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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% CeO₂ stabilised ZrO₂ 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.

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% CeO₂ stabilised ZrO₂ 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.

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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 (Y³⁺) substitution of zirconium (Zr⁴⁺) 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 ZrO₂ 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^{4+} , instead of Y^{3+} 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 $\text{Ce}^{3+/4+}$ (compared to Y^{3+}), 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 to 16 mol% CeO_2 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_2O_3 , TiO_2 or Fe_2O_3 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_2 can be enhanced even more by co-doping 3Y-TZP with small amounts of both alumina and lanthania [14] or alumina and germania [15].

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_2 or TiO_2 revealing that alloying with TiO_2 accelerated the grain growth and suppressed densification, but alloying with less than 6 mol% of CeO_2 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_2O_3 is more effective than CeO_2 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_2O_3 , 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^{3+} and Gd^{3+}) reduce the grain growth efficiently, but other oversized solutes with the same valence as zirconium, like Ce^{4+} , 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 $[M'_{Zr} \cdot V_o'']$ defect clusters in the space charge layer at the grain boundaries, without affecting the mechanical properties [27].

In the present work, Ca^{2+} has been used as a co-doping ion (up to 3 mol% CaO) in ceria-doped zirconia (10Ce-ZrO₂ and 12Ce-ZrO₂) in order to refine its microstructure and increase the mechanical properties. The selection of Ca^{2+} is justified by its low valence and very large ionic size (ionic radius of Ca^{2+} and Zr^{4+} are 112 and 84 pm respectively), which is expected to substantially reduce the grain size and increase the hardness and strength of ceria-stabilized zirconia ceramics.

2. Experimental procedure

2.1. Sample preparation

Commercial co-precipitated ceria-stabilized zirconia powders with 10 and 12 mol% ceria (CEZ-10 and CEZ-12, Daiichi Kigenso Kagaku Kogyo) containing 0.25 wt% Al_2O_3 were mixed with different amounts of CaO (ReagentPlus® 99.9%, Sigma-Aldrich) in ethanol using 5 mm diameter zirconia balls (grade TZ-3Y, Tosoh) on a multidirectional mixer (Turbula T2F, WAB) for 24h. Both zirconia compositions had similar particle sizes in the range of 0.5–1 μm as reported by the supplier [28]. CEZ-12 was supplied in the form of spray dried granules. The particle size of the CaO powders was in the range 10–35 μm as observed in the SEM. After milling and mixing, the dried powders were sieved (315 μm mesh) and shaped by uniaxial pressing at 50 MPa followed by cold isostatic pressing at 250 MPa (EPSI). The green samples were sintered in air in a conventional small (with a cavity size of about 1 L) high-temperature furnace (LHT 02/17, Nabertherm) for 2h at 1500°C with a heating rate of 10°C/min. This temperature and time

1 were selected in order to improve the densification of the calcia-containing ceramics, as a
2 reduction of grain boundary mobility was expected, which could affect their sinterability. The
3 different compositions will be designated by X-Y where X and Y are the molar concentration of
4 ceria and calcia respectively.
5

6 The sintered ceramics were either in the form of discs of ~13.5 mm diameter and ~1.5 mm thick
7 or prismatic bars with dimensions ~3x4x45 mm. All samples were ground and polished following
8 the standard methods up to 3 µm diamond paste with a final polishing step using a 0.5 µm silica
9 suspension on the surfaces to be analysed.
10

11 The density of the samples was measured by the Archimedes method immersing the samples in
12 ethanol.
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14 2.2. Microstructural characterization

15 The grain size distribution was determined on polished surfaces and posterior thermal etching
16 at 1200 °C for 20 min, using the linear intercept method on more than 1000 grains per condition
17 from micrographs obtained by scanning electron microscopy (SEM, XL-30FEG, FEI). The
18 reported values are as-measured without any correction factor.
19

20 X-ray diffraction analysis (XRD, 3003-TT, Seifert) was performed on polished surfaces using Cu
21 K_α radiation at 40 kV and 40 mA, with a scan speed of 2 s/step and a scan step size of 0.02° in
22 the 20–90° 2θ range. In order to quantify the different phases, Rietveld refinements were
23 performed using TOPAS-Academic software (Bruker AXS). The phases were refined as:
24 monoclinic zirconia (*m*) with space group P21/c, tetragonal zirconia (*t*) with space group
25 P4₂/nmc and cubic zirconia (*c*) with space group *Fm* $\bar{3}$ *m*.
26

27 Hydrothermal degradation tests were performed in an autoclave in full steam atmosphere at 134
28 °C and 0.2 MPa pressure during 30 hours. The surface monoclinic content (*V_m*) was measured
29 by XRD analysis, and calculated according to the equation proposed by Garvie et al. [29] and
30 modified by Toraya et al. [30]:
31

$$32 V_m = \frac{1.311[I_m(\bar{1}11) + I_m(111)]}{1.311[I_m(\bar{1}11) + I_m(111)] + I_t(101)} \quad (1)$$

33 with *I_m* and *I_t* the intensity of the monoclinic and tetragonal peaks respectively.
34

35 High-resolution scanning transmission electron microscopy (HRSTEM) combined with energy
36 dispersive X-ray spectroscopy (EDS) was used to analyse thin foils on an aberration-corrected
37 transmission electron microscope (ARM200F, JEOL) operating at 200 kV, using a high-angle
38 annular dark-field (HAADF) detector. Thin-foil preparation for TEM analysis involved mechanical
39 thinning with diamond lapping films and polishing down to 100 µm before final preparation to
40 electron transparency using a JEOL Cryo Ion Slicer at 6 kV.
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2.3. Mechanical characterization

The biaxial flexure strength was measured on discs (5-8 specimens per condition) with a ball-on-three-balls testing fixture with 6 mm diameter balls using a servo-hydraulic testing machine (8511, Instron) [31], [32]. The maximum biaxial stress (σ_{max}) was calculated using the equation proposed by Fett et al. [33]:

$$\sigma_{max} \cong \frac{3F(1+\nu)}{4\pi t^2} \left[2 \ln \left(\frac{R}{\alpha t} \right) + \frac{1-\nu}{1+\nu} \left(\frac{R}{R_D} \right)^2 \right] \quad (2)$$

where F is the applied load, ν the Poisson ratio (taken as 0.28), t the thickness of the disc, R_D the disc radius, R the flexure radius (~ 0.35 mm) and $\alpha = 0.2$.

The fracture toughness was measured from small cracks in single-edge V-notched prismatic specimens (SEVNB) with a starting notch generated by ultra-short pulsed laser ablation (UPLA) (Ti : Sapphire, 120 fs, 795 nm, 1 kHz). The pulse energy used was 7–8 μ J (depending on the composition), and a scanning speed of 50 μ m/s. Four or six passes were needed to achieve the desired total crack depth of about 40 μ m. It was formed by an extremely sharp short notch, about 20 μ m deep and with a typical tip radius of less than 1 μ m, and by a narrow highly microcracked zone in the direction of the notch of similar length as the notch. Five V-notched bar specimens per condition were tested in a servo-hydraulic testing machine (model 8511, Instron) using a four-point bending test configuration with spans of 40/20 mm under a constant stress rate of ~ 100 MPa/s. The full description and assessment of the method can be found elsewhere [34]–[37].

The Vickers indentation fracture toughness test (VIF) was also used by indenting with a load of 294 N and measuring the radial crack patterns by means of laser scanning confocal microscopy (LEXT OLS3100, Olympus). This was carried out with the only objective to compare the results with those obtained by using single-edge cracked prismatic specimens, since the limitations of the indentation method are well known [38]. The equation used to calculate the indentation toughness was that of Niihara et al. for Palmqvist cracks [39]:

$$K_{Ic} = 0.018H\sqrt{a} \left(\frac{E}{H} \right)^{0.4} \left(\frac{c-a}{a} \right)^{-1/2} \quad (3)$$

where H is the Meyer's hardness measured by a Vickers indenter with a load of 98.1 N, E the elastic modulus (taken as 200 GPa from [40]), a a half of the diagonal of the indentation imprint and c the distance between the center of the indentation and the crack tip. For small indentation cracks, this equation can be used as far as $0.25 \lesssim (c-a)/a \lesssim 2.5$. However, in high toughness zirconia ceramics the transformation induced upon indentation takes place up to a distance of about a from the border of the imprint, so that indentation cracks shorter than $(c-a)/a \lesssim 1$ are severely affected by the transformation around the imprint. Therefore, the indentation method was only used when $(c-a)/a$ in equation 3 was between 1 and 2.5.

Confocal micro-Raman spectroscopy (inVia Qontor, Renishaw) was used to estimate the amount of monoclinic phase and to compare the phase transformability of the different ceramic

compositions. A Nd:YAG laser (wavelength 532nm) was used, with a spectrum integration time of 1 s. Single point measurements on the fracture surfaces of discs and bars and 2D mappings around Vickers indentations were performed. The monoclinic phase content was quantified applying the formula proposed by Katagiri et al. [41] and assessed by Tabares et al. [42].

Fracture surfaces were investigated using a SEM coupled with a focused ion beam (dual beam SEM/FIB) (Neon 40, Zeiss). The volume fraction of monoclinic phase on the fracture surfaces was estimated by XRD and calculated according to equation 1.

3. Results

3.1. Microstructure

Table 1 summarizes the microstructural and constituent phase characteristics in the CaO co-doped Ce-ZrO₂ ceramics. After sintering, monoclinic ZrO₂ was only detected in the 10-0, as shown in the XRD pattern presented in Figure 1, together with the presence of cracks on the surface. Hence, because of the presence of a high fraction of monoclinic phase, this specific composition was discarded for further analysis.

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

Designation	CeO ₂ (mol%)	CaO (mol%)	Density (g/cm ³)	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

Figure 1. XRD patterns of polished surfaces of 10 and 12CeO₂-ZrO₂ with 0, 1 or 3 mol% CaO addition. The main peaks of the monoclinic (m-ZrO₂), tetragonal (t-ZrO₂) and cubic (c-ZrO₂) phases are marked.

Rietveld analysis revealed an increasing cubic ZrO₂ content upon calcia addition, which is reflected in a slight change of shape of the peaks around 35° and 60° 2θ in Figure 1 (more remarkable in 10-3 and 12-3 compositions). Calcia is a strong stabilizer of the tetragonal phase in pure zirconia up to about 5 mol% CaO, where cubic ZrO₂ starts to form under equilibrium conditions. Therefore, it is expected that when used as a co-dopant in 10 or 12 mol% CeO₂, relatively small concentrations of calcia may already induce the cubic ZrO₂ phase formation. However, no information on the ternary ZrO₂-CeO₂-CaO equilibrium phase diagram seems to be available in literature. It should also be noted that the stabilization mechanisms of both dopants are different: CaO stabilizes the tetragonal phase by introducing anionic oxygen vacancies similarly to Y₂O₃, whereas CeO₂ stabilizes the t-ZrO₂ phase by dilating the cation network decreasing the strain energy and the relief of oxygen overcrowding [43], [44].

Calcia addition contracts both the tetragonal and cubic ZrO₂ unit cells, as shown in Figure 2a and b. Although the ionic radius of Ca²⁺ is larger than the radius of Ce⁴⁺ (112 pm and 97 pm respectively), the lattice contraction can be explained by the formation of oxygen vacancies [23]. For the 12Ce-ZrO₂ grades, the most thermodynamically stable t-ZrO₂ phase, i.e. the t-ZrO₂ phase with the lowest tetragonality or phase transformability, appears to be 12-1, but the transformability increases with further CaO addition (see Figure 2c). For the 10Ce-ZrO₂ grades, the transformability of the tetragonal phase also increases with calcia content. However, most of the t-ZrO₂ phase in 10-0 spontaneously transformed after cooling and only those t-ZrO₂ grains with the lowest tetragonality remained.

Figure 2. Lattice parameters of the (a) tetragonal and (b) cubic ZrO₂ phase, and (c) tetragonality of the t-ZrO₂ phase in the 10Ce and 12Ce-ZrO₂ doped with different amounts of calcia. The tetragonal data are presented using pseudo-cubic (distorted fluorite) unit cell.

Grain size measurements clearly showed that the large grains observed in the 10-0 and 12-0 disappeared with the addition of small amounts of calcia (≥ 1 mol%), which narrows and shifts the grain size distribution to smaller values (Figure 3). The reduction in grain size was already strong with only 1 mol% CaO addition. When co-doping with 3 mol% CaO, larger grains (pointed out by the arrows in Figure 3) can be identified in a finer grained matrix, which are attributed to the presence of higher volume fractions of larger cubic ZrO₂ grains, as revealed by Rietveld analysis (see Table 1).

Figure 3. Grain size distribution histograms of (a) 10Ce-ZrO₂ and (b) 12Ce-ZrO₂ with 0, 1 and 3 mol% CaO addition. The arrows indicate the appearance of a bimodal distribution.

TEM-EDS elemental mappings of 12-1 revealed a slight segregation of especially Ca but also Al and Ce to the grain boundaries (as illustrated in Figure 4a), together with a local grain boundary depletion of Zr. A substantially higher concentration of both Ca and Ce can be found in some grains, as shown in Figure 4b. Diffraction analysis of the same grains revealed that the dopant-rich larger grain has a cubic crystal structure, whereas the smaller grains with lower Ca and Ce stabiliser content have a tetragonal crystal structure (see Figure 4c).

Figure 4. HRSTEM EDS elemental mappings of the a) and b) 12-1 sample. c) TEM diffraction analysis of the same region as in b).

TEM-EDS point analysis were performed in different grains and on grain boundaries. A summary of the measured average composition, averaged over 3–5 point analysis measurements on 10 different grains, is provided in Table 2.

Table 2. Average concentration (in mol%) as determined by TEM-EDS point analysis inside tetragonal and cubic ZrO_2 grains and on the t-t and t-c grain boundaries (GB) in the 12-1 sample.

	CaO (mol%)	CeO ₂ (mol%)	Al ₂ O ₃ (mol%)	ZrO ₂ (mol%)
t grains	0.4 ±0.2	9.1 ±0.2	0.8 ±0.2	89.4 ±0.3
c grains	2.2 ±0.2	13.9 ±0.4	1.4 ±0.1	82.3 ±0.3
t-t GB	1.2 ±0.5	10.3 ±0.8	1.3 ±0.2	86.9 ±1.3
t-c GB	2.5 ±0.3	12.7 ±0.8	1.8 ±0.1	82.8 ±1.0

Figure 5 shows the XRD patterns of polished surfaces after 30 hours hydrothermal autoclave testing in steam at 134 °C, which theoretically corresponds to more than a human lifespan under *in vivo* conditions [45]. Only the 10-3 grade shows a small amount of monoclinic ZrO_2 phase, as estimated by equation 1 to be about 8 vol%.

Figure 5. XRD patterns of the surface of the different ceramic compositions after hydrothermal testing for 30 h. The arrow points at a small monoclinic peak detected on the 10-3 grade.

3.2. Mechanical properties

Table 3. Mechanical properties of 10 and 12Ce-ZrO₂ ceramics with 0, 1 and 3 mol% calcia.

Designation	Grain size (μm)	Hardness (GPa)	Biaxial tensile strength (MPa)	Fracture toughness (MPa√m)		Monoclinic content on fracture surface of discs (vol%)
				SEVNB	VIF	
10-0	1.99±0.75	6.2±0.1	--	--	--	>70
10-1	0.53±0.23	11.9±0.1	922±77	4.3±0.1	Small cracks	8.5±1.9
10-3	0.64±0.35	12.2±0.1	678±30	4.4±0.1	No cracks	20.0±2.1
12-0	1.27±0.74	9.6±0.1	591±53	4.5±0.1	No cracks	32.6±5.7
12-1	0.60±0.24	12.7±0.1	899±151	3.9±0.1	5.7±0.1	< 3
12-3	0.65±0.31	12.9±0.2	680±44	3.8±0.1	5.5±0.1	15.1±5.0

SEVNB= Single Edge V-Notch Beam method

VIF= Vickers Indentation Fracture method

Table 3 summarises the mechanical properties of the different compositions. The influence of CaO co-stabilization is strong as revealed by the increased hardness upon only 1 mol% calcia addition, as shown in Figure 6. This effect can be attributed to the strong reduction in grain size. The difference in hardness between 10-1 and 10-3 and between 12-1 and 12-3 is slight, but the 12Ce-ZrO₂ grades are harder than the 10Ce-ZrO₂ ones.

Figure 6. Meyer's hardness measured by 98.1 N Vickers indentation.

Similar biaxial flexure strengths are achieved for the co-doped 10 and 12Ce-ZrO₂, being higher for 1 mol% CaO (see Figure 7a). The average amount of monoclinic ZrO₂ phase on the fracture surfaces of the broken discs is severely reduced by the addition of CaO. By increasing the calcia concentration from 1 to 3 mol%, there is a small increase in the fracture surface monoclinic fraction and a decrease in flexure strength (Figure 7b).

Figure 7. a) Biaxial tensile strength (the value for 10-0 is taken from [40]) and b) volume fraction of monoclinic ZrO₂ phase on fracture surfaces,

The evolution of the t-ZrO₂ phase transformability with calcia addition was also studied by means of micro-Raman spectroscopy around Vickers indentations. Figure 8 shows the m-ZrO₂ content maps for the different ceramic grades confirming the trend in m-ZrO₂ volume measured on the fractured disc surfaces (Figure 7b).

Figure 8. Monoclinic phase content maps around 98.1 N Vickers indentations obtained by micro-Raman spectroscopy.

In some compositions, i.e. 10-3 and 12-0, no indentation cracks were formed. In 10-1 and 10-3 they were extremely short for applying Niihara indentation fracture toughness equation, that is, they did not fulfil the condition $(c-a)/a > 0.25$ (equation 3), even with an indentation load of 294N. Regarding the 10-0 composition, it was not investigated since the material was initially

mostly monoclinic. Well-developed crack radial patterns, suitable for applying Niihara's equation, were only formed in 12-1 and 12-3.

One must recall the lack of reliability of the indentation fracture toughness testing method, which has been extensively discussed in literature [38]. It has been stated that it is not a reliable technique to measure the fracture toughness of ceramics, and therefore other standardized methods should be used. However, the use of the indentation fracture toughness is here justified in order to compare with literature values. In addition, measuring the transformation zone around the Vickers imprints gives a very useful measurement of the degree of t-m transformability, but not necessarily of the fracture toughness.

From the flexure strength point of view, the key parameters are the size of the processing defects and the material's fracture toughness, unless unconstrained t-m transformation on the tensile surface takes place, originating defects from which fracture follows. This different possible behaviour of zirconia ceramics is illustrated in the plots of strength versus fracture toughness of Swain and Rose [46].

Here, the fracture toughness was determined from artificial small defects in the form of shallow single edge cracks, machined by UPLA as described in section 2.3. The K_{Ic} values obtained from these short straight edge cracks are summarised in Figure 9a. It should be noted that these values do not correspond to the often reported plateau levels of K_{Ic} for 10 and 12Ce-ZrO₂ ceramics (about 15 and 7 MPa√m respectively [47]), which are obtained by fracture mechanics testing standard methods from long cracks or by using Vickers indentation fracture toughness with very small indentation cracks. Instead, they rather represent the effective fracture toughness of small and not initially shielded cracks [36], for which the contribution of t-m toughening is rather small or negligible. Here, when it has been possible to measure fracture toughness by both methods, as in 12-1 and 12-3 grades, the values obtained are clearly different. Thus, by the SEVNB method with small cracks, the values found (3.9 and 3.8 MPa√m respectively) are significantly smaller than those obtained by Vickers indentation fracture toughness (5.7 and 5.5 MPa√m respectively).

Figure 9. a) Fracture toughness as measured by SEVNB. b) SEM images of fracture surfaces showing three different regions: notch (A), microcracked area (B) and regular fracture (C).

1 The fracture surfaces of the notched specimens were investigated by means of SEM, as shown
2 in Figure 9b, where the notch surface (region A), the fracture surface corresponding to the
3 microcracked area in front of the notch root (region B) and the final fracture surface (region C)
4 are clearly revealed as reported previously [34]–[37]. A higher magnification of the later surface
5 is shown in Figure 10, where it can be appreciated that when adding CaO, the clean
6 intergranular fracture in the 10-0 and 12-0 grades changed to a partially transgranular fracture.
7 Large cubic ZrO₂ grains that were pulled out during fracture can be clearly observed, as marked
8 by the white arrows in Figure 10. The area of fracture surface corresponding to cubic grains
9 increased with the amount of CaO addition as expected from the larger presence of this phase.
10 Figure 10 also clearly illustrates the strong reduction in grain size when adding 1 or 3 mol%
11 CaO to both 10 and 12 mol% CeO₂ ceramic grades. As already revealed on polished surfaces
12 (see Figure 3), 12-3 shows a bimodal grain size distribution with large c-ZrO₂ grains in a finer
13 grained t-ZrO₂ matrix.
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Figure 10. SEM images of fracture surfaces of notched specimens. Arrows point at cubic grains pulled out during the fracture leaving clean geometric intergranular fracture surfaces.

On a final note, the as-sintered ceramics showed an increasing greenish shade with increasing calcia content, being more notorious in the bulk, as observed in Figure 11a. The typical yellowish coloration of Ce-TZP ceramics, both on the surface and in the bulk, could be recovered by an additional conventional heat treatment (1200 °C for 1h) in a tubular furnace with air ventilation (ST-18, Hobersal), shown in Figure 11b. The change in colour could be attributed to a partial ceria reduction during the sintering process due to a lack of oxygen supply, as different colorations have been reported in literature when sintering Ce-TZP ceramics in different atmospheres and in reduced partial oxygen pressure. This effect seems to be related to the production of vacancies due to an oxygen deficiency [48]–[56]. Thus, it seems that ceria-stabilized zirconia ceramics are very sensitive to the oxygen supply in the furnace during

sintering, being able to reduce even in air in small conventional sintering furnaces, typically resulting in a colour gradient with a darker bulk and a brighter surface. No difference in hardness, indentation fracture toughness and transformability was observed between as-sintered (greenish) and heat-treated (yellowish) ceramics.

Figure 11. Color appearance of the ceramics (a) as-sintered and (b) after a heat treatment with air ventilation at 1200 °C for 1h.

4. Discussion

The high amount of monoclinic ZrO_2 content in the 10-0 grade can be explained by the increase in grain size during sintering at 1500 °C. This sintering temperature was used for all compositions in order to reach nearly full densification of the calcia-doped compositions. However, it produced large grains in the 10-0 specimens, which caused thermally-induced spontaneous transformation during cooling due to the relatively low stabilizer content [7], [17]. Spontaneous transformation to monoclinic after sintering has also been reported in literature for the same composition even at lower sintering temperatures, implying the M_s temperature of this material is above room temperature [47]. Moreover, the possible partial reduction of ceria (from Ce^{4+} to Ce^{3+}) during sintering can decrease the amount of dopant in the grains due to Ce^{3+} segregation to the grain boundaries [54], [57], [58], making them more prone to spontaneous transformation during cooling, producing micro- and macrocracks that affect the mechanical properties. It has been reported that the t-m transformation can be promoted in Ce-ZrO_2

ceramics by ceria reduction, obtaining mechanical properties which are sensitive to the sintering atmosphere and annealing temperature and time [58], [59].

It is remarkable that the addition of only 1 mol% calcia **strongly** enhances the stability of the tetragonal phase, reduces the grain size and increases the cubic volume fraction as determined by Rietveld analysis. In the 10-1 and 12-1 compositions, the increase in cubic ZrO_2 phase content is rather small, only about 5 and 7% respectively. The substantially **reduction** grain size from 1.3–2.0 μm for the compositions without calcia to about 0.6 μm for the specimens with 1 mol% CaO (see Table 1) is the main reason for the increase in hardness, with a concomitant further stabilization of the tetragonal phase, making t-m transformation more difficult [60]. This is clearly revealed in the analysis of the t-m transformation of 10-1 and 12-1 by micro-Raman around Vickers indentations (Figure 8), on the fracture surfaces of discs (Figure 7b), as well as on the fracture surface of SEVNB specimens (not shown here), where the amount of monoclinic phase is practically absent or strongly reduced. Not only the grain size influenced the transformability of the t- ZrO_2 grains, but also the presence of Ca^{2+} decreased the tetragonality and transformability of the t- ZrO_2 phase compared to that in 12Ce- ZrO_2 (see Figure 2c).

The distribution of solutes in the tetragonal and cubic ZrO_2 phases present with calcia co-doping is inhomogeneous. In these compositions, the cubic ZrO_2 phase is highly enriched in Ce and Ca solutes while the overall stabilizer content in the tetragonal neighbouring grains is lowered (see Table 2). This has been directly observed by TEM in 12-1 (see Figure 4 and Table 2) with a Ca concentration in the cubic grains more than five times higher than in the tetragonal grains. As the cubic ZrO_2 volume fraction increases considerably with 3 mol% CaO addition (see Table 1), this effect is expected to be even more significant in these compositions, as more cubic grains will be formed and poorer doped tetragonal grains will be **present**. This is reflected in **the increased transformability of the tetragonal phase when increasing the CaO composition from 1 to 3 mol%** (see Figure 2c, Figure 7b and Figure 8). The presence of a higher fraction of the intrinsically harder **and more brittle c- ZrO_2 phase [61] in 10-3 and 12-3 is compensated by a higher transformability of the tetragonal phase of these compositions**, so that their hardness **and Vickers indentation fracture are** comparable to 10-1 and 12-1, respectively.

The biaxial strength **of the two zirconia-ceria grades increased significantly** upon 1 mol% CaO addition because of the reduction in **tetragonal grain size and transformability. The high transformability and fracture toughness of 10-0 and 12-0 makes the strength likely to be controlled by the critical stress for t-m transformation. By contrast, the strong reduction in transformability of 12-1 seems to indicate that the strength is controlled by the fracture toughness and the size of natural flaws and not by the critical transformation stress [45].** Regarding 10-1, its behaviour is rather in the transition between both mechanisms since **although its transformability is strongly reduced with respect to 10-0, there is still significant t-m transformation around Vickers indentation imprints (see Figure 8).**

Co-doping with 3 mol% calcia reduced the bending strength to about 700 MPa for both Ce-ZrO₂ compositions. This is in line with an increasing presence of cubic phase in both compositions in the form of large grains as revealed on the fracture surfaces (see Figure 10).

The indentation fracture toughness could only be measured for the 12-1 and 12-3 compositions, in which cracks had suitable lengths to comply with the requirements of Niihara's equation (see equation 3) [62]. The indentation fracture toughness was 5.7 MPa√m for 12-1 and 5.5 MPa√m for 12-3, that is, very similar values and also close to those of 3Y-TZP (~5.5 MPa√m [21]) with a similar grain size. This can be understood considering that, although 12-1 is slightly less transformable than 12-3, it also has slightly less cubic phase than 12-3.

The higher transformability of 12-3 was not expected because of its higher total stabiliser content. It could be explained considering that the tetragonal phase composition does not have necessarily the equilibrium composition, since it is impoverished in stabiliser content by the presence of the cubic phase as shown in Table 2, increasing its transformability, seen as an increase of tetragonality in Figure 2c.

It can be noticed that the fracture toughness for the base materials (without calcia) obtained from notched specimens was rather low compared with the high values often quoted by other methods [47], [63]. Although the starting artificial unshielded cracks for measuring fracture toughness were small, they were long enough to control the fracture process in these compositions. Therefore, the flexure strength depends on the size of the crack length and of the shape of the R-curve. The low and similar K_{Ic} values measured for both materials are then related to the initial fracture toughness of the R-curve without hardly any contribution of t-m transformation toughening. It means that there is not stable crack extension before unstable fracture, because the starting crack is too small and the slope of the R-curve is not steep enough. Fracture was not controlled by the critical transformation stress on the surface of the flexure specimens, since the fracture stress applied on the tensile surface in the precracked specimens (~315 MPa) is lower than the reported values for the critical stress for t-m transformation (around 600 MPa in 11 mol% CeO₂ [8]).

Finally, all grades had a high ageing resistance, with only a small amount (< 10 vol%) of monoclinic phase detected for the 10-3 grade after 30h in water steam. This composition was expected to be the more susceptible to LTD, as it was also the more transformable with the highest t-ZrO₂ phase tetragonality among the CaO-doped ceramics studied (see Figure 2c, Figure 7b and Figure 8), and also because of the assumed higher oxygen vacancies introduced by Ca²⁺ into the pristine oxygen vacancy-free Ce-ZrO₂ material. The detrimental influence of the cubic phase in a 3Y-TZP on the ageing resistance due to the dopant deprivation of the tetragonal grains has been observed previously in literature [64]. However, as the ageing resistance of Ce-ZrO₂ base compositions is much higher than for 3Y-TZP [5], the influence of the impoverished tetragonal grains is lower than in 3Y-TZP.

5. Conclusions

In summary, the addition of 1 or 3 mol% CaO to 10 and 12Ce-ZrO₂ ceramics effectively reduces the grain size, increasing the hardness, fracture strength and cubic ZrO₂ phase content without compromising the hydrothermal ageing resistance. The CaO addition promotes the formation of a larger grained cubic ZrO₂ phase which accumulates a substantial amount of the stabilizing Ca²⁺ and Ce⁴⁺ cations. This reduces the stabiliser content of the tetragonal ZrO₂ phase making the ceramic more transformable when the amount of CaO is increased from 1 to 3 mol%.

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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 ₂ (mol%)	CaO (mol%)	Density (g/cm ³)	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

Table 2. Average concentration (in mol%) as determined by TEM-EDS point analysis inside tetragonal and cubic ZrO₂ grains and on the t-t and t-c grain boundaries (GB) in the 12-1 sample.

	CaO (mol%)	CeO ₂ (mol%)	Al ₂ O ₃ (mol%)	ZrO ₂ (mol%)
t grains	0.4 ±0.2	9.1 ±0.2	0.8 ±0.2	89.4 ±0.3
c grains	2.2 ±0.2	13.9 ±0.4	1.4 ±0.1	82.3 ±0.3
t-t GB	1.2 ±0.5	10.3 ±0.8	1.3 ±0.2	86.9 ±1.3
t-c GB	2.5 ±0.3	12.7 ±0.8	1.8 ±0.1	82.8 ±1.0

Table 3. Mechanical properties of 10 and 12Ce-ZrO₂ ceramics with 0, 1 and 3 mol% calcia.

Designation	Grain size (μm)	Hardness (GPa)	Biaxial tensile strength (MPa)	Fracture toughness (MPa√m)		Monoclinic content on fracture surface of discs (vol%)
				SEVNB	VIF	
10-0	1.99±0.75	6.2±0.1	--	--	--	>70
10-1	0.53±0.23	11.9±0.1	922±77	4.3±0.1	Small cracks	8.5±1.9
10-3	0.64±0.35	12.2±0.1	678±30	4.4±0.1	No cracks	20.0±2.1
12-0	1.27±0.74	9.6±0.1	591±53	4.5±0.1	No cracks	32.6±5.7
12-1	0.60±0.24	12.7±0.1	899±151	3.9±0.1	5.7±0.1	< 3
12-3	0.65±0.31	12.9±0.2	680±44	3.8±0.1	5.5±0.1	15.1±5.0

SEVNB= Single Edge V-Notch Beam method

VIF= Vickers Indentation Fracture method

Figure 1
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Figure 2
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Figure 3
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a)

b)

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Figure 1. XRD patterns of polished surfaces of 10 and 12CeO₂-ZrO₂ with 0, 1 or 3 mol% CaO addition. The main peaks of the monoclinic (m-ZrO₂), tetragonal (t-ZrO₂) and cubic (c-ZrO₂) phases are marked.

Figure 2. Lattice parameters of the (a) tetragonal and (b) cubic ZrO₂ phase, and (c) tetragonality of the t-ZrO₂ phase in the 10Ce and 12Ce-ZrO₂ doped with different amounts of calcia. The tetragonal data are presented using pseudo-cubic (distorted fluorite) unit cell.

Figure 3. Grain size distribution histograms of (a) 10Ce-ZrO₂ and (b) 12Ce-ZrO₂ with 0, 1 and 3 mol% CaO addition. The arrows indicate the appearance of a bimodal distribution.

Figure 4. HRSTEM EDS elemental mappings of the a) and b) 12-1 sample. c) TEM diffraction analysis of the same region as in b).

Figure 5. XRD patterns of the surface of the different ceramic compositions after hydrothermal testing for 30 h. The arrow points at a small monoclinic peak detected on the 10-3 grade.

Figure 6. Meyer's hardness measured by 98.1 N Vickers indentation.

Figure 7. a) Biaxial tensile strength (the value for 10-0 is taken from [39]) and b) volume fraction of monoclinic ZrO₂ phase on fracture surfaces.

Figure 8. Monoclinic phase content maps around 98.1 N Vickers indentations obtained by micro-Raman spectroscopy.

Figure 9. a) Fracture toughness as measured by SEVNB. b) SEM images of fracture surfaces showing three different regions: notch (A), microcracked area (B) and regular fracture (C).

Figure 10. SEM images of fracture surfaces of notched specimens. Arrows point at cubic grains pulled out during the fracture leaving clean geometric intergranular fracture surfaces.

Figure 9. Color appearance of the ceramics (a) as-sintered and (b) after a heat treatment with air ventilation at 1200 °C for 1h.