

## Synthesis, microstructure and mechanical properties of ceria stabilized tetragonal zirconia prepared by spray drying technique

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**Abstract.** Ceria stabilized zirconia powders with ceria concentration varying from 6 to 16 mol% were synthesized using spray drying technique. Powders were characterized for their particle size distribution and specific surface area. The dense sintered ceramics fabricated using these powders were characterized for their microstructure, crystallite size and phase composition. The flexural strength, fracture toughness and microhardness of sintered ceramics were measured. High fracture toughness and flexural strength were obtained for sintered bodies with 12 mol% of CeO<sub>2</sub>. Flexural strength and fracture toughness were dependent on CeO<sub>2</sub> concentration, crystallite size and phase composition of sintered bodies. Correlation of data has indicated that the transformable tetragonal phase is the key factor in controlling the fracture toughness and strength of ceramics. It has been demonstrated that the synthesis method is effective to prepare nanocrystalline tetragonal ceria stabilized zirconia powders with improved mechanical properties. Ce–ZrO<sub>2</sub> with 20 wt% alumina was also prepared with flexural strength, 1200 MPa and fracture toughness, 9.2 MPa√m.

**Keywords.** Zirconia; ceria stabilized zirconia; nanocrystalline; spray drying; toughened ceramics; mechanical properties.

### 1. Introduction

Ceria stabilized tetragonal zirconia polycrystalline ceramics possess distinct advantages over other conventional structural ceramic materials (Garvie *et al* 1975; Evans and Cannon 1986) because of their better thermal stability in moist environments (Matsumoto 1978), wider range of solid solubility in tetragonal region and coefficient of thermal expansion matching with that of iron alloys (Tsukuma and Shimada 1985; Nettleship and Stevens 1987). Consequently, ceria stabilized zirconia ceramics have been investigated extensively for structural applications.

The highly improved mechanical properties in these transformation toughened ceramics are related to the stress induced transformation of the metastable tetragonal grains to the monoclinic phase at the crack tips (McMeeking and Evans 1982; Chen and Reyes-Morel 1986; Hannink *et al* 2000). Therefore, the transformability of the metastable tetragonal phase in the process zone plays a dominant role in the ultimate attainable mechanical properties of these materials. The grain size and microstructure of these materials are difficult to control in conventional technique such as ball milling for powder preparation. The larger ball milled particles sinter at much higher temperature leading to considerable grain growth, which does not permit retention of desired tetragonal

phase and high values of mechanical properties in the material (Wang *et al* 1992). Most of the earlier studies on CeO<sub>2</sub>–ZrO<sub>2</sub> system are with powders prepared by conventional methods and the results are inconsistent due to the poor homogeneity and sinterability of the powders (Wang *et al* 1992). Recently few attempts have been made to prepare CeO<sub>2</sub>–ZrO<sub>2</sub> using chemical methods and only a limited effort has been made to understand the effect of CeO<sub>2</sub> content and grain size on the mechanical properties of the system (Wang *et al* 1992; Maschio *et al* 1992). Various additives and sintering aids have also been tried to improve sintered density and flexural strength of the material (Maschio *et al* 1998; Kojima *et al* 2000).

Recently high purity, chemically homogenous and reactive ceria stabilized zirconia powders have been prepared by chemical methods (Yin *et al* 1999; Matsui and Ohgai 1999) and sintered ceramics having considerably high density and transformable tetragonal phase have been obtained using these powders. However, little effort has been made to establish structure–property correlation in the sintered ceramics (Yoshioka *et al* 1992).

The objective of the present paper is, therefore, to study the effect of ceria doping on phase composition, crystallite size and mechanical properties such as flexural strength and fracture toughness of zirconia ceramics. Effort has also been made to enhance strength of Ce–TZP ceramics by incorporating 20 wt% alumina as a second phase (Cutler *et al* 1991).

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## 2. Experimental

### 2.1 Preparation of powders and Ce–ZrO<sub>2</sub> ceramics

The following raw materials were used for preparation of ceria stabilized zirconia powders: (i) ZrOCl<sub>2</sub>·8H<sub>2</sub>O (IRE Ltd., 99% purity) and (ii) ceric ammonium nitrate (CDH, > 99% purity).

The zirconium oxychloride was recrystallized and converted into nitrate as per procedure described elsewhere (Lal *et al* 1993) and doped with required amounts of ceric ammonium nitrate solution to prepare composite nitrate solution of the following compositions: (i) 6 mol% CeO<sub>2</sub>–94 mol% ZrO<sub>2</sub> (6Ce–ZrO<sub>2</sub>), (ii) 8 mol% CeO<sub>2</sub>–92 mol% ZrO<sub>2</sub> (8Ce–ZrO<sub>2</sub>), (iii) 10 mol% CeO<sub>2</sub>–90 mol% ZrO<sub>2</sub> (10Ce–ZrO<sub>2</sub>), (iv) 12 mol% CeO<sub>2</sub>–88 mol% ZrO<sub>2</sub> (12Ce–ZrO<sub>2</sub>), (v) 14 mol% CeO<sub>2</sub>–86 mol% ZrO<sub>2</sub> (14Ce–ZrO<sub>2</sub>), and (vi) 16 mol% CeO<sub>2</sub>–84 mol% ZrO<sub>2</sub> (16Ce–ZrO<sub>2</sub>).

The mixed solutions were spray dried in a lab model Spray Drier (Anhydro, Denmark) and calcined at 500°C for 4 h. The calcined powders were deagglomerated in an attritor, mixed with binder and compacted at a hydraulic pressure of 175 MPa followed by pressure less sintering of the compacts at 1400°C for 2 h.

Alumina toughened Ce–TZP was prepared by attrition milling of 99.9% purity alumina powder with spray dried 12Ce–TZP powder in the ratio 20 : 80 by weight. The compaction and sintering parameters were same as in case of Ce–ZrO<sub>2</sub> ceramics.

### 2.2 Characterization of powders and Ce–ZrO<sub>2</sub> ceramics

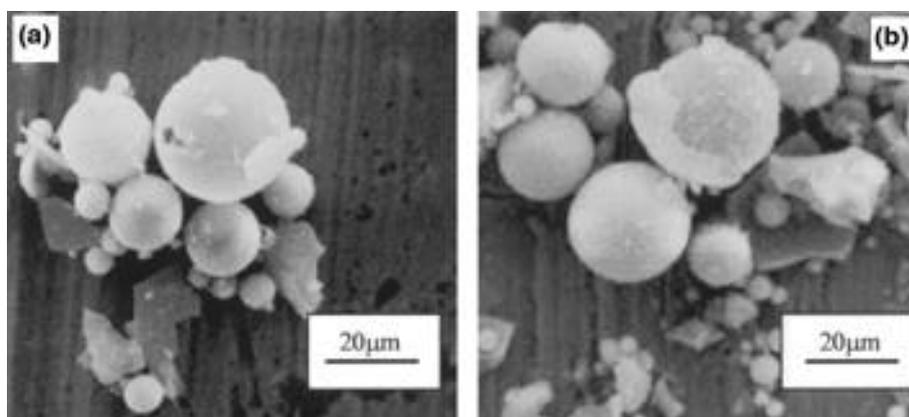
The attrited powders of 6Ce–ZrO<sub>2</sub> and 16Ce–ZrO<sub>2</sub> were characterized for their particle size distribution by laser beam diffraction technique (Mastersizer-2000, Malvern Instruments) and surface area by BET technique (Surface Area Analyser model 2200, Micromeritics Inc.) The density of sintered ceramics was measured using Archi-

medes method. The microstructure was studied by SEM (Jeol, JSM-840). Sintered specimens were cut into bars of 2.5 × 3.5 × 30 mm<sup>3</sup> and polished to 1 μm finish using diamond paste for evaluation of mechanical properties. Flexural strength was measured by 3 pt. bend test with a span of 20 mm at a crosshead speed of 0.5 mm/min and the fracture toughness was measured using SENB technique (Gokhale *et al* 1994). The hardness of the specimen was measured by micro indentation technique. X-ray diffraction techniques were used to determine crystallite size, compositional homogeneity and percentage of monoclinic (*m*), transformable tetragonal (*t*), non-transformable tetragonal (*t'*) and cubic (*c*) phases in sintered ceramics. Monochromatic CuK<sub>α</sub> radiation was used in the present work. Crystallite size was calculated using the (11 $\bar{1}$ )<sub>*m*</sub>, (111)<sub>*m*</sub> and (111)<sub>*t*</sub> diffraction peaks using Scherrer formula (Klug and Alexander 1954). Compositional homogeneity of sintered ceramics was examined using a Williamson Hall plot (Osendi *et al* 1985) and also by EDAX analysis.

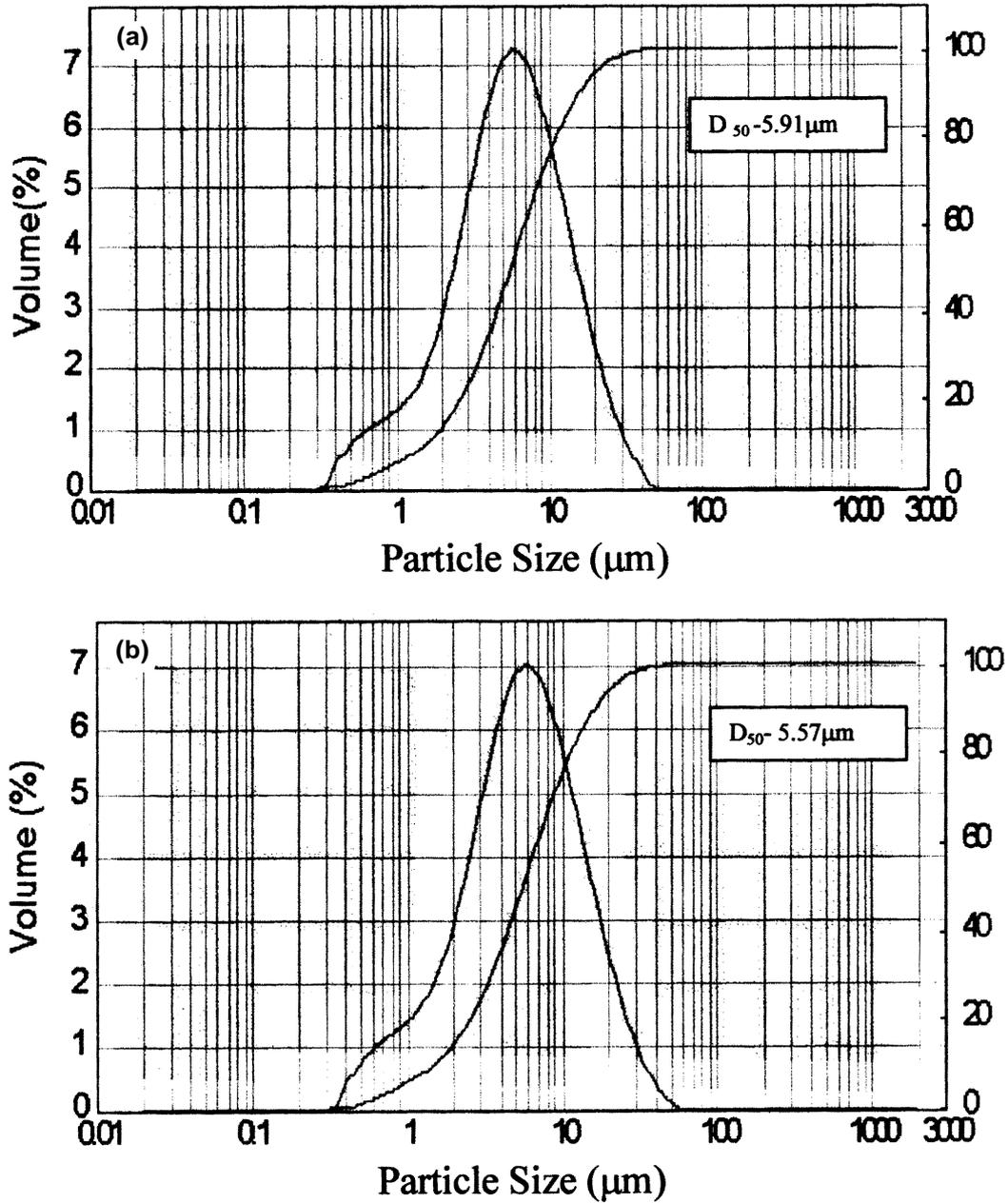
## 3. Results and discussion

SEM photomicrographs of calcined 6Ce–ZrO<sub>2</sub> and 16Ce–ZrO<sub>2</sub> powders are shown in figure 1. The particle agglomerates are spherical and in the range 3–30 μm. Figure 2 shows the particle size distribution of the above powders. The particle size, *D*<sub>50</sub> for the powders are 5.91 μm and 5.57 μm, respectively. It is observed that the amount of dopant (ceria concentration) has no effect on particle size distribution of zirconia powders. Similar effect has also been observed for surface area of these powders, which is in the range 50–55 m<sup>2</sup>/g for all the compositions.

The sintered density, proportions of *m*, *t*, *t'* and *c* phases and crystallite size of different compositions of sintered ceramics are shown in table 1. The sintered density of ceramics is > 98.2% except for 6Ce–ZrO<sub>2</sub>. The



**Figure 1.** SEM photomicrographs of calcined ceria doped zirconia powders: (a) 6Ce–ZrO<sub>2</sub> and (b) 16Ce–ZrO<sub>2</sub>.



**Figure 2.** Particle size distribution of ceria stabilized zirconia powders: (a) 6Ce-ZrO<sub>2</sub> and (b) 16Ce-ZrO<sub>2</sub>.

**Table 1.** Variation of density, crystallite size, phase composition and grain size with composition of sintered Ce-ZrO<sub>2</sub> ceramics.

Composition	Density (% theoretical)	Crystallite size (nm)	Phase composition (mol%)			Average grain size (μm)
			<i>m</i>	<i>t + t'</i>	<i>c</i>	
6Ce-ZrO <sub>2</sub>	97.05	30.0	22	78 + 0	0	2.5
8Ce-ZrO <sub>2</sub>	98.26	27.1	10	90 + 0	0	2.3
10Ce-ZrO <sub>2</sub>	98.42	24.0	0	100 + 0	0	2.2
12Ce-ZrO <sub>2</sub>	98.60	22.5	0	100 + 0	0	2.0
14Ce-ZrO <sub>2</sub>	98.60	21.3	0	77 + 23	0	1.9
16Ce-ZrO <sub>2</sub>	98.60	20.6	0	42 + 46	12	1.9

lower density is due to the higher monoclinic phase leading to development of microcracks during sintering. It may be seen that the powders containing 6 and 8 mol% CeO<sub>2</sub> contain *m* + *t* phases, powders having 10, 12 and 14 mol% CeO<sub>2</sub> are fully tetragonal whereas 16 mol% CeO<sub>2</sub> addition gives rise to cubic phase. The axial ratio (*c/a*) decreases with increase in CeO<sub>2</sub> concentration from 6 to 16 mol%. The amount of metastable transformable tetragonal (*t*) phase decreases and non-transformable tetragonal (*t'*) phase increases with increase in ceria concentration above 12 mol%. Our results are in close agreement with earlier observations (Quinelato *et al* 2000) for powders synthesized from polymer precursor. It has also been observed that crystallite size of zirconia ceramics decreases with increase in ceria concentration. This is in accordance with thermodynamic equation for free energy for phase transformation (Lange 1982). The ceramics with 10 and 12 mol% CeO<sub>2</sub> exhibit maximum transformable tetragonal (*t*) phase for a crystallite size of 24 and 22 nm, respectively. To achieve maximum fracture toughness and

strength in Ce–ZrO<sub>2</sub> the sintered ceramics should have nearly theoretical density and maximum amount of transformable tetragonal phase which is possible if the crystallite size is between 22 and 24 nm. Figure 3 shows XRD patterns of sintered 6Ce–ZrO<sub>2</sub>, 12Ce–ZrO<sub>2</sub> and 16Ce–ZrO<sub>2</sub> ceramics taken at room temperature. The (400) reflections exhibit 4 peaks for two types of tetragonal phases, transformable *t* phase (at  $2\theta = 72.90^\circ, 74.36^\circ$ ) and non-transformable *t'* phase (at  $2\theta = 73.42^\circ, 74.16^\circ$ ) with axial ratio (*c/a*) 1.017 and 1.008, respectively. The Williamson Hall plots obtained from data of these XRD patterns is shown in figure 4. The slopes of the curves are zero which shows the absence of lattice strain and thereby confirms the compositional homogeneity of the material. The amount of Ce in 12Ce–ZrO<sub>2</sub> powders has been found to be  $12.65 \pm 0.2$  wt% by EDAX analysis which is in close agreement with the actual 13.0 wt% added during preparation.

Figure 5 shows variation of hardness, flexural strength and SENB fracture toughness of sintered ceramics with

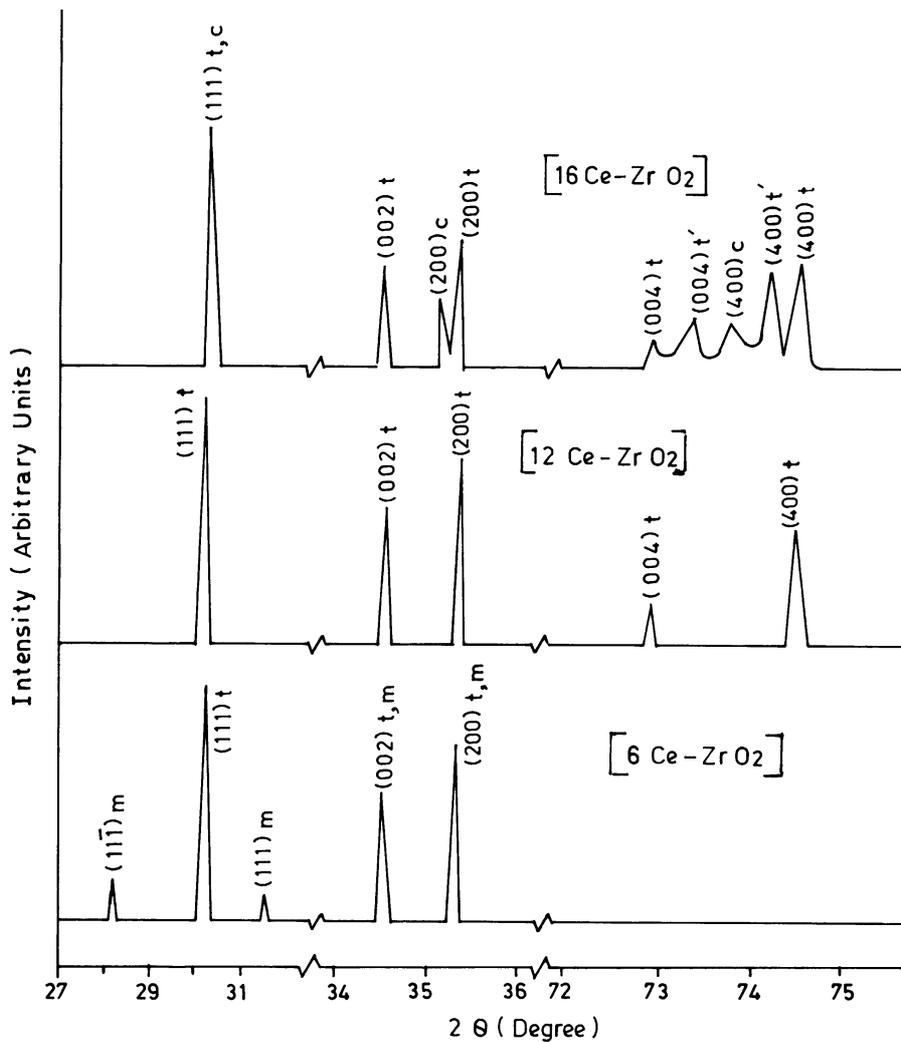


Figure 3. XRD patterns of ceria stabilized zirconia ceramics.

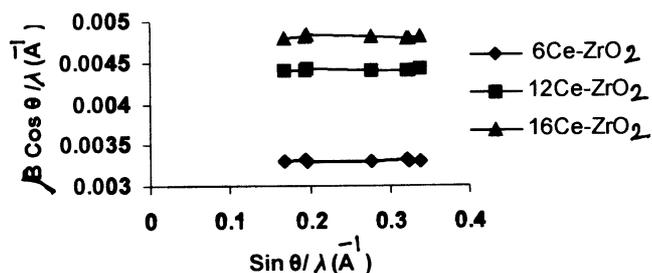


Figure 4. Williamson Hall plot for ceria stabilized zirconia ceramics.

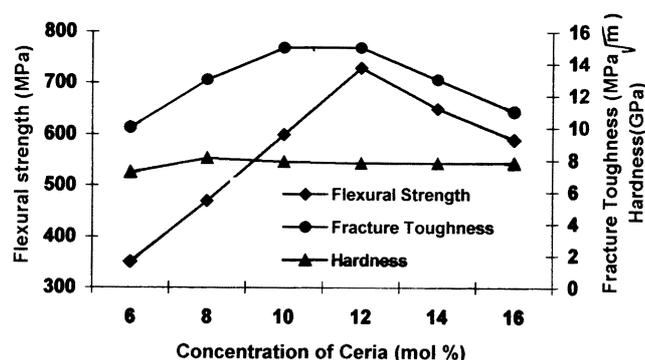


Figure 5. Variation of mechanical properties with ceria concentration in zirconia ceramics.

amount of  $\text{CeO}_2$  in zirconia. It may be seen that the flexural strength and fracture toughness increase sharply with increase in ceria concentration up to 12 mol% and start decreasing slowly with further increase in ceria concentration. This may be attributed to increase in transformable tetragonal phase in the material up to 12 mol%  $\text{CeO}_2$  concentration and thereafter decrease in transformable tetragonal phase and increase in non transformable tetragonal phase with further increase in ceria concentration. The similar trend in values of flexural strength and fracture toughness signifies that flexural strength is controlled by stress induced transformation toughening and flaw size in the sintered ceramics is very small which can be attributed to high purity, fine and homogeneous powders prepared using spray drying technique. The transformable tetragonal (*t*) phase and consequently the flexural strength and fracture toughness are maximum at a critical crystallite size of  $\sim 22$  nm. The material with lower crystallite size does not transform to monoclinic phase in the stress field of a propagating crack thereby reducing the fracture toughness as well as strength of the material. With crystallite size above the critical value, the *t* phase transforms spontaneously to monoclinic phase without absorption of energy at the crack tip leading to lower fracture toughness. The flexural strength (730 MPa) and fracture toughness ( $15 \text{ MPa}\sqrt{\text{m}}$ ) achieved in the present work using spray dried powder are higher than the

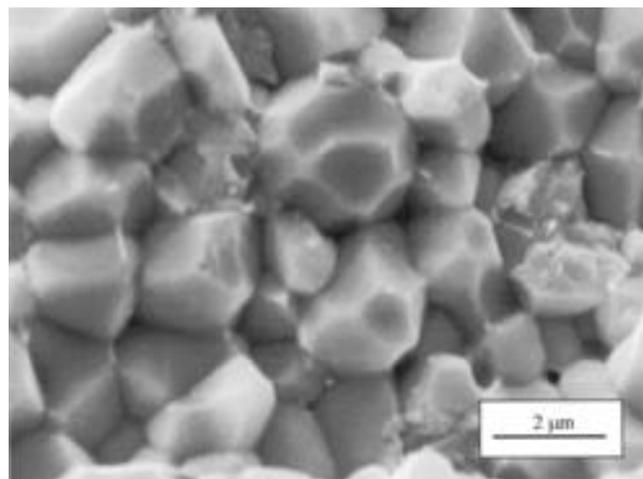


Figure 6. SEM photomicrograph of ceria stabilized zirconia ceramics.

earlier reported values (Tsukuma and Shimada 1985; Chen and Brook 1989; Wang *et al* 1992; Quinelato *et al* 2000).

The variation of ceria content in zirconia has very little effect on the hardness of  $\text{Ce-ZrO}_2$ . The hardness of 6Ce- $\text{ZrO}_2$  has been found to be slightly lower due to its lower density and microcracks. SEM photomicrograph of sintered 12Ce- $\text{ZrO}_2$  ceramics is shown in figure 6. The average grain size was about  $2 \mu\text{m}$ . The lower grain size and high density of ceramics in the present studies may be attributed to fine starting powders and lower sintering temperature. The finer grains have vital role in achieving higher flexural strength in the present study. The data generated in the present study are useful in developing material with desired mechanical strength by controlling the crystallite size and optimizing the concentration of ceria in  $\text{ZrO}_2$ . The addition of 20 wt% alumina in 12Ce-TZP gives the much improved strength (1200 MPa) with moderate toughness ( $9.2 \text{ MPa}\sqrt{\text{m}}$ ) as compared to earlier study (Cutler *et al* 1991). Thus the properties similar to Y-TZP ceramics can also be achieved in Ce-TZP by alumina addition with added advantage of low temperature thermal stability.

#### 4. Conclusions

In the present study a correlation between microstructure and mechanical properties of  $\text{Ce-ZrO}_2$  has been carried out. It has been demonstrated that high purity, fine and chemically homogeneous powders can be prepared by spray drying technique. These powders can be sintered by pressureless sintering at  $1400^\circ\text{C}$ . It has been demonstrated that the volume fraction of metastable transformable tetragonal phase is dependent on ceria concentration. Fracture toughness and strength increase with increase in the amount of transformable tetragonal phase in the ceramics. The excellent mechanical properties of ceramics

are attributed to the fine, spherical and reactive starting powders with good compositional homogeneity.

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