



## Effect of calcia co-doping on ceria-stabilized zirconia

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### ABSTRACT

Ceria-stabilized zirconia ceramics are characterised by excellent hydrothermal stability and high fracture toughness, but the fracture strength and hardness are lower than that of conventional 3Y-TZP, which is sensitive to low temperature degradation in humid environments. In the present work, the influence of small concentrations of calcia on the microstructure, mechanical properties and hydrothermal ageing resistance of 10 and 12 mol% CeO<sub>2</sub> stabilised ZrO<sub>2</sub> has been assessed. The addition of only 1 mol% of CaO had a strong refining effect on the microstructure resulting in an increased hardness and strength but reduced stress activated tetragonal-to-monoclinic transformability. The addition of 3 mol% CaO however enhanced the transformability with respect to 1 mol% CaO and preserved the high resistance to hydrothermal degradation of Ce-TZP.

### 1. Introduction

Tetragonal polycrystalline zirconia stabilized with 3 mol% of yttria (3Y-TZP) is widely used in dentistry owing to its biocompatibility, aesthetic appearance and excellent mechanical properties, which are related to its relatively high fracture toughness,  $K_{Ic}$ , and its small grain size [1,2]. The stabilization of the tetragonal phase at room temperature is possible by the yttrium (Y<sup>3+</sup>) substitution of zirconium (Zr<sup>4+</sup>) and concomitant formation of charge neutralizing oxygen vacancies. The main mechanism for the high  $K_{Ic}$  is transformation toughening, i.e. the transformation of the tetragonal ZrO<sub>2</sub> phase (*t*) into the monoclinic phase (*m*) by the tensile stresses around the crack tip. This is accompanied by a local volume expansion that induces a reaction compressive stress, reducing in this way the stress intensity factor at the crack tip [3]. However, the *t*→*m* phase transformation can also occur spontaneously at the surface in contact with humid environments inducing surface microcracking and an increase in roughness. This phenomenon, referred to as low-temperature degradation (LTD), is the main issue for the long-term reliability of 3Y-TZP in humid environmental applications [4]. The exact mechanism responsible for LTD is still not fully understood, but it is related to the annihilation of oxygen vacancies induced by the diffusion of water species from the surface in humid environments [5,6].

Tetragonal zirconia can also be stabilized at room temperature by cerium, Ce<sup>4+</sup>, instead of Y<sup>3+</sup> cations, without inducing oxygen vacancies. However, ceria stabilized zirconia (Ce-TZP) has a substantially larger grain size than 3Y-TZP, which is partly due to the need of higher

sintering temperatures and/or longer times for full densification. The grain growth of Ce-TZP at low temperatures is slow due to the slow diffusion kinetics of Ce<sup>3+/4+</sup> (compared to Y<sup>3+</sup>), requiring higher sintering temperatures, producing a larger and broader grain size distribution due to the absence of an effective grain growth retarding mechanism as it occurs in 3Y-TZP [7]. Dense 7–16 mol% CeO<sub>2</sub> stabilised zirconia ceramics with different grain sizes were fabricated and evaluated in terms of hardness, strength and fracture toughness by Tsukuma et al. [8]. They found a high fracture toughness, but also low hardness and fracture strength, which was associated with the relatively large micrometer grain size and high transformability under stress of the metastable tetragonal phase.

As the mechanical properties strongly depend on the grain size, it is expected that limiting the grain growth during sintering will decrease the high *t*-*m* transformability and increase the strength and hardness of Ce-TZP. In principle, this can be achieved by the addition of specific solutes which might segregate to the grain boundaries during sintering, reducing their mobility by a solute drag mechanism [7,9,10].

The effect of solutes has been previously investigated mainly in 3Y-TZP, where the addition of specific additives or impurities such as Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> or Fe<sub>2</sub>O<sub>3</sub> was established to be beneficial, acting as sintering aids or affecting *t*-phase stability and ageing resistance [11]. For instance, small amounts of homogeneously distributed alumina (less than 0.5 wt.%) can improve the LTD resistance [12,13]. Recent studies suggest that the ageing resistance of *t*-ZrO<sub>2</sub> can be enhanced even more by co-doping 3Y-TZP with small amounts of both alumina and lanthanum [14] or alumina and germania [15].

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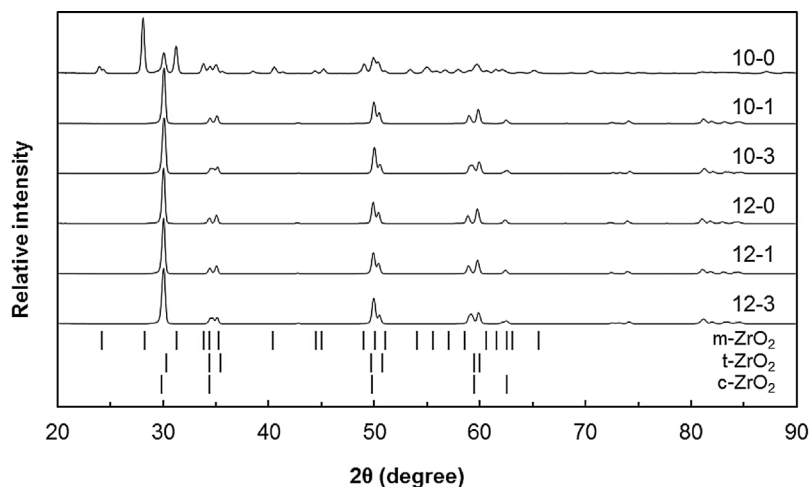
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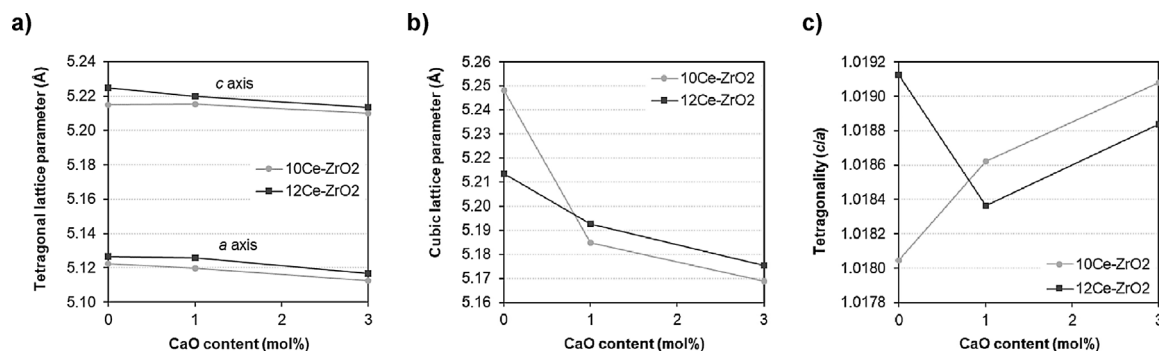
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**Table 1**  
Composition, density, grain size and constituent phases of the ceramics sintered for 2 h at 1500 °C.

Designation	CeO <sub>2</sub> (mol%)	CaO (mol%)	Density (g/cm <sup>3</sup> )	Avg. grain size (μm)	Monoclinic phase (wt%)	Tetragonal phase (wt%)	Cubic phase (wt%)
10-0	10	0	–	1.99 ± 0.75	76.7	20.5	< 3
10-1	10	1	6.14 ± 0.04	0.53 ± 0.23	< 1	91.8	8.2
10-3	10	3	5.99 ± 0.03	0.64 ± 0.35	< 1	65.1	34.9
12-0	12	0	6.19 ± 0.02	1.27 ± 0.74	< 1	97.0	< 3
12-1	12	1	6.17 ± 0.01	0.60 ± 0.24	< 1	89.9	10.1
12-3	12	3	6.07 ± 0.01	0.65 ± 0.31	< 1	61.8	38.2



**Fig. 1.** XRD patterns of polished surfaces of 10 and 12CeO<sub>2</sub>-ZrO<sub>2</sub> with 0, 1 or 3 mol% CaO addition. The main peaks of the monoclinic (m-ZrO<sub>2</sub>), tetragonal (t-ZrO<sub>2</sub>) and cubic (c-ZrO<sub>2</sub>) phases are marked.



**Fig. 2.** Lattice parameters of the (a) tetragonal and (b) cubic ZrO<sub>2</sub> phase, and (c) tetragonality of the t-ZrO<sub>2</sub> phase in the 10Ce and 12Ce-ZrO<sub>2</sub> doped with different amounts of calcia. The tetragonal data are presented using pseudo-cubic (distorted fluorite) unit cell.

One of the first studies on the influence of different oxides on the grain size of 3Y-TZP was carried out by Sato et al. [16]. They co-doped 3Y-TZP with 0–12 mol% of either CaO, MgO, CeO<sub>2</sub> or TiO<sub>2</sub> revealing that alloying with TiO<sub>2</sub> accelerated the grain growth and suppressed densification, but alloying with less than 6 mol% of CeO<sub>2</sub> caused no significant changes in grain size. CaO was the most effective oxide in reducing the tetragonal grain size, and cubic zirconia phase was already detected with only 2 mol% CaO addition [16].

In ceria-doped zirconia, partial substitution of ceria by yttria also resulted in a reduced grain size and in a more stabilized tetragonal structure, which increased the hardness but decreased the fracture toughness [17–21]. As Y<sub>2</sub>O<sub>3</sub> is more effective than CeO<sub>2</sub> regarding grain size refinement and tetragonal stability, co-doping zirconia with proper proportions of ceria and yttria results in a reduced grain size with respect to a Ce-TZP and a better LTD resistance than Y-TZP ceramics [7,16–18].

Grain growth in zirconia is strongly related to the composition and phase content, as observed in zirconia doped with Y<sub>2</sub>O<sub>3</sub>, where the grain growth of cubic grains can be two orders of magnitude faster than that of tetragonal grains alloyed with the same cation, but it can be

strongly suppressed if both phases coexist [22]. Grain growth depends strongly on the ionic radius and valence of the solutes. Oversized divalent and trivalent ions (such as Y<sup>3+</sup> and Gd<sup>3+</sup>) reduce the grain growth efficiently, but other oversized solutes with the same valence as zirconium, like Ce<sup>4+</sup>, have no effect [23–25]. The resistance to grain boundary mobility is related to the segregation of these ions at the grain boundaries and it increases with a higher solute concentration and a larger valence difference between the solute and the host cation [22,26].

The cation radius of the dopant also influences the ageing resistance of 3Y-TZP, obtaining an enhanced LTD resistance with large as well as with small cation trivalent dopants due to the stronger bond of the [M'<sub>Zr</sub>·V<sub>O</sub>'] defect clusters in the space charge layer at the grain boundaries, without affecting the mechanical properties [27].

In the present work, Ca<sup>2+</sup> has been used as a co-doping ion (up to 3 mol% CaO) in ceria-doped zirconia (10Ce-ZrO<sub>2</sub> and 12Ce-ZrO<sub>2</sub>) in order to refine its microstructure and increase the mechanical properties. The selection of Ca<sup>2+</sup> is justified by its low valence and very large ionic size (ionic radius of Ca<sup>2+</sup> and Zr<sup>4+</sup> are 112 and 84 p.m. respectively), which is expected to substantially reduce the grain size and

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