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Powder Preparation, Mechanical and Electrical Properties of Cubic Zirconia Ceramics

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Abstract

Cubic zirconia ceramics, doped either with 8 mol% Y_2O_3 or with 12 mol% MgO and CaO, were prepared from precursor material obtained via co-precipitation with ammonia from aqueous metal chloride solutions. Precipitation experiments with and without the addition of surfactant were carried out. Different methods of drying were employed followed by calcination and attrition steps to obtain oxidic precursors. The powders were characterized by particle size distribution, scanning electron microscopy and specific surface areas. Following isostatic compaction the oxide powders were sintered at 1600 and 1700°C for 4 h. The effects of the powder characteristics and the drying procedures on the mechanical properties of the sintered bodies were investigated.

1 Introduction

Pure zirconia is known to have three polymorphs under atmospheric pressure, with monoclinic, tetragonal and cubic symmetry. The cubic and tetragonal forms are unstable at room temperature. The temperature range of the stability of these phases, however, can be lowered by doping zirconia with other oxides, such as Y_2O_3, CaO or MgO.[1-3] The content of the dopants determines whether the tetragonal or the cubic phase will be stabilized.

Cubic zirconia doped either with Y_2O_3, MgO or CaO is found to have a rather low bend strength.[4-6] The mechanical properties of the sintered ceramics, however, depend strongly on the powder characteristics, such as particle size and particle size distribution, and on the morphology as well as agglomeration of the starting oxides[7] and on the thermal treatment.[8] Different ways to co-precipitate doped amorphous hydroxide precursors, various drying procedures as well as attrition milling of the calcined oxides have been investigated in this study to learn about the effects of the powder characteristics and sintering procedures on the mechanical properties of cubic zirconia.

Zirconia with fluorite structure exhibits considerable electrical conductivity at elevated temperatures[9-15] due to the migration of oxygen vacancies introduced by the stabilizers. The specific conductivities and the temperature dependences of the conductivities will be reported.

2 Experimental Procedure

2.1 Sample preparation

Aqueous solutions of $ZrOCl_2{\cdot}8H_2O$ (Merck, Germany) (0·2 mol dm^{-3}) containing the appropriate amounts of $Y(NO_3)_3{\cdot}5H_2O$, $MgCl_2{\cdot}6H_2O$ and $CaCl_2{\cdot}2H_2O$ (all from Merck) were prepared. In some experiments sodium laurylsulfate (0·05 g dm^{-3}) was added to both the metal salt solutions and to the aqueous ammonia. The co-precipitation process was carried out by spraying the aqueous metal salt solutions into vigorously stirred concentrated ammonia solutions. The pH was kept above 10 during the precipitation by adding excess amounts of ammonia solution. Stirring was continued for 1 h after spraying was completed. The co-precipitated hydroxides were then filtered and washed with distilled water until no Cl^- ion was present in the filtrate. Further powder treatments were carried out as follows: (i) hydroxides prepared in the presence of sodium laurylsulfate were either spray dried or washed with ethanol and dried at 100°C in air, (ii) hydroxides made by co-precipitation without adding sodium laurylsulfate were washed with ethanol and dried at 100°C in air. All hydroxides were calcined at 750°C for 2 h. The spray-dried hydroxides were used as

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obtained from the calcination. The calcined oxide powders from the other preparation techniques were attrited in 1-propanol for 4 h with zirconia balls (2 mm diameter, 1000 min^{-1}).

Pellets (10 mm diameter × 4 mm height) and blocks (25 × 20 × 40 mm) were compacted isostatically at 70 MPa. The blocks for bend strength measurements were presintered at 1000°C for 1 h and cut to a geometry of 4 × 5 × 30 mm. The specimens were then sintered at 1600°C and 1700°C, respectively, for 4 h. The heating rate was 5°C min^{-1} until 1200°C and 3°C min^{-1} up to the final sintering temperature. The sintered bodies were then ground to the respective dimensions and diamond polished to a 3 μm finish on the tensile surface. The edges of the tensile surfaces were chamfered. Density, three-point bend strengths, Vickers hardness and fracture toughness were measured from the ceramic specimens. Etching was performed in potassium hydrogensulfate melts at 250°C for 10 min.

2.2 Characterization

The doped zirconia powders were investigated by X-ray diffraction (Rigaku D/max IIA, Japan) for the phase content. The particle sizes and particle size distributions were determined by a laser particle sizer (Coulter LS 130, USA), the specific surfaces were measured by BET on a Quantasorb system (Quantachrome, USA). The densities of the sintered specimens were measured by the means of Archimedes' principle in iso-octane (2,2,4-trimethylpentane). Theoretical densities were calculated following the theory of Ingel and Lewis[16] from the lattice parameters.[6,17,18] The Vickers hardness and fracture toughness were tested on the polished surfaces using a Vickers diamond indenter with a load (P) of 100 N. The K_{Ic} values were calculated as: $K_{Ic} = 0{\cdot}0824\ P\ c^{-3/2}$.[19–21] Three-point bend strengths were measured on 3 × 4 × 30 mm specimens with 20 mm span width, using six to 10 bars for each composition and sintering temperature. The load was increased by 12 N s^{-1}. Scanning electron micrographs of the specimen were made on a JEOL-JSM-T300A electron microscope (Jeol, Japan). Light microscopy studies were made on a Neovar-Pol microscope (Reichert, Austria). Grain sizes of the sintered bodies were obtained from the intercept technique. The crystallite sizes were calculated from the BET specific surface areas according to the formula:

$d = 6\ (\rho\ A_s)^{-1}$ (where d is crystallite size, A_s specific surface area and ρ theoretical density of the oxide). The electrical conductivities were measured by the d.c. four-probe technique between 380 and 1080°C. Contacts were made with platinum paint.

3 Results

3.1 X-ray diffraction

The dried hydroxide powders were amorphous according to X-ray diffraction; the calcined powders and the sintered bodies showed only the peaks of the cubic phase (Fig. 1). There was no observable phase transformation due to surface treatment (polishing) or upon fracture.

3.2 Powder characteristics

The average particle sizes, the specific surface areas and the calculated crystallite sizes are sum-

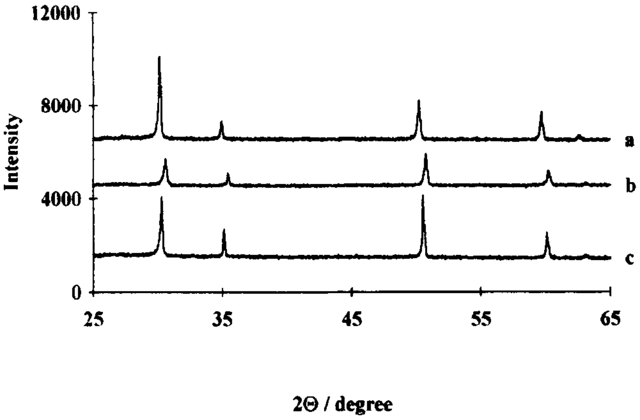

Fig. 1. X-ray diffraction of cubic zirconias sintered at 1700°C; (a) doped with 8 mol% Y_2O_3; (b) doped with 12 mol% MgO; (c) doped with 12 mol% CaO.

Table 1. Average particle sizes and specific surface areas of co-precipitated and calcined doped cubic zirconia powders[a]

Sample	Average particle size (vol. stat.) (μm)	Average particle size (number. st.) (μm)	Specific surface area ($m^2\ g^{-1}$)	Average crystallite size[b] (nm)
8Y[c]	19·5	1·85	–	–
8Y[d]	12·5	0·18	42·4	23·8
8Y[e]	2·0	0·18	49·9	20·2
8Y[f]	1·9	0·21	39·4	25·6
8Y[g]	0·7	0·17	48·2	20·9
12Mg[c]	26·6	2·83	–	–
12Mg[d]	8·9	0·19	26·8	37·4
12Mg[e]	8·6	0·18	46·5	21·6
12Mg[f]	2·8	0·24	30·8	32·6
12Mg[g]	0·6	0·16	45·5	22·0
12Ca[c]	24·1	1·95	–	–
12Ca[d]	7·5	0·18	43·7	23·2
12Ca[e]	5·1	0·18	26·9	37·6
12Ca[f]	1·9	0·24	39·0	26·0
12Ca[g]	0·7	0·17	53·8	18·8

[a] 8Y: doped with 8 mol% Y_2O_3, 12Mg: doped with 12 mol% MgO, 12Ca: doped with 12 mol% CaO.
[b] Calculated from the specific surface area.
[c] Co-precipitated without sodium laurylsulphate and calcined.
[d] Co-precipitated with sodium laurylsulphate and calcined.
[e] Co-precipitated with sodium laurylsulphate, spray dried and calcined.
[f] Co-precipitated without sodium laurylsulphate, calcined and attrited.
[g] Co-precipitated with sodium laurylsulphate, calcined and attrited.

marized in Table 1. The particle size distributions are shown in Figs 2–4. Precipitation without sodium laurylsulfate followed by calcination resulted in strongly agglomerated powders with average particle sizes of about 20–26 μm. Adding sodium laurylsulfate to the co-precipitation process yielded particle sizes around 7–13 μm. Spray drying of the co-precipitated hydroxides led to a reduction in the particle sizes, but hard agglomerates were subsequently formed during the calcination process. These hard agglomerates prevented proper densification during the sintering process. The spray-dried and calcined powders consisted of dense spheres of 2–5 μm diameter as shown in Fig. 5. All calcined powders with the exception of the spray-dried samples were attrited, leading to considerably smaller particle sizes. The attrited powders were rather homogeneous in particle size distribution as shown in Figs 6 and 7. The particles consisted of prime crystallites with diameters below 50 nm (Fig. 7) in agreement with crystallite diameters calculated from the specific surface areas (Table 1).

3.3 Density and grain size

Densities of the sintered bodies are summarized in Table 2. The relative densities of the specimens

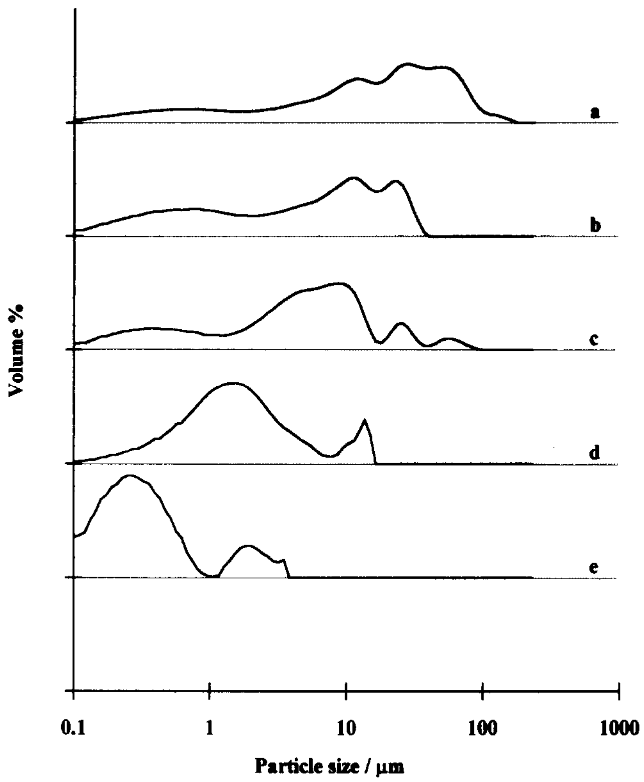

Fig. 3. Particle size distribution of zirconia powders doped with 12 mol% MgO: (a) co-precipitated without sodium laurylsulphate and calcined; (b) co-precipitated with sodium laurylsulphate and calcined; (c) co-precipitated with sodium laurylsulphate, spray dried and calcined; (d) co-precipitated without sodium laurylsulphate, calcined and attrited; (e) co-precipitated with sodium laurylsulphate, calcined and attrited.

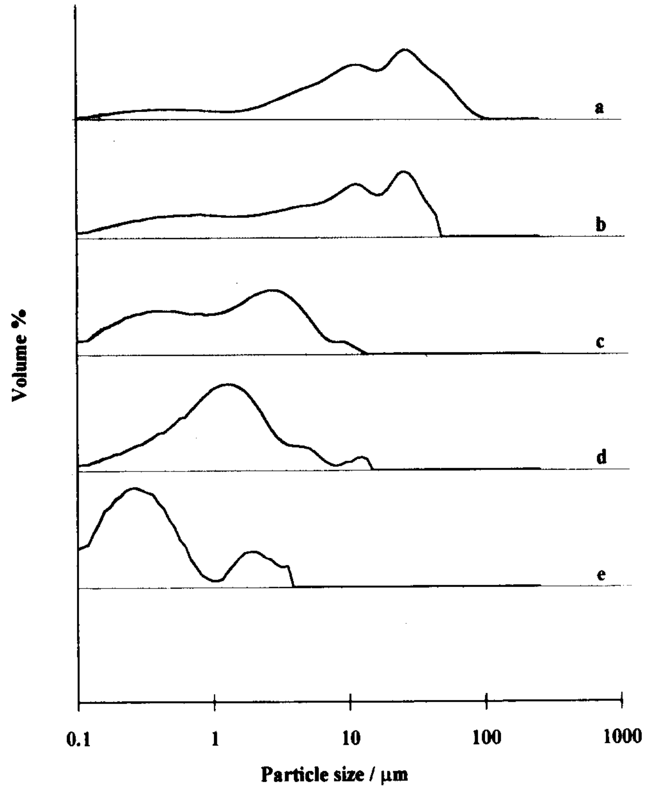

Fig. 2. Particle size distribution of zirconia powders doped with 8 mol% Y_2O_3: (a) co-precipitated without sodium laurylsulphate and calcined; (b) co-precipitated with sodium laurylsulphate and calcined; (c) co-precipitated with sodium laurylsulphate, spray dried and calcined; (d) co-precipitated without sodium laurylsulphate, calcined and attrited; (e) co-precipitated with sodium laurylsulphate, calcined and attrited.

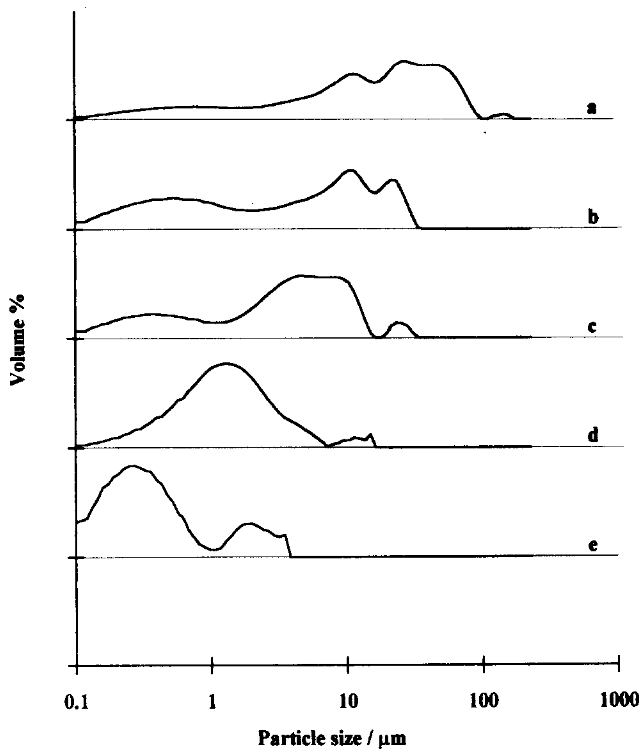

Fig. 4. Particle size distribution of zirconia powders doped with 12 mol% CaO: (a) co-precipitated without sodium laurylsulphate and calcined; (b) co-precipitated with sodium laurylsulphate and calcined; (c) co-precipitated with sodium laurylsulphate, spray dried and calcined; (d) co-precipitated without sodium laurylsulphate, calcined and attrited; (e) co-precipitated with sodium laurylsulphate, calcined and attrited.

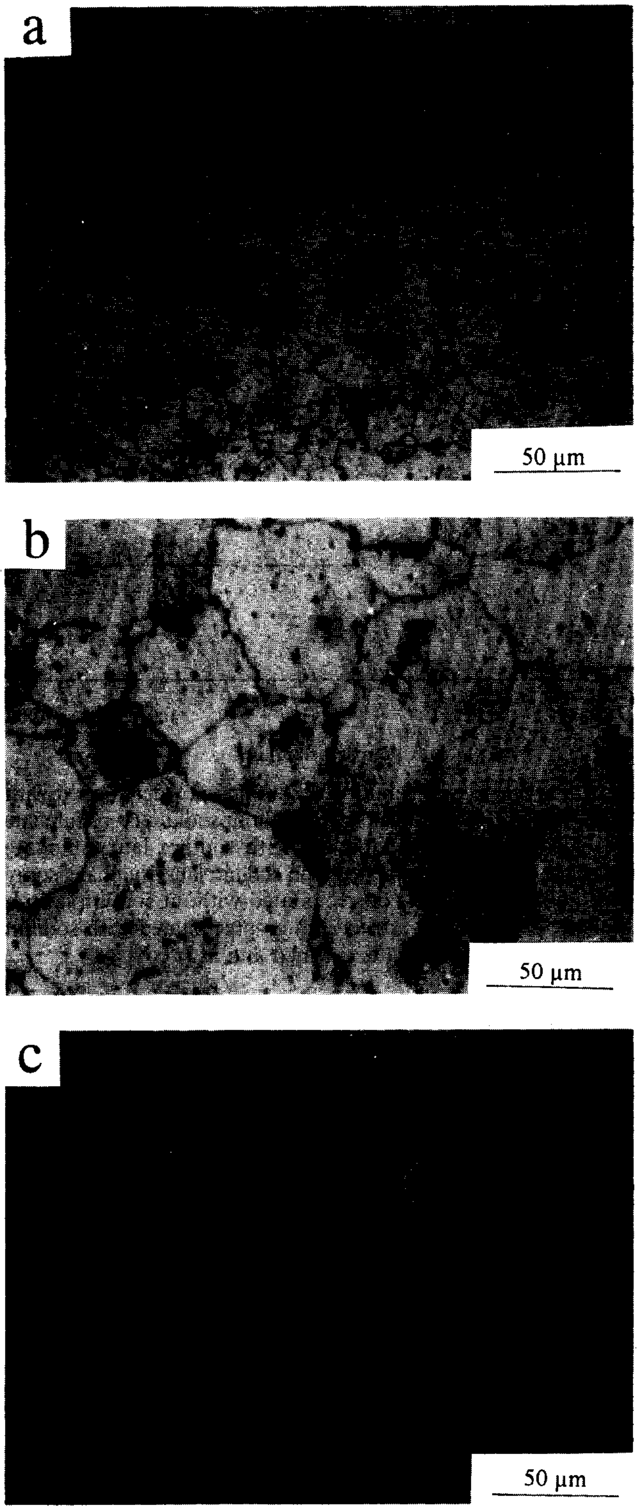

Fig. 5. Scanning electron micrographs of the calcined oxides from spray-dried hydroxides co-precipitated in the presence of sodium laurylsulphate. Magnification: 10 000×. (a) Doped with 8 mol% Y_2O_3; (b) doped with 12 mol% MgO; (c) doped with 12 mol% CaO.

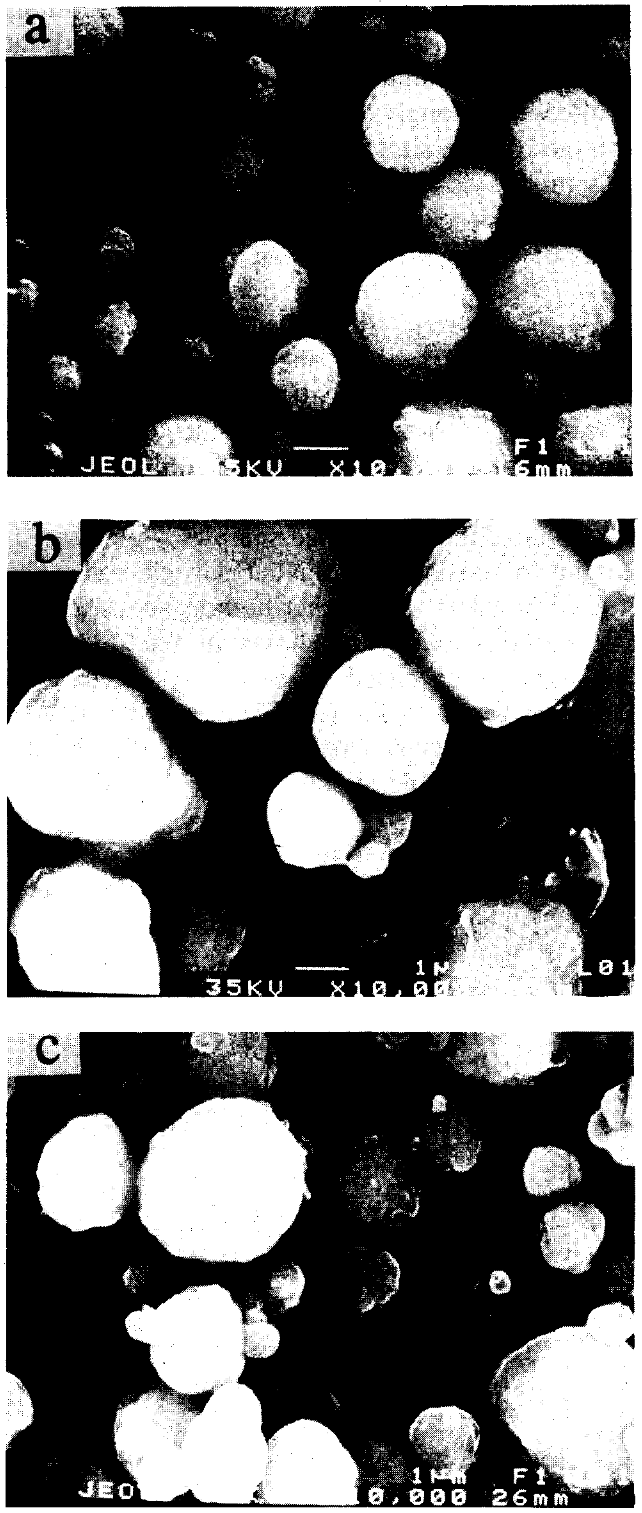

Fig. 6. Scanning electron micrographs of the calcined and attrited oxides from hydroxides co-precipitated without sodium laurylsulphate. Magnification: 20000×. (a) Doped with 8 mol% Y_2O_3; (b) doped with 12 mol% MgO; (c) doped with 12 mol% CaO.

prepared from the attrited powders and sintered at 1600°C were >96% and reached 97–99% for specimens sintered at 1700°C. The densification process for bodies made from the spray-dried powders yielded relative densities <90%. These rather low values are due to the poor sinterability of the hard agglomerates formed during the calcination, which were not destroyed during compaction.

Considerable grain growth was experienced during sintering. Yttria-doped zirconia sintered at 1700°C exhibited grain sizes of about 20 to 25 µm, magnesia- and calcia-doped bodies gave grain sizes of 30 to 40 µm (Fig. 8).

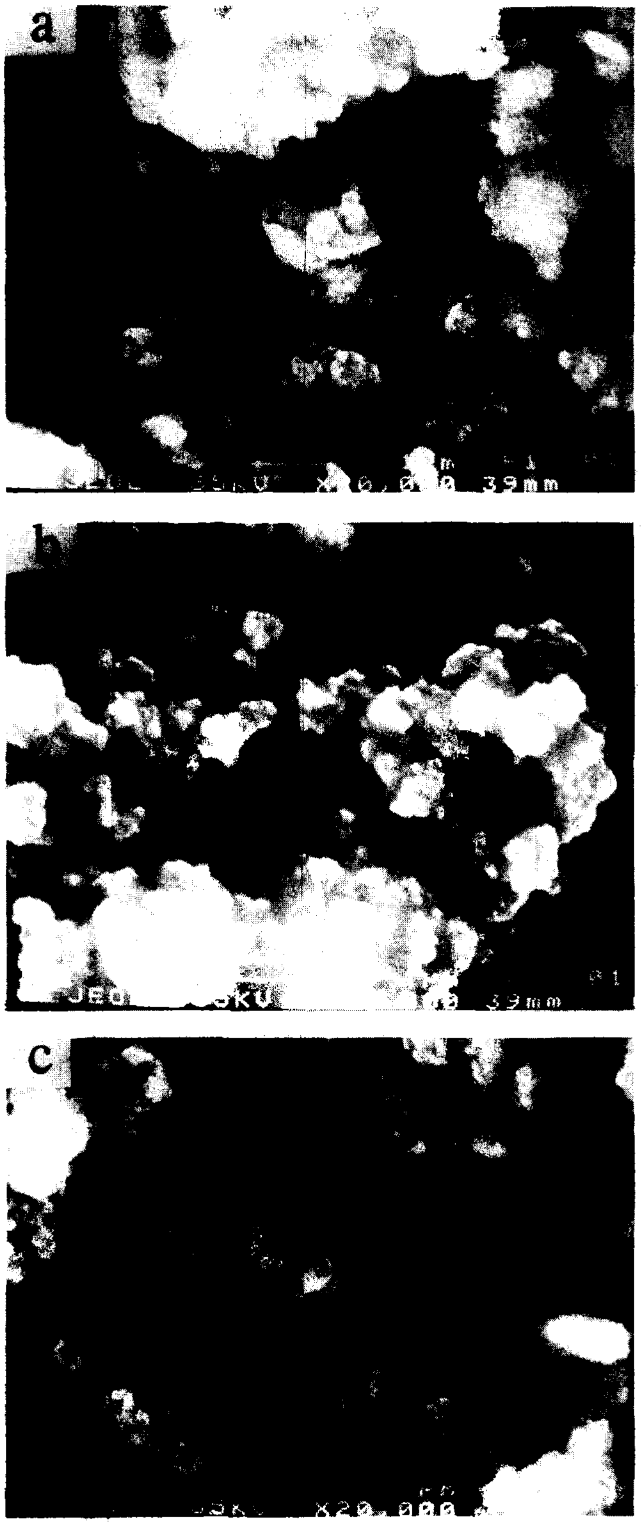

Fig. 7. Scanning electron micrographs of the calcined and attrited oxides from hydroxides co-precipitated in the presence of sodium laurylsulphate. Magnification: 30 000×. (a) Doped with 8 mol% Y_2O_3; (b) doped with 12 mol% MgO; (c) doped with 12 mol% CaO.

Table 2. Densities, relative densities and Vickers hardnesses and K_{Ic} values of doped, cubic zirconia ceramics[a]

Sample	*Sintering temp. (°C)*	*Density ($g\ cm^{-3}$)*	*Relative density (%)*[b]	*Vickers hardness (GPa)*	K_{Ic} *($MPa\ m^{1/2}$)*
8Y[c]	1600	5·74	96	9·4	2·4
8Y[d]	1600	5·29	89	3·3	1·8
8Y[e]	1600	5·73	96	17·6	2·6
8Y[f]	1600	5·19	87	7·8	2·3
8Y[c]	1700	5·73	96	9·2	3·1
8Y[d]	1700	5·33	90	3·8	2·1
8Y[e]	1700	5·75	97	18·1	2·9
8Y[f]	1700	5·36	90	9·8	2·4
12Mg[c]	1600	5·67	98	12·6	3·9
12Mg[d]	1600	5·18	89	5·0	2·5
12Mg[e]	1600	5·75	99	16·5	4·3
12Mg[f]	1600	5·10	88	5·6	2·5
12Mg[c]	1700	5·67	98	13·7	4·2
12Mg[d]	1700	5·27	91	8·9	2·6
12Mg[e]	1700	5·75	99	16·2	4·4
12Mg[f]	1700	5·17	89	7·1	2·4
12Ca[c]	1600	5·61	98	8·5	2·5
12Ca[d]	1600	5·51	96	11·3	2·4
12Ca[e]	1600	5·69	99	15·8	4·5
12Ca[f]	1600	5·15	90	5·2	2·2
12Ca[c]	1700	5·62	98	9·6	3·5
12Ca[d]	1700	5·56	97	12·4	3·1
12Ca[e]	1700	5·72	99	15·8	4·5
12Ca[f]	1700	5·16	90	7·0	2·3

[a] 8Y: doped with 8 mol% Y_2O_3, 12Mg: doped with 12 mol% MgO, 12Ca: doped with 12 mol% CaO.
[b] Percentage of the theoretical density, the latter calculated by the theory of Ingel and Lewis[18] from the lattice parameters.[6,19,20]
[c] Co-precipitated without sodium laurylsulphate, calcined and attrited.
[d] Co-precipitated with sodium laurylsulphate and calcined.
[e] Co-precipitated with sodium laurylsulphate, calcined and attrited.
[f] Co-precipitated with sodium laurylsulphate, spray dried and calcined.

3.4 Vickers hardnesses and K_{Ic} values

The application of surface-active material during co-precipitation followed by attrition of the calcined powders increased the Vickers hardnesses of the ceramics significantly (Table 2). The hardnesses reached 18·1 GPa for the yttria-, 16·2 GPa for the magnesia- and 15·8 GPa for the calcia-stabilized specimen sintered at 1700°C. The fracture toughnesses of the ceramics also improved when attrited powders were used as precursor material.

3.5 Strength

The measured three-point bend strengths with standard deviations, the Weibull moduli and the grain sizes are given in Table 3. Samples prepared from attrited precursor material obtained from co-precipitation with addition of laurylsulfate showed an increase in bend strength from 63 to 91 MPa for yttria-stabilized, from 71 to 98 MPa for the magnesia-stabilized and from 60 to 75 MPa for the calcia stabilized cubic zirconias sintered at 1700°C compared with samples precipitated without surface-active substances.

3.6 Conductivity

The electrical conductivities at 1000°C of the ceramics prepared from hydroxides co-precipitated with sodium laurylsulfate were measured to be 0·12, 0·072 and 0·032 S cm^{-1} for the yttria-,

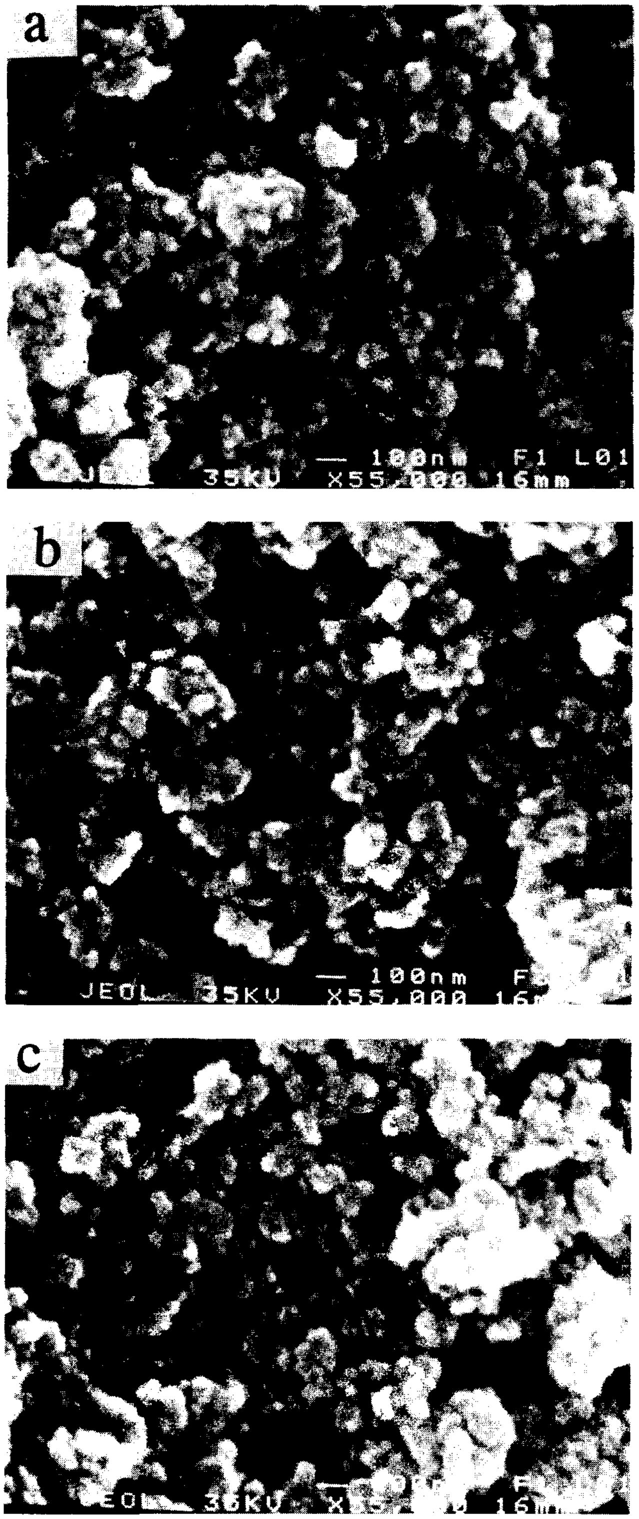

Fig. 8. Optical micrographs of the polished and etched surfaces of ceramics sintered at 1700°C. Magnification 400×. (a) Doped with 8 mol% Y_2O_3; (b) doped with 12 mol% MgO; (c) doped with 12 mol% CaO.

Table 3. Three-point bend strengths and Weibull moduli of doped cubic zirconia ceramics[a]

Sample	*Sintering temp.* (°C)	*Three-point bend strength (MPa)*	*Standard deviation (MPa)*	*Weibull modulus,* m	*Grain size (μm)*
8Y[b]	1600	60	12	4·0	24
8Y[b]	1700	63	9	7·0	26
8Y[c]	1600	82	12	3·7	16
8Y[c]	1700	91	17	2·9	20
12Mg[b]	1600	55	8	6·5	14
12Mg[b]	1700	71	14	4·5	28
12Mg[c]	1600	89	5	11·7	28
12Mg[c]	1700	98	15	5·2	41
12Ca[b]	1600	61	15	3·7	29
12Ca[b]	1700	60	11	5·1	35
12Ca[c]	1600	74	12	5·7	33
12Ca[c]	1700	75	12	3·6	40

[a] 8Y: doped with 8 mol% Y_2O_3, 12Mg: doped with 12 mol% MgO, 12Ca: doped with 12 mol% CaO.

[b] Co-precipitated without sodium laurylsulphate, calcined and attrited.

[c] Co-precipitated with sodium laurylsulphate, calcined and attrited.

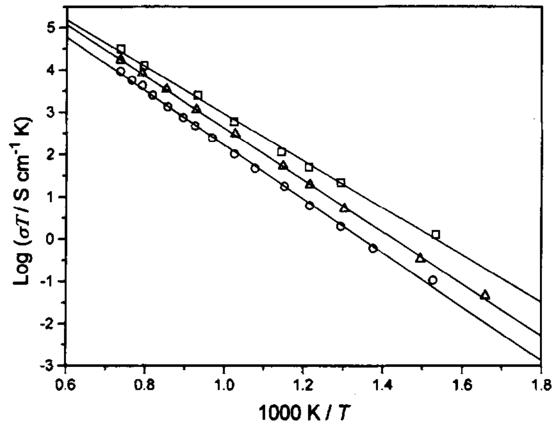

Fig. 9. Log(σT) versus $1/T$ plots for the conductivities (σ) of doped cubic zirconia: □, doped with 8 mol% Y_2O_3; Δ, doped with 12 mol% MgO; ○, doped with 12 mol% CaO.

magnesia- and calcia-doped samples, respectively. The temperature dependences of the total ionic conductivities of the doped samples are shown in Fig. 9 as Arrhenius plots. Literature data for cubic zirconia doped with 8 mol% yttria at 1000°C vary between 0·036 and 0·13 S cm^{-1} (Ref. 9) and 0·16 S cm^{-1}.[10,11] Values between 0·16 and 0·19 S cm^{-1} have been measured for tapes by a two-point a.c. technique.[12] Measurements on commercially available yttria-doped zirconias yielded specific conductivities of between 0·09 and 0·125 S cm^{-1}.[13] The conductivities measured by us compare well with the data reported in literature. The specific conductivities of our yttria-doped samples decreased to about 0·09 S cm^{-1} upon annealing at 1000°C for 30 days. Decreases in the conductivities of yttria-doped zirconias have been reported recently.[11,13] The specific conductivities at 1000°C for zirconia doped with 12 mol% calcia have been reviewed.[9,15] The published values ranged between 0·004 and 0·067 S cm^{-1}.

4 Conclusions

The mechanical properties of the sintered bodies depended strongly on the wet-chemical preparation techniques, the drying procedures and the attrition of the oxidic precursors. Spraying aqueous solutions of the respective metal chlorides into aqueous ammonia resulted in prime crystallites with diameters below 50 nm. These crystallites aggregated during the precipitation step to particles several μm in size. The particle sizes after calcination were affected by both the addition of surfactant during the co-precipitation process and the drying procedure. Addition of the surfactant during the precipitation step yielded soft agglomerates which broke during the attrition step. The best mechanical properties and the highest relative densities (96–99%) were obtained for powders co-precipitated with addition of surfactant, which were attrited after calcination; the worst properties were obtained for powders which were not subjected to attrition. Spray drying of the hydroxides yielded hard, spherical particles with poor densification behaviour, yielding sintered bodies with relative densities below <90%.

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