phase to be obtained, Y and Zr propionate solution yields the formation of a precipitate during drying. As this precipitate appears to be amorphous by X-ray diffraction, its phase composition cannot be determined. However, we can consider it as a mixture of both Y and Zr propionates. Further calcination (exothermic effect around 325 °C) yields the formation of Y_2O_3 and ZrO_2 as fine powders, that react with each other allowing the Y_2O_3–ZrO_2 solid solution to be formed. Possible heterogeneities within the propionate precipitate can explain the formation of free Y_2O_3 as well as m-ZrO_2.

For the C precursor, the coexistence of Cl^- ions in the starting mixture makes the interpretation much more difficult. After organic burning, the powder behaves in the same way as precursors A and B yielding the formation of a three phase mixture. It has also been observed that complete decomposition is only achieved at higher temperatures in relation with the presence of residual chlorides.

5. Conclusions

Using $Zr(C_3H_7O)_4$ and $Y(NO_3)_3 \cdot 6H_2O$-isopropanol solution as the starting materials one can obtain YSZ precursor with the most homogeneous chemical composition among the four investigated routes based on metal-organic compounds. YSZ with a pure cubic phase and a mean grain size of a few microns can be obtained through calcination of the precursor at low temperatures.

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