

Synthesis of ultrafine pure and yttria-stabilized hafnia by solid-state reaction at relatively low temperature

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Highly reactive, ultrafine powders of pure hafnia as well as stabilized hafnia (8 mol % yttria) have been synthesized at relatively low temperature (500 °C) by solid-state reaction between standard coarse-grained powders of sodium metaphosphate (NaPO₃) and sodium hafnate (Na₂HfO₃). The reaction product was found to be a two-phase mixture of sodium orthophosphate (Na₃PO₄) and hafnia. Subsequently, the orthophosphate phase was removed by washing with dilute nitric acid. The as-prepared powders were extremely fine (particle size < 20 nm) and crystalline (cubic fluorite structure). After cold pressing and heating to 1650 °C, the materials retained a fine-grained microstructure. Stable cubic HfO₂ with Y₂O₃ addition (8 mol %) was obtained at a temperature which was not too high (1650 °C).

1. Introduction

The synthesis of ceramics with fine particle size and uniform microstructure has been a main area in the field of materials for many years. Preparation of highly reactive zirconia, partially or fully stabilized, for applications in many fields, such as chemical gas sensors, high-temperature refractories, has been carried out using techniques such as attrition milling, coprecipitation from solutions of inorganic salts or alkoxides, and reaction sintering.

However, these techniques have some restrictive aspects: they are sometimes difficult to control (pH value in the coprecipitation process), costly, and often not easy to obtain [1–6]. Recently, a method which avoids the use of solution precursors as in some of the above-mentioned techniques and based on a solid-state reaction, has been used for the synthesis of an ultrafine zirconia powder at low temperature [7].

Zirconium and hafnium are both group IVB elements and show large structural and chemical similarities. This is also true for their oxides.

Like ZrO₂, hafnium oxide (HfO₂) exhibits a non-quenchable monoclinic to tetragonal phase transformation, but at a higher temperature (1750 °C). However, HfO₂ and ZrO₂ can be transformed into cubic crystal structures, free of this destructive transformation by the addition of CaO, MgO or Y₂O₃. The cubic structure (fluorite type) commonly called “stabilized hafnia” is stable from room temperature to the melt. It has been shown [8] that Y₂O₃-stabilized HfO₂ is the most resistant to destabilization at high temperatures. Hafnia is a promising ultra-refractory material for nuclear applications (control rods or neutron shielding) due to its high melting point (≈ 2900 °C), extreme chemical inertness, and strong

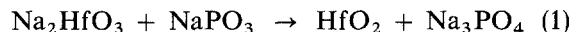
thermal neutron capture cross-section. However, the synthesis of this pure or stabilized oxide requires the use of very high temperatures (≈ 2000 °C), so this synthesis is expensive and not easy to carry out.

With the intention of preparing ultrafine, highly active powder of pure and yttria-stabilized hafnia, a technique based on solid-state reaction at relatively low temperature has therefore been used.

2. Experimental procedure

The synthesis was carried out by solid reaction between sodium hafnate, Na₂HfO₃, and sodium metaphosphate, NaPO₃, at 500 °C. Compound Na₂HfO₃ is not commercially available and was first prepared by heating at 900 °C for 90 h, appropriate amounts of hafnium oxide powder (crystallite size 1–3 μm) and sodium carbonate. In a second step, Na₂HfO₃ and NaPO₃ powders were ground, mixed into equimolar amounts and heated in air for 150 h at 500 °C in a platinum crucible.

The following chemical reaction occurred



The kinetic of reaction was slow at 500 °C but increased at 700 °C. The sodium orthophosphate, Na₃PO₄, was removed by repeated washings with dilute nitric acid, followed by deionized water and ethanol washings. The alcohol-washed powder was stored at 40 °C for complete drying in an oven.

Phase analysis was performed using X-ray powder diffraction (CuK_α radiation). Microstructure and particle size of the powder were examined by transmission electron microscopy (TEM) and by scanning electron microscopy for sintered bodies.

3. Characterization of as-prepared hafnium oxide powder

3.1. X-ray diffraction

The as-prepared hafnia powder was crystallized and the X-ray pattern showed a single phase with cubic symmetry (fluorite type), high intensity and sharpness for peaks of the structure. As shown later, this cubic phase is metastable; however, no structural change with time at room temperature was detected on the diagram after the powder was exposed even for several months in air.

3.2. Electron microscopy

The particle size of the powder was determined from a powder ultrasonically dispersed in a solution of absolute ethyl alcohol. A drop of the dispersion was deposited on to a carbon substrate on a copper mesh screen. The as-prepared powder was extremely fine with submicrometre particle size (≈ 20 nm) (Fig. 1) and there was evidence that the larger particles were agglomerated. The agglomerates present in the powder appear to be relatively weakly bound so they will be broken down during the subsequent powder compaction process.

3.3. Thermal evolution of ultrafine hafnia

Hafnia powder was heat treated in the range room temperature to 1650°C after cold-pressing (3 t cm^{-2}). No particular advantage was gained in connection with the sintering by exceeding this pressing value. X-ray diffraction diagrams of submicrometre HfO_2 show a structural evolution as the temperature was raised. So at 500°C both the allotropic forms of HfO_2 can be observed: the initial cubic phase and the monoclinic form which begins to grow. Up to 700°C , the ratio of the two forms is inverted, the monoclinic phase increasing while the cubic phase progressively decreases. This fact indicates a metastable state for this cubic phase. The transformation is achieved at 850°C and then only the monoclinic phase is observed in the range $850\text{--}1600^\circ\text{C}$.

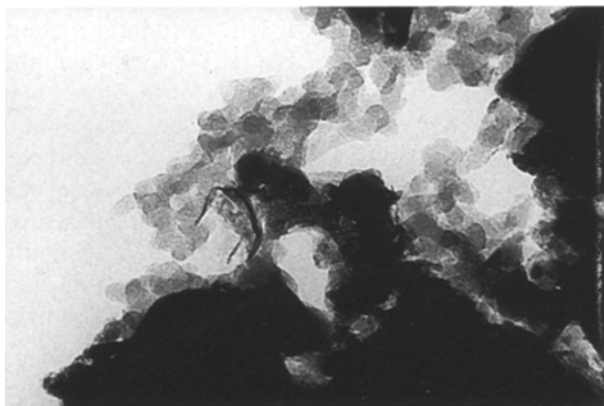


Figure 1 Transmission electron micrograph of as-prepared HfO_2 powder ($\times 150000$).

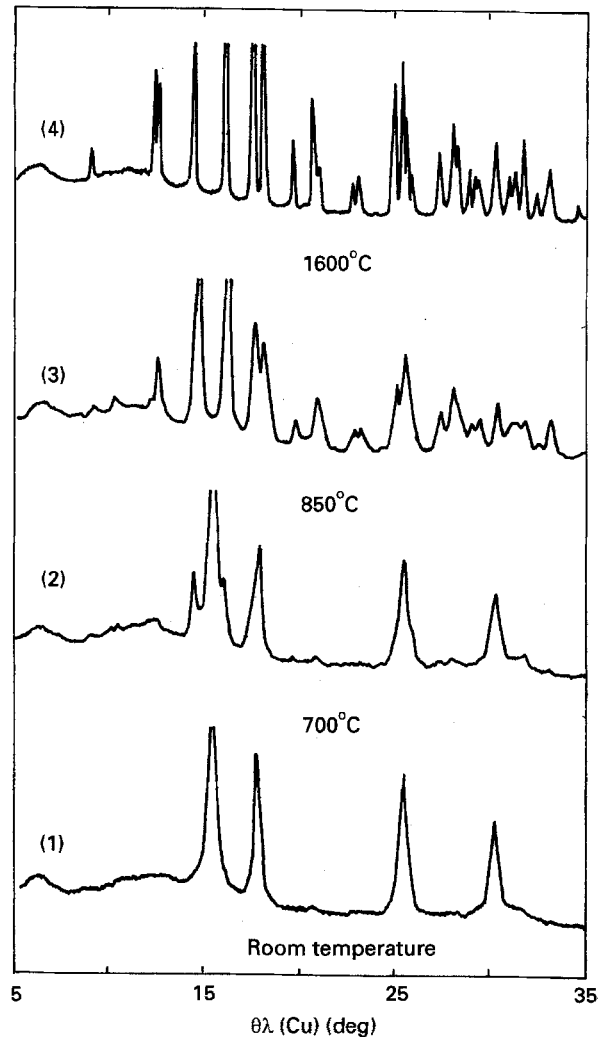


Figure 2 X-ray pattern evolution of HfO_2 versus heat treatment. (1) Room temperature, cubic form (cfc); (2) 700°C , cubic (cfc) + monoclinic forms; (3) 850°C , monoclinic form; (4) 1600°C , monoclinic form.

TABLE I Evolution of monoclinic phase and crystallite size for pure HfO_2 versus temperature

Heat-treatment temperature, T ($^\circ\text{C}$) (15 h)	Monoclinic structure (%)	Crystallite size (nm)
40	0	20
500	4	20
700	22.5	20
850	100	20–25
1500	100	600
1650	100	0.3–0.5 μm

Fig. 2 shows evolution of the X-ray patterns of HfO_2 with temperature.

The relative phase fractions of monoclinic and cubic HfO_2 were determined using the method given by Toraya *et al.* [9]. The fraction, R , of the monoclinic HfO_2 phase is

$$R = \frac{I_m(\bar{1}11) + I_m(111)}{I_m(\bar{1}11) + I_m(111) - I_c(111)} \quad (2)$$



Figure 3 Transmission electron micrograph of HfO_2 powder heated at 850°C for 19 h ($\times 300\,000$).

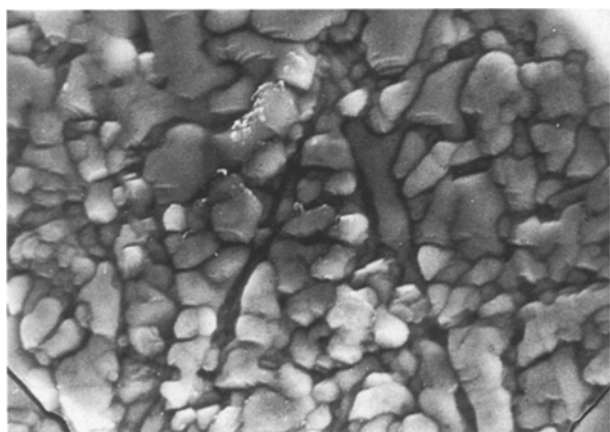


Figure 4 Scanning electron micrograph of a polished HfO_2 pellet after heating for 6 h at 1650°C ($\times 20\,000$).

where I_m and I_c are the integral intensities of the monoclinic and cubic phases, respectively.

The concentrations of the monoclinic structure for samples treated at various temperatures are given in Table I.

Evolution of the crystallite size of HfO_2 with temperature (Table I) was observed by TEM. The as-prepared powder was extremely fine with an average size of 20 nm. Up to 850°C , the size of the particles was constant (Fig. 3) indicating that the size was not connected with the metastable cubic–monoclinic transformation experienced by the material. At higher temperatures (850 – 1650°C), the particle size grew and reached 600 nm and 0.3 – $0.5\ \mu\text{m}$ at 1500 and 1650°C , respectively (Fig. 4).

It can be noted that even after heating to 1650°C , the materials retain a submicrometre grain size.

3.4. Discussion

Synthesis of submicrometre hafnia by solid-state reaction at relatively low temperature leads to a comparison of this process with a technique often reported in earlier works and based on hydrolytic decomposition of alkoxides [10]. Both methods, although differing in their principles, components and reaction conditions,

TABLE II Thermal evolution of hafnia prepared from different modes

Hydrolytic decomposition of alkoxides	Solid-state reaction at 500°C
As-prepared: amorphous	As-prepared: crystallized cubic fluorite structure (cfc)
460°C : amorphous + monoclinic phases	500°C : cubic + monoclinic phases
$> 500^\circ\text{C}$: monoclinic phase	850°C : monoclinic phase

yield an ultrafine hafnia with particle size < 20 nm. However, the powder from hydrolytic decomposition was initially amorphous and this state was retained up to 460°C . From 460 – 480°C , the X-ray diagrams exhibited a mixture of the amorphous and monoclinic states. At higher temperature only the monoclinic phase was noted.

Garvie [11], in an earlier work, reported that metastable tetragonal HfO_2 could not be prepared from aqueous solution. When an hydrous precipitate was heated, the sequence of phases observed was amorphous \rightarrow monoclinic.

The synthesis reported in the present work leads to the conversion at relatively low temperature of a standard coarse-grained hafnia powder into an ultrafine crystallized one, with a metastable cubic fluorite structure. At 500°C , a mixture of cubic and monoclinic forms was observed on the X-ray patterns, and at 850°C only the monoclinic phase was noted.

Techniques based on hydrolytic decomposition of alkoxides or precipitation from aqueous solution to prepare ultrafine hafnia yielded an amorphous as-prepared powder which, after further heat treatment, did not show a metastable cubic state as was noted with the solid-state reaction process at relatively low temperature.

Our results can be related to the metastable cubic state observed [12] in the case of zirconia powder prepared from hydrolytic decomposition of alkoxides.

The structural evolution with temperature of hafnia synthesized from these modes is summarized in Table II.

4. Synthesis of ultrafine yttria-stabilized hafnia

Addition of yttrium oxide to HfO_2 produces a cubic fluorite structure. In the HfO_2 – Y_2O_3 system, the fluorite phase extends from 8 mol% to more than 40 mol% Y_2O_3 at 1800°C [13]. The composition HfO_2 –8 mol% Y_2O_3 was retained to carry out the synthesis of ultrafine stabilized HfO_2 powder by solid-state reaction at a relatively low temperature. The hafnia–yttria composition was prepared initially either by coprecipitating hafnium oxychloride and yttrium oxide in hydrochloric acid solution and then calcining the coprecipitate for 65 h at 900°C , or by solid-state reaction of mixed standard coarse-grained hafnia and yttria at high temperature ($> 1600^\circ\text{C}$).

X-ray diffraction diagrams of the products showed crystalline peaks with the positions corresponding to

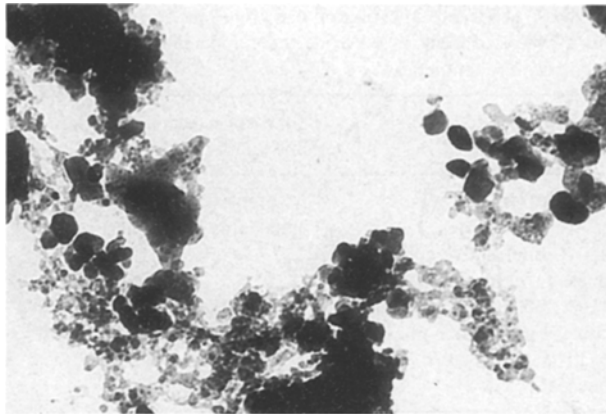


Figure 5 Transmission electron micrograph of as-prepared yttria-stabilized (8 mol %) hafnia ($\times 120\,000$).

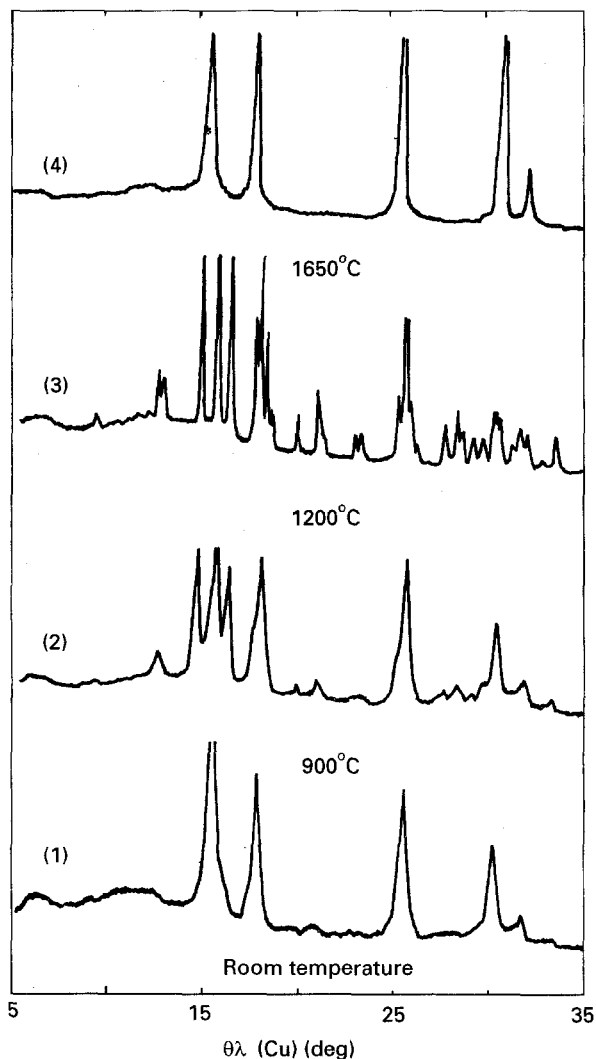


Figure 6 X-ray pattern evolution of stabilized yttria (8 mol %) hafnia versus temperature. (1) Room temperature, cubic fluorite phase (cfc); (2) 900°C, cubic + monoclinic (weak) phases; (3) 1200°C, cubic + monoclinic phases; (4) > 1650°C, cubic phase (cfc).

the cubic phase. The calculated lattice parameter of this phase (fluorite structure) was $a = 0.511$ nm, in good agreement with the above-mentioned values [13].

Powder of basic composition then undergoes all stages of the synthesis route by solid-state reaction at

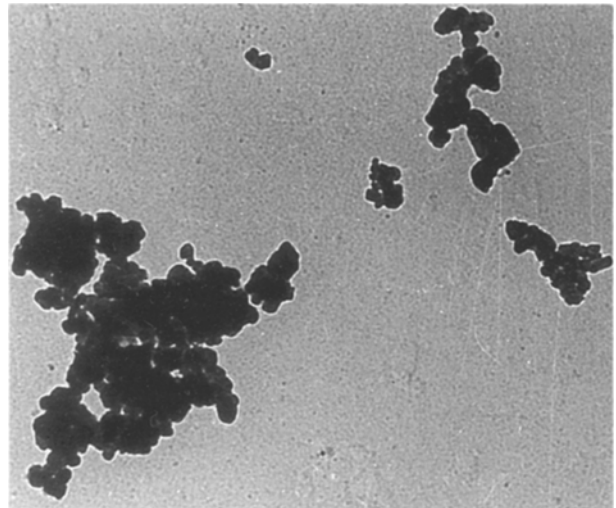


Figure 7 Transmission electron micrograph of yttria-stabilized (8 mol %) hafnia treated for 15 h at 900°C ($\times 60\,000$).

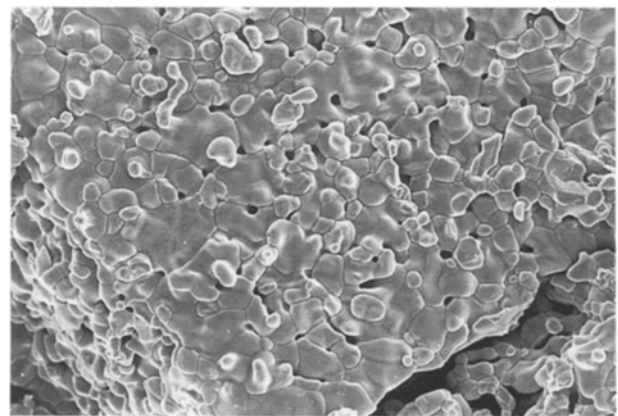


Figure 8 Scanning electron micrograph of a fresh fracture of yttria-stabilized (8 mol %) hafnia pellet, treated for 7 h at 1650°C ($\times 2500$).

relatively low temperature (500°C) as previously reported, and was used to prepare pure hafnia.

4.1. Characterization of as-prepared yttria-stabilized hafnia

The as-prepared powder was crystallized with cubic fluorite structure. No structural evolution with time (several months) was observed for the powder stored in air at room temperature.

The same TEM examination technique described for pure hafnia was used and shows an as-prepared powder extremely fine with particle size ≈ 6 nm (Fig. 5). As noted earlier, the particle size of the as-prepared powder of pure hafnia was ≈ 20 nm. Addition of Y_2O_3 to HfO_2 for the studied composition leads to stabilize hafnia (cubic structure) and also to a reduction in the particle size of the powder.

Similar results were reported for calcia-stabilized zirconia compared with pure zirconia synthesized by the mixed liquid technique [14].

4.2. Thermal behaviour

Ultrafine as-prepared HfO_2 -8 mol % Y_2O_3 powder after cold-pressing (3 t cm^{-2}) was heated for 15 h at various temperatures up to 1700°C . The X-ray diffraction pattern of products showed that the cubic fluorite structure was retained up to 600°C . Above this temperature a cubic \rightarrow monoclinic phase transformation has progressively occurred in the material. The amount of cubic phase decreased as the temperature increased, indicating that the cubic phase is metastable. At 1200°C , both monoclinic and cubic forms were in nearly equal amounts. A reverse behaviour occurred at 1500°C from monoclinic to cubic phase. This trend became more marked with increased temperature and at 1650°C only cubic HfO_2 was noted. This phase was retained during cooling to room temperature and recycling of the same sample, indicating a complete state of equilibrium for the studied composition over the temperature range investigated.

The structural evolution of yttria (8 mol %)-stabilized hafnia with temperature is summarized in Fig. 6.

Particle-size evolution of this material with temperature was analysed by TEM. The as-prepared powder was extremely fine ($\approx 6 \text{ nm}$). After heat treatment at 900°C , an average particle size of 30–50 nm was observed (Fig. 7) with a tendency to agglomerate. Examination by SEM of fresh fractures of sintered bodies revealed a fine-grained microstructure with particle size of 80, 100, 300 nm at 1200, 1500, 1580°C , respectively, and at 1650°C an average grain size of 1–3 μm .

The particle size increases with a more or less linear dependence up to 1500°C ; above this temperature the increase is higher but the grain size remains on a micrometre scale. It can be noted (Fig. 8) that internal porosity is absent in the grains and weak on the grain boundaries.

5. Discussion

It was interesting for this powder composition to compare the material obtained by solid-state reaction at relatively low temperature with that prepared by hydrolytic decomposition of alkoxides [15]. Particle sizes from both techniques were ultrafine ($< 10 \text{ nm}$). However, the solid-state reaction at relatively low temperature is easy to carry out and uses classic and cheap components. The ultrafine as-prepared powder, having a high reactivity, will improve the reaction conditions during further heat treatments and will lead to uniformity and homogeneity of the material and so improved properties. The product from hydrolytic decomposition of alkoxides was amorphous, like pure hafnia prepared from the same way. Above 480°C , powder was progressively crystallized in a cubic structure. As the temperature was increased to 1100°C , the amount of cubic phase decreased, indicating a metastability for this form, whereas a higher concentration of monoclinic form was observed up to 1300°C . However, this later began to diminish rapidly when the temperature reached $\approx 1500^\circ\text{C}$. At the same time, stable cubic phase grew and at $\approx 1650^\circ\text{C}$ only this phase was observed. Thus, the technique

TABLE III Thermal evolution of yttria (8 mol %)-stabilized hafnia synthesized from the alkoxide route and solid-state reaction at relatively low temperature

Alkoxide method	Solid-state reaction at relatively low temperature
As-prepared: amorphous	As-prepared: crystallized metastable cubic phase (cfc)
480°C : metastable cubic phase (cfc) (beginning)	
1100 – 1300°C : metastable cubic + monoclinic phases	1200°C : metastable cubic + monoclinic phases
1650°C : stable cubic phase (cfc)	$> 1650^\circ\text{C}$: stable cubic phase (cfc)

based on hydrolytic decomposition of alkoxides leads to an initially amorphous powder being obtained. On the other hand, the solid-state reaction at relatively low temperature and from phosphate yields a crystallized initial product (metastable cubic form). Further thermal evolution of powders synthesized from both techniques was similar, and the same sequence of phases (metastable cubic \rightarrow monoclinic \rightarrow stable cubic) was observed.

Table III shows the thermal evolution of yttria (8 mol %)-stabilized hafnia prepared by these methods.

6. Conclusions

Ultrafine ($< 20 \text{ nm}$), highly reactive powders of pure and yttria (8 mol %)-stabilized hafnia have been synthesized at relatively low temperature (500°C) by solid-state reaction between standard coarse-grained powders (1–3 μm) of sodium metaphosphate (NaPO_3) and Na_2HfO_3 compound. The as-prepared powders were crystalline (cubic fluorite structure). Further heat treatments up to 1650°C induced a structural evolution of the materials with the sequence of phases: metastable cubic \rightarrow monoclinic for pure hafnia, and metastable cubic \rightarrow monoclinic \rightarrow stable cubic for yttria-stabilized hafnia. The particle size of products after cold-pressing and sintering remained on a micrometre scale even after heating to 1650°C and their microstructures were homogeneous. Stable cubic HfO_2 with Y_2O_3 (8 mol %) addition was obtained at a not too high temperature (1650°C). This solid-state reaction process is attractive to convert, at relatively low temperature, a standard coarse-grained powder into ultrafine one, which is highly reactive and homogeneous and which will be a promising starting material to prepare "high-tech" ceramics. Another advantage of this process is the use of classic, cheap and easy to synthesize reaction components.

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*Received 22 June 1993
and accepted 17 August 1994*