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Phase stability and microstructural characteristics of 12 mol% (Mg, Ca)-PSZ prepared via polymeric route

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Abstract

Urea-formaldehyde resin was used as a precursor for the processing of ultrafine 12 mol% (Mg, Ca)-PSZ powders with uniform morphology. 12 mol% CaO stabilized zirconia was subjected to extensive cracking on reheating between 1400 and 1500 °C. The cracking phenomenon was found to be due to the tetragonal to monoclinic phase transformation. MgO equal to CaO was added at 3, 6 and 9 mol% to improve the stability of tetragonal zirconia. The crystallization of tetragonal zirconia from the amorphous powders occurs between 400 and 500 °C. The stability of tetragonal zirconia was found to increase with addition of MgO. The addition of MgO, combined with fast heating during hot pressing, activates the densification process by acting as a sintering aid and reducing the relative degree of structural coarsening. Optimized stability of tetragonal zirconia and good microstructure were achieved at equal proportions of MgO and CaO.

Keywords: Ca-PSZ; (Mg; Ca)-PSZ; Polymeric route; Tetragonal zirconia stability

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1. Introduction

Interest in zirconia-based ceramics is attributed to their unique set of properties. The very high melting temperature of zirconia makes it a prime candidate for refractory applications. Zirconia is a candidate material for components that are subjected to high thermal shock resistance, high temperature and corrosive environments. Zirconia has been utilized in seals, engines, cutting tools, sensors, and thermal barrier coatings [1].

Pure zirconia undergoes a number of reversible phase transitions during heat treatment. The most destructive is the transformation of tetragonal to monoclinic phase resulting in 4% volume change [2]. The best method to exploit the properties of zirconia is improvement of sinterability by stabilization of the high temperature phases to room temperature. Control over the stability is achieved by doping zirconia with one or more of the fluorite stabilizer oxides [3]. CaO [4], MgO [5], Y_2O_3 [6] and CeO_2 [7] are used to achieve either fully or partially stabilized zirconia.

Calcia and magnesia are the most extensively used oxides to stabilize zirconia at their high temperature polymorphs because of their cheap precursors and refractory potential [8]. However, CaO and MgO stabilized zirconia show poor stability due to the extensive tetragonal to monoclinic phase transformation resulting in extensive cracking in certain applications [9]. Precipitation, eutectoid decomposition, and crystallization of zirconia proceed very slowly and equilibrium is difficult to achieve. Wu et al. [10] found that high density and small grain size can be achieved by the use of multiple additives i.e. CaO (or Y_2O_3) together with MgO.

Calcia (12 mol%) stabilized zirconia (CSZ) powders showed the coexistence of monoclinic and cubic solid solutions between 1180 and 1325 °C. In sintered samples, the cubic solid solution decomposition reaction follows the metastable extension of the boundary line separating the two-phase regions from that of the cubic solid solution. On cooling, tetragonal solid solution precipitate forms within the cubic matrix and partially transforms into monoclinic on cooling [11].

Different routes have been utilized for processing of fine powders including co-precipitation [12], alkoxide [13], and citrate routes [14]. The main defect is the

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agglomeration of powders [15]. In the current work, urea-formaldehyde polymeric gels were used as a precursors for the synthesis of 12 mol% (Mg, Ca)-PSZ. Phase analysis and microstructure characteristics were assessed.

2. Experimental work

2.1. Materials

Reagent grade urea (BDH Ltd., Poole UK), commercial formaldehyde solution (37%) and ethylene glycol (Aldrich) were used as organic precursors for resin preparation. Zirconium oxychloride (Aldrich), magnesium nitrate (Aldrich) and calcium nitrate (Aldrich) were used as salt precursors.

2.2. Preparation of gel

The polymerization reaction between urea and formaldehyde was utilized to form polymer resins hosting the respective inorganic cations. The reaction starts at pH ~ 8.5 during stirring and reflux at 70 °C for 15 min to form methylol urea-formaldehydes; monomethylol and dimethylol urea-formaldehyde were formed. The reaction was terminated at pH ~ 3 through simultaneous addition of ethylene glycol and salt solutions. The different gels were prepared using urea, formaldehyde, ethylene glycol, and zirconium oxychloride in a ratio of 1:2:1:1. Water and other byproducts were vacuum distilled at 70 °C. The flow chart of preparation technique is displayed in Fig. 1. Transparent polymeric gels have been achieved with no signs of precipitation, in which cations are occluded in the structure. Details of the preparation conditions were previously reported [16–19]. The compositions of mixes are shown in Table 1. Gels were dried in a furnace at 110 °C/24 h.

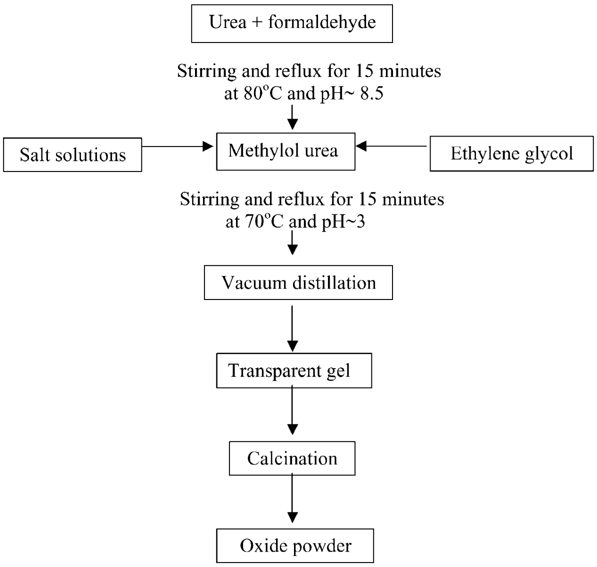

Fig. 1. Flow chart of the preparation method.

Table 1
Compositions of the different powders

Mixes	Z_6	Z_7	Z_8	Z_9	Z_{10}
CaO mol%	12	00	9	6	3
MgO mol%	00	12	3	6	9

2.3. Characterization of powders

Selected gels (Z_6, Z_9 and Z_{10}) were crushed in an agate mortar: 300 mgs of the gel powders were used for DTA analysis up to 800 °C at a rate of 5 °C/min using a Bähr 701 DTA.

The dried gels were calcined up to 600 °C/2 h at a heating rate of 1 °C/minute. During calcination, samples were soaked at 180, 300 and 600 °C for 2 h. The temperatures were suggested from DTA analysis. Parts of the resulting powders were pressed at a uniaxial pressure of 250 MPa using 2% PVA as a binder. The pressed samples (Z_6, Z_7, Z_8, Z_9 and Z_{10}) were used for determination of the thermal shrinkage of powders up to 1300 °C at a heating rate 5 °C/min using a Bähr 801 dilatometer. The phase compositions of powders calcined at 600 °C were determined using a Philips 1710 XRD apparatus. The crystallite size was calculated from the XRD broadening of peaks with hkl (111) using Scherrer formula; $D = 0.9\lambda/\beta\cos\theta$.

2.4. Densification of powders

Powders calcined at 600 °C were pressed uniaxially at 250 MPa, without binder, to discs 1.5 cm diameter and 0.5 cm high. The pressed samples were heated at 1000 °C/2 h and 1500 °C/2 h at a heating rate of 5 °C/min.

Other powder samples were pressed uniaxially without a binder at 150 MPa into discs 5 cm diameter and 0.5 cm thick, followed by hot pressing at 35 MPa for 20 min at 1400 °C. Phase compositions of the samples were studied by XRD at ambient temperature. The amount of monoclinic phase was calculated using the equation of Porter and Heuer [2].

The different samples, sintered either by uniaxial pressing at 1500 °C/2 h or by hot pressing at 1400 °C, were subjected to polishing. The polished samples were carefully washed with water and thermally etched at 1350 °C/3 h. The etched samples were coated with gold and the microstructure was verified using SEM, type JSM-6400, operating at 20 kV.

3. Results and discussion

The DTA analysis of selected gels (Z_6. Z_9, Z_{10}) performed up to 800 °C showed two small exothermic peaks at 220 and 285 °C as displayed in Fig. 2. The two peaks are related to gel decomposition. Another broad

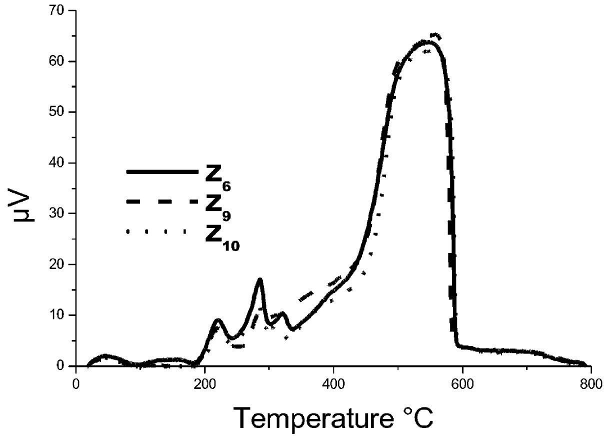

Fig. 2. DTA of selected mixes.

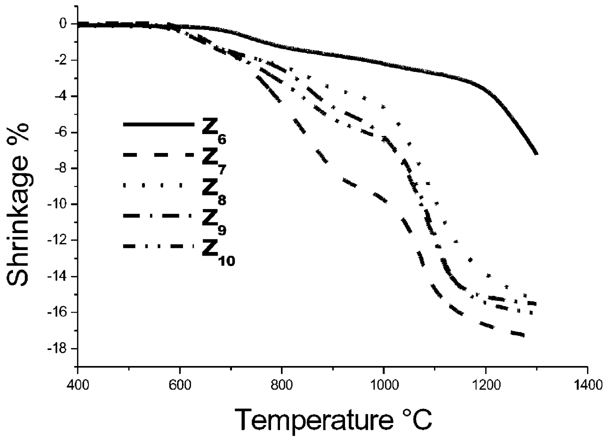

Fig. 3. Thermal shrinkage of powders.

exothermic peak occurs between 350 and 580 °C; it represents overlap of the dissociation reaction and the crystallization of cubic and tetragonal zirconia solid solutions.

The dilatometer behavior of the different powders is shown in Fig. 3. Shrinkage starts at about 570 °C. The sintering reactions of the different mixes proceed by essentially a one step reaction. Mix Z_6 displayed lower shrinkage, 7% up to 1300 °C. Higher shrinkage is shown by Z_7, 17%. The addition of MgO replacing CaO in mixes Z_8, Z_9 and Z_{10} increases shrinkage to about 15%. The presence of MgO in Z_8, Z_9 and Z_{10} strongly improves sintering, giving strong evidence for densification by MgO.

The XRD analysis of the different powders calcined up to 600 °C showed the crystallization of cubic and tetragonal solid solutions as shown in Fig. 4. The calculated crystallite size is about 5 nm for Z_6. Appreciable increases in the crystallite size of Z_8 and Z_9 resulted from addition of MgO, to about 6 nm.

The XRD analysis of the different powders uniaxially pressed at 250 MPa and sintered at 1500 °C/2 h gave a mixture of tetragonal and monoclinic phases. Ca-PSZ, mix Z_6, cracked, probably as a result of the complete transformation of tetragonal to monoclinic phase as shown in Fig. 5A. Mg-PSZ, mix Z_7, showed the presence of tetragonal and monoclinic zirconia phases, Fig.5B. The amount of monoclinic phase is estimated to be about 30%., In MgO-containing mixes Z_8, Z_9 and Z_{10}, the stability of tetragonal zirconia increased and the amount of monoclinic zirconia decreased to less than 10%: Fig. 5C–E.

The microstructural results of samples uniaxially pressed at 250 MPa and fired at 1500 °C/2 h are shown in Fig. 6. Mix Z_6 shows fine grains about 200 nm. Long crack-like pores occur around grain boundaries and seem to be continuous: Fig. 6A and B. In mix Z_7, the particle size is about 400 nm. Pores exist at the triple junction formed at the intersection of grain boundaries, Fig. 6C. Large grains, 1μm in size, observed in mixes Z_6 and Z_7 actually consist of several smaller grains. In mix Z_8, the resin structure was preserved as shown in Fig. 6D. The spherical grains reach about 1 μm in size. Mix Z_9 has a bimodal grain size distribution including submicron grains (less than 400 nm) in the junctions and the main grains (1–2 μm) formed through diffusion: Fig. 6E. Pores occur at the triple junctions.

Hot pressed samples of Z_6 completely disintegrated on reheating between 1400 and 1500 °C/2 h, possibly as a result of tetragonal to monoclinic phase transformation. The microstructure of sample Z_9, hot pressed at 1400 °C for 20 min at 35 MPa is shown in Fig. 7. Narrow grain size distributions in the range of 0.4–2 μm occurs as shown in Fig. 7A. Spherical grains and polygonal pseudo-cubic grains develop. At higher magnification,

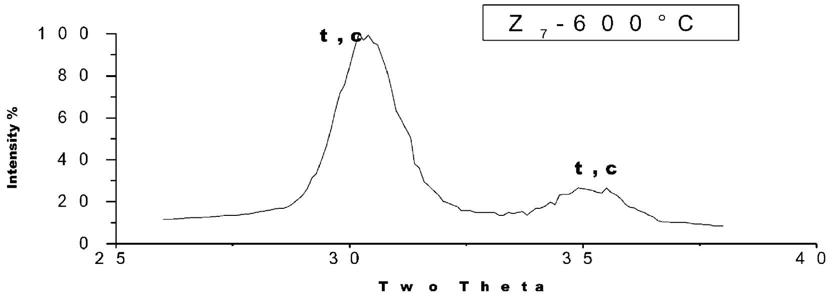

Fig. 4. XRD of powder calcined at 600 °C.

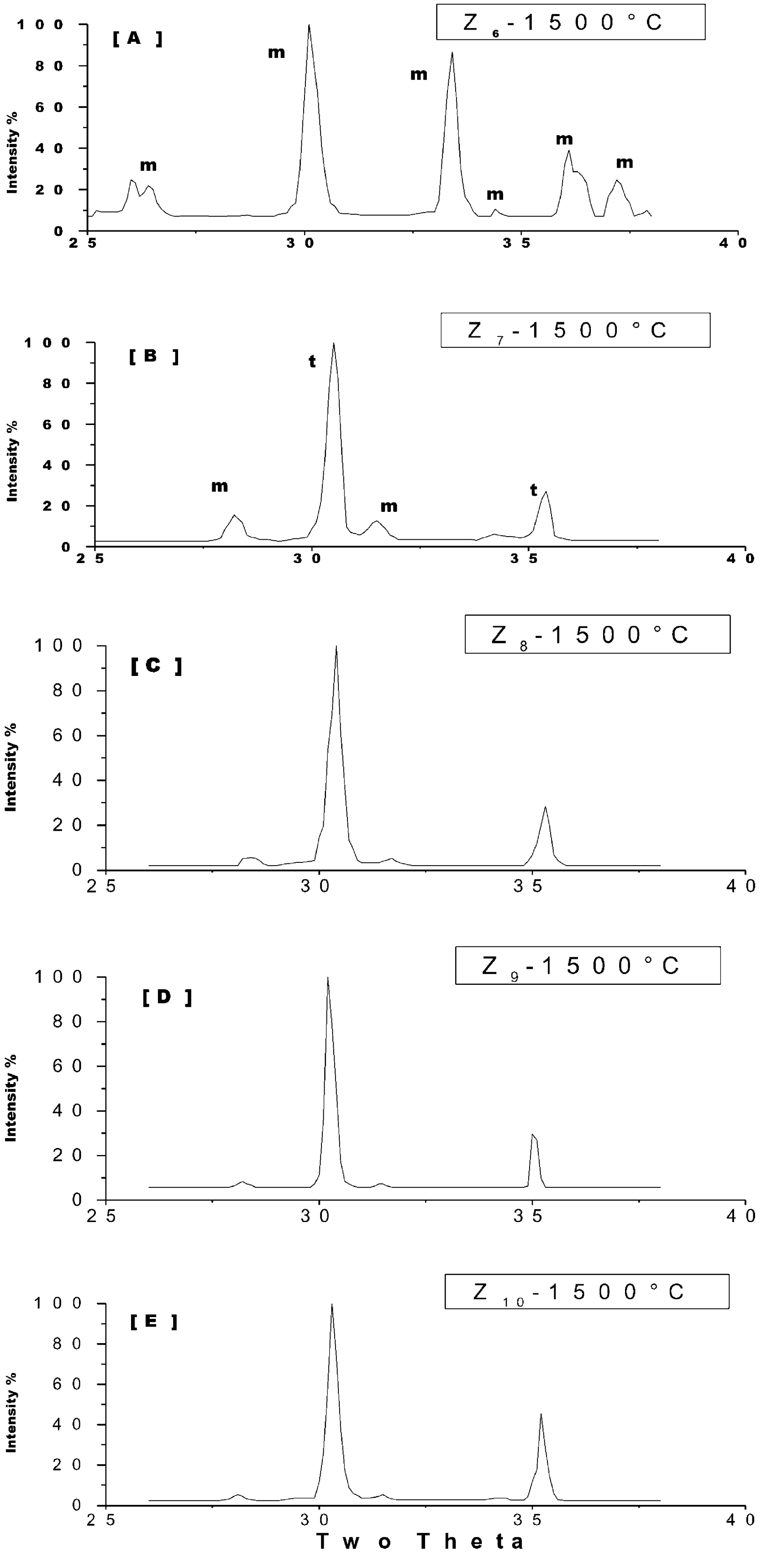

Fig. 5. XRD of samples uniaxially pressed, fired at 1000/2 h and 1500 °C/2 h m.: monoclinic t: tetragonal c: cubic.

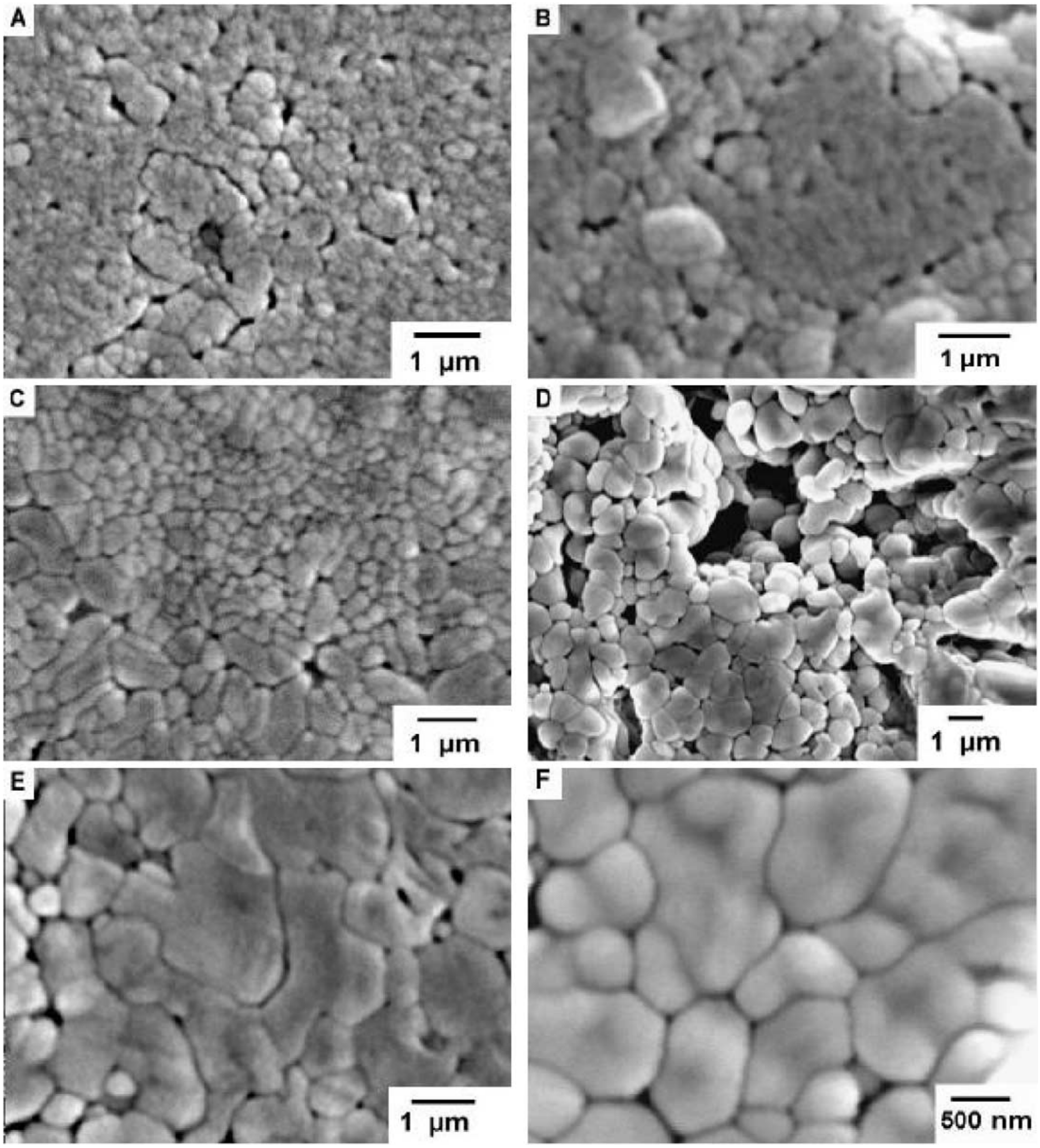

Fig. 6. SEM of mixes uniaxially pressed and fired at 1000 °C/2 h and 1500 °C/2 h; (A,B): Z_6, (C) Z_7, (D) Z_8, (E) Z_9, (F) Z_{10}.

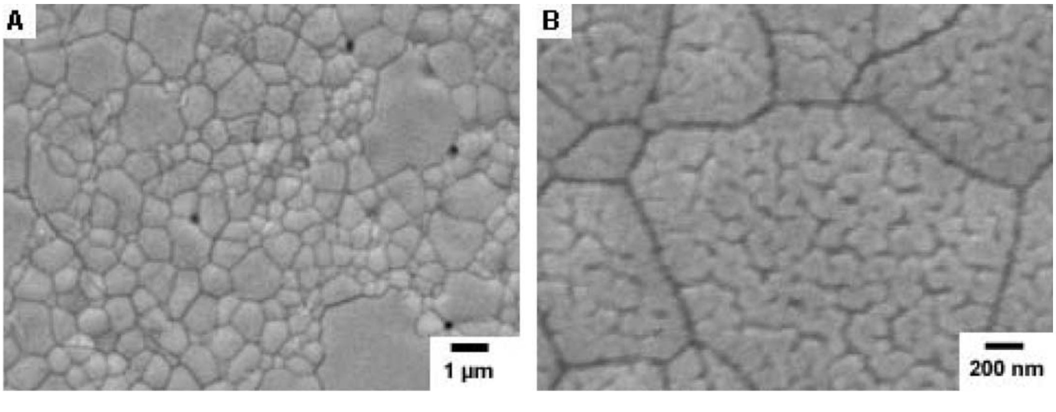

Fig. 7. SEM of Z_9 pressed at 1400 °C for 20 min at 35 MPa and thermally etched at 1350 °C/3 h.

the large polygonal grains are comprised of small tetragonal grains about 100 nm as shown in Fig. 7B. The grains formed within the cubic matrix by nucleation and crystallization partially transform into monoclinic phase forming PSZ. MgO thus has a strong effect on the degree of coarsening. The densification reaches 96.9% without cracks following processing of mix Z_9 at 1400 °C/2 h.

4. Conclusion

[1]. The presence of MgO with CaO improves the stability of tetragonal zirconia and enhances densification at lower sintering temperatures (1400 °C).

[2]. 12 mol% CaO stabilized zirconia cracked on reheating between 1400 and 1500 °C as a result of undergoing the tetragonal to monoclinic phase transformation.

[3]. The addition of MgO, combined with fast heating during hot pressing at 1400 °C, activates densification and reduces the degree of grain growth.

[4]. The best combination of tetragonal zirconia and good microstructure were achieved in Z_9, containing equal proportions of MgO and CaO.

References

[1] M.M. Schwartz, Handbook of Structural Ceramics, McGraw-Hill Inc, New York, 1992.

[2] D.L. Porter, A.H. Heuer, Microstructural development in MgO–partially stabilized zirconia (Zr-PSZ), J. Am. Ceram. Soc. 63 (5) (1979) 219–224.

[3] E. Mustafa, Microstructure and mechanical properties of PSZ toughened alumina ceramics prepared via polymeric sol–gel route, PhD thesis from Faculty of Science, Cairo University, May 1997.

[4] S. Kumar, P. Pramamik, Innovative chemical method preparation of calcia stabilized zirconia powders, Trans. J. Br. Ceram. Soc. 94 (3) (1995) 123–126.

[5] R.R. Hughan, R.H. Hannink, Precipitation during controlled cooling of magnesia partially stabilized zirconia, J. Am. Ceram. Soc. 69 (7) (1986) 556–563.

[6] J. Luo, R. Stevens, Tetragonality of nanosized 3Y-TZP powders, J. Am. Ceram. Soc. 82 (7) (1999) 1922–1924.

[7] S. Yin, S.U. Uchida, Y. Fujishio, M. Ohmori, T. Sato, Preparation of porous ceria doped tetragonal zirconia ceramics by capsule free hot isostatic pressing, Trans. J. Br. Ceram. Soc. 98 (1) (1999) 19–23.

[8] W.D. Kingrey, H.K. Brown, D.R. Uhlmann, Introduction to ceramics, 2nd Edition, John Wiley and Sons, New York, 1976.

[9] R.M. Dickerson, M.V. Swain, A.H. Heuer, Microstructural evolution in Ca-PSZ and the room-temperature instability of tetragonal zirconia, J. Am. Ceram. Soc. 70 (4) (1987) 214–220.

[10] S. WU, R.J. Brook, Sintering additives for zirconia ceramics, Trans. J. Br. Ceram. Soc. 82 (1983) 260–264.

[11] J.R. Hellmann, V.S. Stubican, Stable and metastable phase relations in the system ZrO_2–CaO, J. Am. Ceram. Soc. 66 (4) (1983) 260.

[12] S. Maschio, A. Trovarelli, Powder preparation and sintering behavior of zirconia–20 mol% ceria solid solution prepared by various methods, Trans. J. Br. Cerm. Soc. 94 (5) (1995) 191.

[13] J. Saiki, K. Hirota, O. Yamaguchi, S. Inamura, H. Miyamoto, N. Shiokawa, K. Tsuji, Formation, Transformation and sintering of ZrO_2–MgO compositions prepared from alkoxides, Trans. J. Br. Ceram. Soc. 92 (4) (1993) 161–164.

[14] M.P. Pechini, US Patent 3, 330, 697, 1967.

[15] M.A. Van De Graff, A.S. Burggraaf, Wet chemical preparation of zirconia powders: their microstructure and behaviors, in: N. Claussen (Ed.), Advances in Ceramics, 12, Science and Technology of Zirconia II, Am. Ceram. Soc., Columbus, OH, 1983, pp. 744–765.

[16] E. Mustafa, Ca-PSZ prepared via polymeric sol–gel route, Ceram. Int. 26 (2) (2000) 215–220.

[17] D.M. Ibrahim, E. El-Meliegy, Calcia stabilized tetragonal zirconia powders prepared by urea formaldehyde polymeric route, Trans. J. Br. Ceram. Soc. 99 (4) (2000) 159–163.

[18] D.M. Ibrahim, E. El-Meliegy, MgO as a co-dopant for ceria partially stabilized zirconia, in: N.P. Bansal, J.P. Singh (Eds.), Innovative Processing, Synthesis; Ceramics, Composites IV, Am. Ceram. Soc. Conf. 102, 2000, pp. 341–349.

[19] E. Mustafa, M. Wilhelm, W. Wruss, Microstructure and phase stability of Y-PSZ co-doped with MgO or CaO prepared via polymeric route, Trans. J. Br. Ceram. Soc. 101 (2) (2002) 1–5.