JOURNAL OF MATERIALS SCIENCE 30 (1995) 1495–1499

Preparation of tetragonal ZrO_2–Gd_2O_3 powders

S. BHATTACHARYYA, D.C. AGRAWAL
Materials Science Programme, Indian Institute of Technology, Kanpur 208016, India

ZrO_2–Gd_2O_3 alloys containing 2, 3, 5 and 8 mol. % Gd_2O_3 have been prepared by mixed oxide (MO), hybrid sol–gel (SG), and co-precipitation (CP) routes. No tetragonal (t) phase is retained in the MO method, while 100% t phase is obtained in the calcined CP samples; the SG method leads to only partial stabilization of the t phase. Washing of the CP powders with propan-2-ol leads to unagglomerated powders with increased specific surface area (145 versus 89 $m^2 g^{-1}$) and sintered density (98% versus 79%). Cubic and t′ phase also appear on sintering the samples with > 2 mol. % Gd_2O_3.

1. Introduction

Zirconia ceramics, consisting mainly of tetragonal zirconia polycrystals (TZP), partially stabilized zirconia (PSZ) and zirconia toughened alumina (ZTA), are technologically important primarily because of their exceptionally high values of fracture toughness. The major contribution to the enhanced fracture toughness is believed to come from the tetragonal to monoclinic (t → m) transformation that occurs in the stress field of a propagating crack. The t phase in pure zirconia is not stable at room temperature except when the particle size is extremely small (30 nm). It can be stabilized in particles of larger sizes by alloying ZrO_2 with Y_2O_3, CeO_2 etc. Most of the commercial materials use MgO, CaO and Y_2O_3 as the stabilizing oxides [1]; CeO_2 is also used to a large extent. However in each of these cases certain problems exist. Thus Ca–PSZ [2, 3] and Mg–PSZ [4, 5] require sintering at high temperatures (in the cubic phase field) followed by thermal treatments to optimize the mechanical properties. Y–TZP suffers from property degradation at low temperature (in humid atmosphere) [6] as well as at high temperatures [7]. Ce–TZP has poor sinterability [8], so either high sintering temperature (1600 °C) [9] or hot-pressing is needed; however properties may degrade due to Ce^{4+}/Ce^{3+} reduction during hot-pressing [10]. Because of these difficulties the search for alternate stabilizers has continued. More attention is being devoted to the use of rare earth oxides such as Yb_2O_3 [11], Er_2O_3 [12], Gd_2O_3 [13] as alloying additives to ZrO_2. Of these the effect of Gd_2O_3 on the phase and properties of ZrO_2 has been studied to a very limited extent. Van Dijk *et al.* [13] prepared ZrO_2–Gd_2O_3 solid electrolytes and measured their electrical conductivity. Similar studies have also been reported by Moztarzadeh [14] and Kang *et al.* [15]. Michel *et al.* [16] prepared Gd_2O_3 doped tetragonal zirconia single crystal by skull melting and Leung *et al.* [17] studied the high temperature phase partitioning in ZrO_2–Gd_2O_3 system prepared from aqueous precursors.

The phases obtained in the mixed oxide systems are heavily dependent on the methods of preparation due to slow achievement of equilibrium. In fact, the zirconia toughened ceramic materials used in technology are rarely at equilibrium. Keeping this in view, in the present work ZrO_2 alloyed with Gd_2O_3 has been prepared by three different methods and the sinterability and the extent of stabilization obtained have been studied.

2. Experimental Procedure

2.1. Preparation of ZrO_2–Gd_2O_3 powders

Three different routes, hybrid sol–gel, mixed oxide and co-precipitation, were employed to prepare ZrO_2–Gd_2O_3 gel or powder. The concentration of Gd_2O_3 was 2, 3, 5 and 8 mol. % for the hybrid sol–gel and the co-precipitation routes and 5 mol. % only for the mixed oxide route. The preparation schemes for all the three methods are described below.

2.1.1. Hybrid sol–gel route

In this route the precursors used were zirconium-*n*-propoxide (zr-n-p) (Alfa Products, Danvers, USA), Gd_2O_3 (Indian Rare Earths Ltd., Kerala), acetic acid (S.D. Fine Chemicals, Boisar, India), diethanolamine (Ranbaxy Laboratories, Bombay, India), and propan-2-ol (S.D. Fine Chemicals, Boisar, India). A clear sol was prepared using zr-n-p, propan-2-ol, acetic acid, and diethanolamine in the molar ratio 1:20.8:0.014:0.75. The sol was stirred for 20 min followed by the addition of Gd_2O_3. The mixed sol was further stirred for 30 min after which it was gelled by adding triple distilled water in the ratio zr-n-p:H_2O = 1:0.3. The gel was dried at 100 °C for 24 h. The dried gel was lightly ground and calcined in air at 700 °C for 4 h. The calcined powders were uniaxially compacted at 200 MPa into cylindrical pellets (10 mm ϕ, 3 mm high). The pellets were sintered in air at 1400 °C for 2 h.

0022–2461

2.1.2. Mixed oxide route

In this route, ZrO_2 (Aldrich Chemical Co., UK) and Gd_2O_3 were mixed and ball milled in propan-2-ol medium using alumina balls. The ball milled powder was dried at 100 °C for 24 h, lightly compacted into cylindrical pellets (pressure <40 MPa) and calcined at 1000 °C for 2 or 8 h.

2.1.3. Co-precipitation route

Zr-n-p was dissolved in a mixture of propan-2-ol and diethanolamine. Gd_2O_3 was introduced as $Gd(NO_3)_3 \cdot 6H_2O$ solution in propan-2-ol. Acetic acid (0.014 mol/mol of zr-n-p) was added to retard the hydrolysis of zr-n-p through the formation of a complex [18]. The resultant clear sol was then added in a drop-wise manner to triple distilled water (H_2O/zr-n-p (v/v) = 500) whereby partial hydrolysis of zr-n-p took place. The complete precipitation of $Zr(OH)_4$ and $Gd(OH)_3$ took place upon adding NH_4OH while stirring. The pH of the solution was always kept above 10.2 to ensure complete precipitation of Zr and Gd hydroxides.

The gelatinous precipitate was stirred for 24 h, allowed to settle and the solvent was filtered off. The precipitate was washed five times with triple distilled water using 750 ml of distilled water for each washing. The precipitate was then divided into two parts: one part was dried as such at 100 °C for 24 h. The other part was further washed with propan-2-ol five times using 300 ml of propan-2-ol for each washing. This precipitate was dried at 80 °C for 24 h. Both the precipitates were calcined in air at 700 °C for 4 h and were uniaxially compacted at 200 MPa into cylindrical pellets (10 mm ϕ, 3 mm high). The sintering was carried out either at 1400 °C for 2 h or at 1600 °C 1 h.

2.2. Characterization

Specific surface area of the washed powders was obtained using a surface area analyser (Quantachrome Corp., UK). Phases in the calcined and sintered samples were determined by X-ray diffraction (XRD) (Rich Seifert Isodebyeflex 2002, Germany). Fourier transform infrared spectroscopy (FTIR) (Perkin Elmer, UK) was carried out on washed powders. Powders were also observed in a transmission electron microscope (TEM) (Model EM 301, Philips) to determine their degree of agglomeration. Density of the sintered samples was determined by Archimedes' method.

3. Results and discussion

3.1. Phase identification

Fig. 1 shows the X-ray diffractograms of the calcined and sintered samples of ZrO_2–2 mol. % Gd_2O_3 made by hybrid sol–gel route. Both the monoclinic (m) and tetragonal (t) phases are present. The fraction of the m phase was calculated from the X-ray peak intensities using the relation [19]

$$X_m = \frac{I_m(1\,1\,\bar{1}) + I_m(1\,1\,1)}{I_m(1\,1\,\bar{1}) + I_m(1\,1\,1) + I_t(1\,1\,1)} \qquad (1)$$

and

$$v_m = \frac{PX_m}{1 + (P - 1)X_m} \qquad (2)$$

where, X_m is the integrated peak intensity ratio, $P = 1.314$ [20] and v_m is the volume fraction of m phase.

Table I lists the volume% of tetragonal, monoclinic and cubic phases in the calcined and sintered samples for all the three processes. The calcined samples from

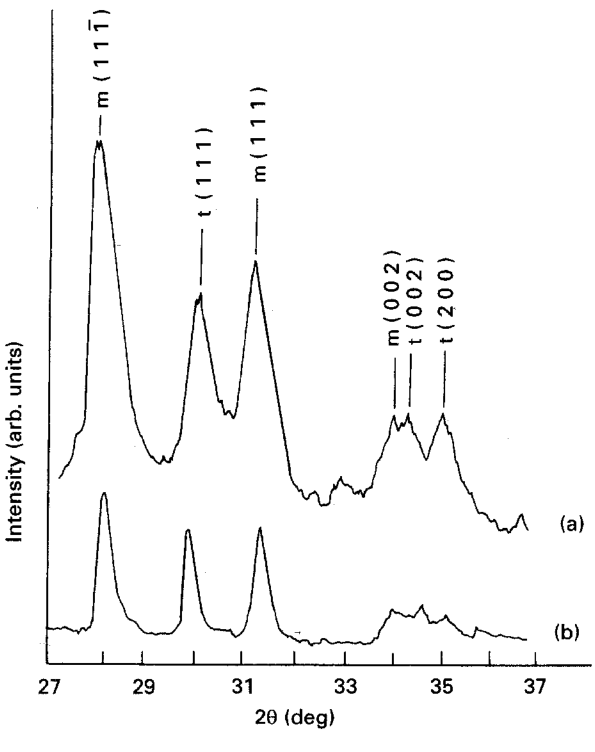

Figure 1 X-ray diffractogram of ZrO_2–2 mol. % Gd_2O_3 prepared by hybrid sol–gel route, (a) calcined (700 °C/4 h), (b) sintered (1400 °C/2 h); the m phase decreases on sintering.

TABLE I Volume% (t + c) phase in the calcined and sintered samples prepared by different methods

	Volume % (t + c) phase				
	Calcined powder			Sintered pellet	
Composition (mol. % Gd_2O_3)	SG route (700 °C/4 h)	MO route (1000 °C/8 h)	CP route (700 °C/4 h)	SG route (1400 °C/2 h)	CP route (1400 °C/2 h)
2	22	0	100	25	100
3	26	0	100	35	100
5	52	0	100	55	100
8	62	0	100	87	100

the hybrid sol–gel route contain both m and t phases. The m phase is present even in the samples with 8 mol. % Gd_2O_3. It has been reported [16, 17] that only 3 mol. % Gd_2O_3 is needed for complete stabilization of t phase. Hence under the calcination conditions used here, all Gd_2O_3 does not go into solution in ZrO_2. This is confirmed by the observed increase in the amount of t phase in the sintered samples.

The samples prepared by the mixed oxide route do not show any t phase after calcination at 1000 °C for 2 h. As this method involves reaction between two crystalline compounds, it is expected that high calcination temperature and longer time would be needed. However even after 8 h at 1000 °C no tetragonal phase was obtained in the calcined samples.

Of the three methods employed, only the co-precipitation route leads to complete stabilization of the t phase for all (2–8 mol. %) Gd_2O_3 contents. X-ray diffractograms of the calcined samples prepared from this method are shown in Fig. 2. In the sintered samples only the 2 mol. % composition is fully tetragonal; the samples with 3, 5 and 8 mol. % Gd_2O_3 have t′ and cubic phases also (Fig. 3).

In the ZrO_2–Gd_2O_3 system, it is known that a tetragonal phase with nonequilibrium concentration of Gd_2O_3 forms first followed by the formation of cubic phase with much higher Gd_2O_3. The Gd_2O_3 partitions between t and c phases [17]. Formation of t′ phase has not been reported but the existence of sharp, distinct peaks in the X-ray diffractograms support the formation of t′ phase in our samples.

3.2. Density

A high sintered density is required for use of ZrO_2 ceramics as structural material, solid electrolytes or oxygen sensors etc. However, the sintered samples from the hybrid sol–gel route as well as co-precipitation route have poor density; a maximum relative density of 0.79 was obtained for ZrO_2–3 mol. % Gd_2O_3 (Fig. 4a); the relative density drops to 0.6 for 5 mol. % Gd_2O_3, reasons for which are not understood. Sintering these samples at a high temperature (1600 °C) does not help; on the other hand it reduces the tetragonal phase to about 12% and some zirconate phase also forms (Fig. 5). It is well known that the presence of hard agglomerates in the green powder results in differential sintering and hence poor sintered density [21, 22]. These hard agglomerates in powders prepared from wet synthesis methods form in the drying stage due to the formation of strong Zr–O–Zr bonds [23]. One way to remove this bond is to wash the powder with non-polar solvents like alcohol, benzene etc. which results in the replacement of OH^- groups by organic group (e.g. ethoxy groups in case of washing by ethyl alcohol). These organic groups prevent the formation of strong Zr–O–Zr bonds during

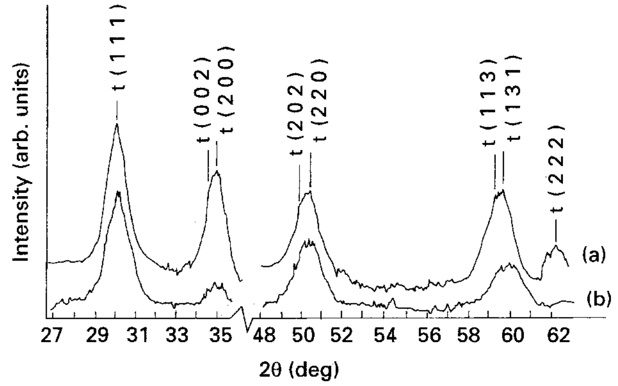

Figure 2 X-ray diffractogram of the calcined sample prepared by co-precipitation route showing only t phase, (a) ZrO_2–2 mol. % Gd_2O_3, (b) ZrO_2–3 mol. % Gd_2O_3.

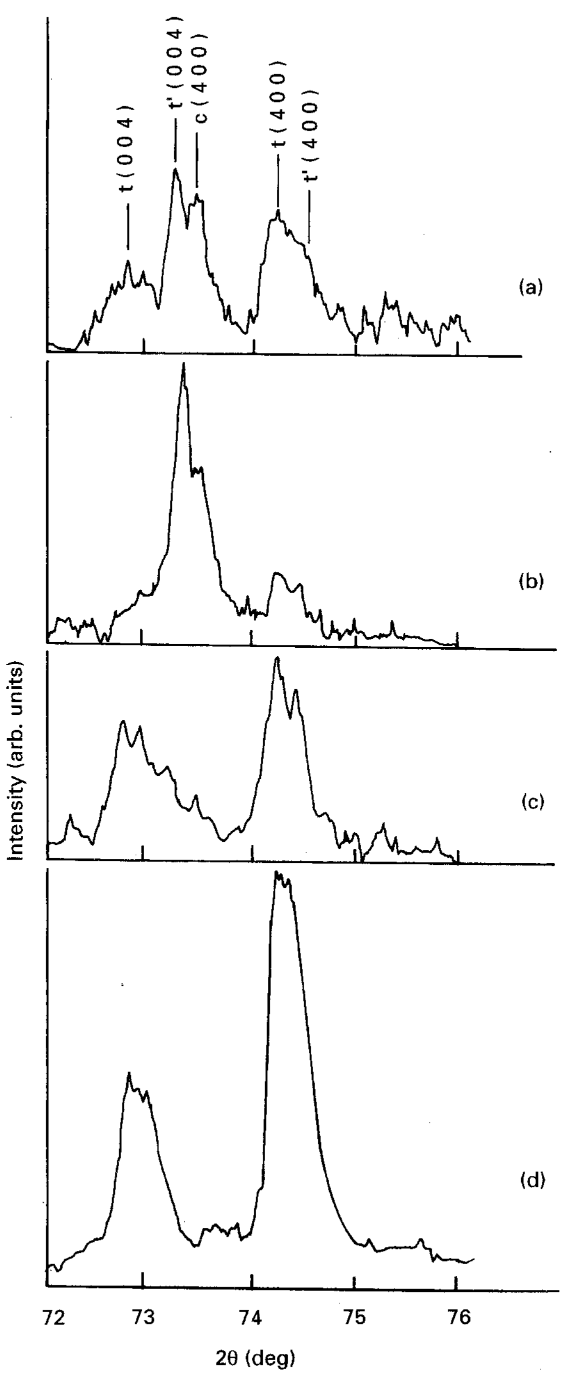

Figure 3 X-ray diffractogram of the sintered ZrO_2–Gd_2O_3 samples prepared by CP route and having different amounts of Gd_2O_3, (a) 8 mol. %, (b) 5 mol. %, (c) 3 mol. % and (d) 2 mol. %; single phase t is obtained only in (d); with higher Gd_2O_3 c and t′ phases also appear.

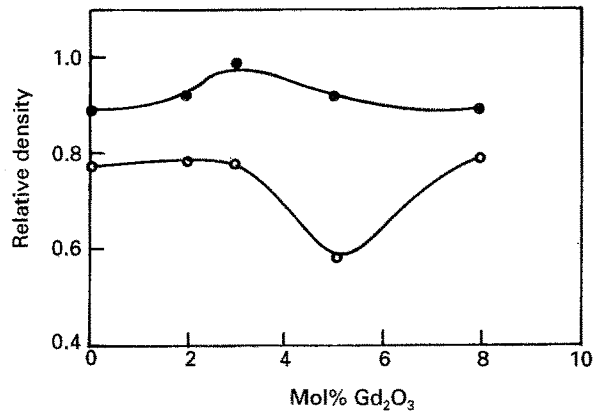

Figure 4 Variation of relative density with the amount of Gd_2O_3 (a) ○, water washed powder, (b) ●, propan-2-ol washed powder.

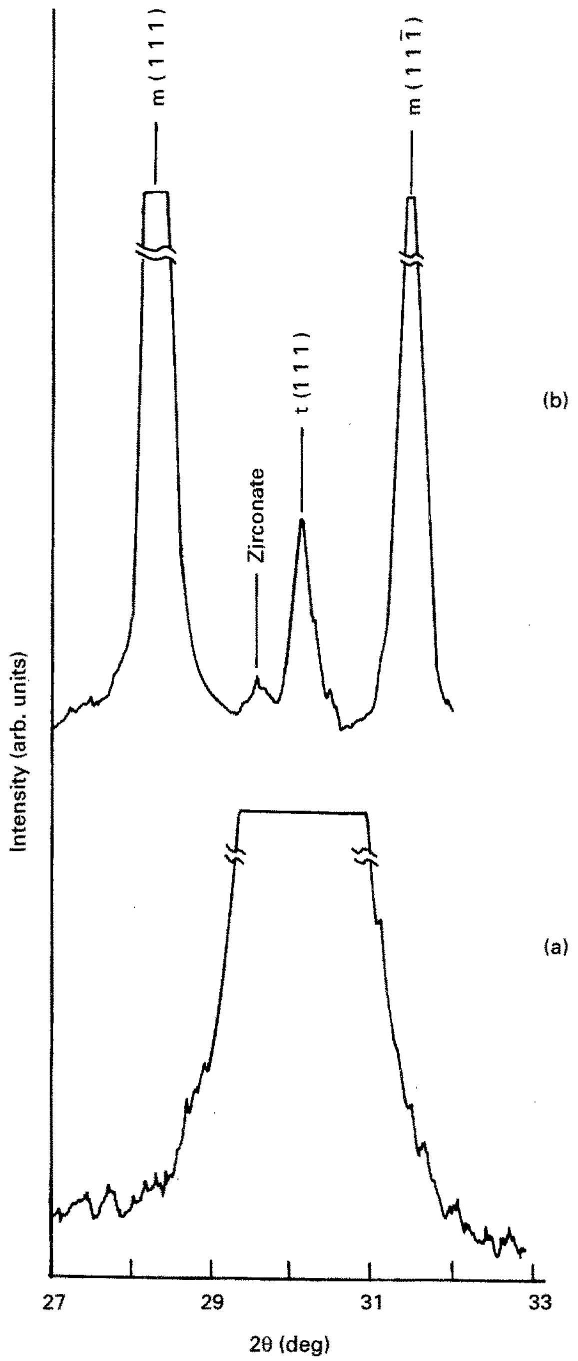

Figure 5 X-ray diffractogram of ZrO_2–2 mol. % Gd_2O_3; (a) calcined at 700 °C for 4 h showing only t phase, (b) sintered at 1600 °C for 1 h showing t, m and zirconate phase. The volume% of t phase decreases to 12% after sintering.

subsequent drying. The solvents generally used are benzene [24], hydrogen peroxide [25], acetone–toluene–acetone [26], alcohol [27] etc. In the present case, the co-precipitated powder was washed with water (to remove excess NH_4OH), followed by propan-2-ol (to remove excess water). Washing with propan-2-ol leads to a very significant increase in the sintered density – a relative density of as high as 0.98 is obtained in the 3 mol. % Gd_2O_3; and for other compositions also it is significantly higher (90%) than that obtained from water washed samples (Fig. 4b). Due to the presence of the propoxy group on the surface of the propan-2-ol washed powders, formation of hard agglomerates is avoided. The FTIR spectra of water washed and alcohol washed powders are shown in Fig. 6. The extensive interaction of the powder with propan-2-ol is shown by the bands at 1070 cm^{-1} due to C–O stretching from the chemically adsorbed propan-2-ol (Fig. 6b); the bands at 923 and 845 cm^{-1} appear to be due to C–O stretching from the physically adsorbed excess propan-2-ol. The broad peak at 3383 cm^{-1} is due to OH^- from the alcohol. This band is also present in the water washed sample (Fig. 6a). It is believed that similar to the case of ethanol washed hydrous ZrO_2 studied by Kaliszewski and Heuer [23], the hydroxyl groups on ZrO_2 in the present case get replaced by propoxy groups during propan-2-ol washing which prevent the formation of Zr–O–Zr bonds and hence agglomeration, during subsequent drying. Absence of hard agglomerates results in higher sintered densities [23]. The specific surface area for the water washed powder was 85 $m^2 g^{-1}$ while it was 147 $m^2 g^{-1}$ for the propan-2-ol washed powder, indicating that the agglomerations are reduced by propan-2-ol washing.

The TEM pictures of the water washed and propan-2-ol washed powders show distinctly different agglomeration behaviour. While water washed powders show large agglomerated crystallites (Fig. 7a), propan-2-ol washed powders show loose or separated crystallites (Fig. 7b). This indicates that propan-2-ol washing produces soft agglomerates which can be easily broken.

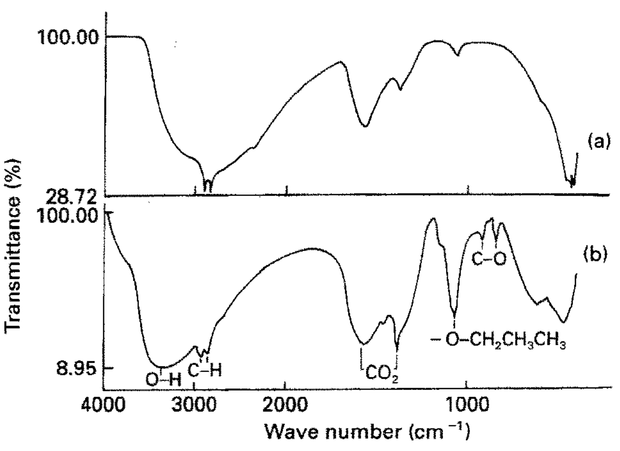

Figure 6 FTIR spectra of (a) water washed powder, (b) propan-2-ol washed powder. The latter figure shows the formation of propoxy groups on the surface of powder as a result of washing.

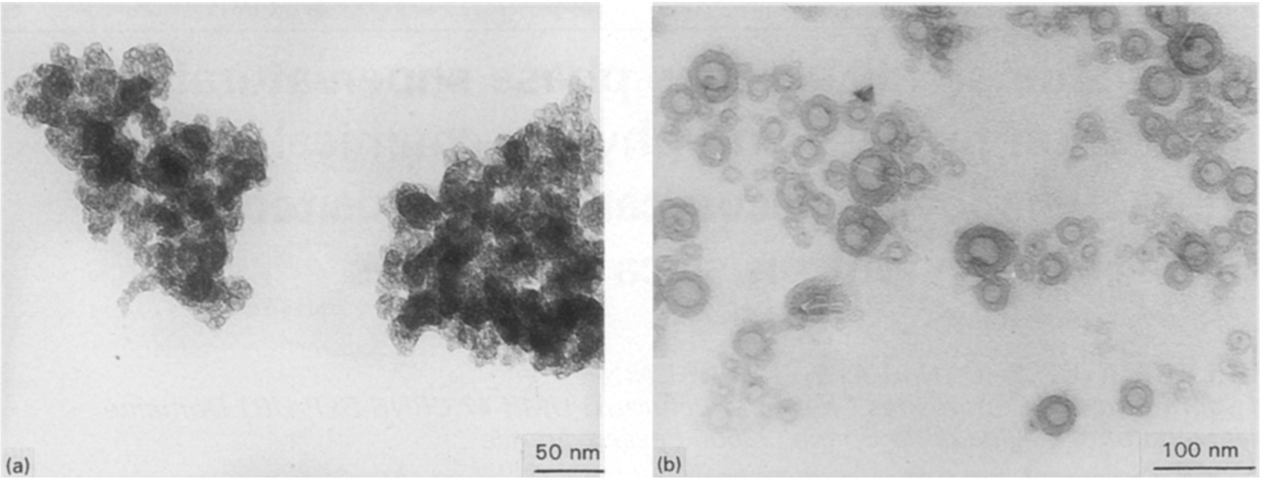

Figure 7 Transmission electron micrographs of (a) water washed powder, (b) propan-2-ol washed powder. The propan-2-ol washed powder shows loose crystallites as compared to water washed powder.

4. Conclusions

From the present study the following can be concluded:

(1) Gd_2O_3 acts to stabilize the tetragonal phase in ZrO_2.
(2) The co-precipitation route is efficient in retaining 100% tetragonal phase in the sintered samples.
(3) In the composition range studied, only ZrO_2–2 mol. % Gd_2O_3 has pure tetragonal phase in the sintered samples. The sintered samples of the other compositions, 3, 5 and 8 mol. % Gd_2O_3, have t′ and c phases besides the t phase. The calcined samples of these compositions have also broad peaks, which indicate that t′ and c phase may also be present after calcination.
(4) The water washed powders have hard agglomerates due to the formation of Zr–O–Zr bonds resulting from the removal of surface OH^- groups during drying of these powders. The presence of these hard agglomerates results in poor sintered density. Washing with propan-2-ol removes these terminal OH^- groups and replaces them with propoxy groups. These groups being non-terminal produce soft agglomerates, which improve densification.

References

1. D. J. GREEN, R. H. J. HANNINK and M. V. SWAIN, in "Transformation Toughening of Ceramics" (CRC Press Inc., 1989) pp. 41.
2. R. H. J. HANNINK, K. A. JOHNSTON, R. T. PASCOE and R. C. GARVIE, in "Advances in Ceramics", Vol. 3 (The American Ceramic Society, Cleveland, 1981) pp. 116.
3. R. M. DICKERSON, M. V. SWAIN and A. H. HEUER, *J. Am. Ceram. Soc.* **70** (1987) 214.
4. R. R. HUGHAN and R. H. J. HANNINK, *J. Am. Ceram. Soc.* **69** (1986) 556.
5. R. R. LEE and A. H. HEUER, *J. Am. Ceram. Soc.* **70** (1987) 208.
6. T. SATO and M. SHIMADA, *J. Am. Ceram. Soc.* **68** (1985) 356.
7. R. H. J. HANNINK, *J. Mater. Sci.* **18** (1983) 457.
8. S. B. BHADURI, A. CHAKRABORTY and R. MOHAN RAO, *J. Am. Ceram. Soc.* **71** (1988) C-410.
9. K. TSUKUMA and M. SHIMADA, *J. Mater. Sci.* **20** (1985) 1178.
10. S. MASCHIO, E. BISCHOFF, O. SBAIZERO and S. MERIANI, in "Zirconia 88", Advances in Science and Technology of Zirconia (Elsevier Applied Science, London, 1989) pp. 171.
11. M. GONZÁLEZ, C. MOURE, J. R. JURADO and P. DURAN, in "Euro-Ceramics" Vol. 1 (Elsevier Applied Science, London, 1989) pp. 2.325.
12. P. DURAN, P. RECIO, J. R. JURADO, C. PASCUAL and C. MOÜRE, *J. Am. Ceram. Soc.* **72** (1989) 2088.
13. T. VAN DIJK and A. J. BURGGRAFF, *Phys. Status Solidi A* **58** (1980) 115.
14. F. MOZTARZADEH, in "Advances in Ceramics", Vol. 24B (The American Ceramic Society, Cleveland, Ohio, 1986) pp. 901.
15. T. K. KANG, T. NAGASAKI, N. IGAWA, K. I. HIUN and H. OHNO, *J. Am. Ceram. Soc.* **75** (1992) 2297.
16. D. MICHEL, L. MAZEROLLES and M. PEREZ. Y. JORBA, *J. Mater. Sci.* **18** (1983) 2618.
17. D. K. LEUNG, C. J. CHAN, M. RÛHLE and F. F. LANGE, *J. Am. Ceram. Soc.* **74** (1991) 2786.
18. G. YI and M. SAYER, *Am. Ceram. Soc. Bull.* **70** (1991) 1173.
19. H. TORAYA, M. YOSHIMURA and S. SOMIYA, *J. Am. Ceram. Soc.* **67** (1984) C-119.
20. H. K. SCHMID, *J. Am. Ceram. Soc.* **70** (1987) 367.
21. T. VASILOS and W. H. RHODES, in "Ultrafine-Grain Ceramics" (Syracuse University Press, 1970) pp. 137.
22. F. F. LANGE and B. I. DAVIS, in "Advances in Ceramics", Vol. 12 (The American Ceramic Society, Cleveland, Ohio, 1983) pp. 699.
23. M. H. KALISZEWSKI and A. H. HEUER, *J. Am. Ceram. Soc.* **73** (1990) 1504.
24. K. S. MAZDIYASNI, C. T. LYNCH and J. S. SMITH, *J. Am. Ceram. Soc.* **48** (1965) 372.
25. M. A. C. G. VAN de GRAFF and A. J. BURGRAFF, in "Advances in Ceramics", Vol. 12 (The American Ceramic Society, Cleveland, Ohio, 1983) pp. 281.
26. R. GOPALAKRISHNAN, T. KOSMAC, V. KRASEVEC and M. KOMAC, in "Sintering '85" (Plenum Press, New York, 1987) pp. 281.
27. C. E. SCOTT and J. S. REED, *Am. Ceram. Soc. Bull.* **58** (1979) 587.

Received 22 October 1993
and accepted 5 September 1994