

Effects of sintering on Y_2O_3 -doped CeO_2

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Properties

ABSTRACT

Purpose: Having high electrical conductivity, Y_2O_3 -doped CeO_2 is a good candidate for various high temperature electrochemical devices, such as solid oxide fuel cells and oxygen gas sensor. However, its inferior mechanical properties compared to its competitors, e.g. ZrO_2 -based electrolytes, has restricted its usage.

Design/methodology/approach: The present work evaluates the sintering behavior and mechanical properties of CeO_2 , and aims to enhance the mechanical properties and sinterability while restricting the grain growth by doping with Y_2O_3 .

Findings: The relative density, rather than the Y_2O_3 concentration, was the most important factor that affected the mechanical properties of CeO_2 . Increase of density resulted in higher hardness and elastic modulus, and lower the fracture toughness of CeO_2 . In the optimum condition, the K_{IC} of 5.1 $MPa.m^{1/2}$, nanohardness of 13.0 GPa, and elastic modulus of 371.5 GPa were obtained for the undoped CeO_2 (density = 98.00%) sintered at 1700°C.

Research limitations/implications: This study does not include sintering at higher temperatures. It is also worth investigating formation of oxygen vacancy or Ce_2O_3 material in the Y_2O_3 -doped CeO_2 .

Practical implications: It is noteworthy that in this study, the high temperature calcination of mixed powders is avoided in order to keep yttria as a second phase (not as a solute) in the ceria matrix. This enables yttria to be more effective to suppress the grain growth.

Originality/value: The objectives are to improve the mechanical properties and to reveal the effects of various parameters, such as density, grain size, and yttria doping on the nano/micro indentation behavior of ceria material.

Keywords: Mechanical properties; Sintering; Grain size; Y_2O_3 -doped CeO_2

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1. Introduction

Cerium oxide (CeO_2 , ceria)-based materials are widely used in various industrial applications [34,35], such as solid oxide electrolysis cells (SOECs) [1], solid oxide fuel cells (SOFCs) [2], and oxygen gas sensor [3]. Being a refractory material, CeO_2 -based materials are difficult to densify even when sintered at higher temperatures, and increase of sintering temperature in order to approach the full density would result in the significant grain growth and deterioration of mechanical [4, 5] and electrical [6] properties of ceria material. In order to suppress the grain

growth, two approaches, either preparing nano powders or using a sintering dopant have been considered.

There have been some works [7, 9] investigating the effect of various dopants, such as MnO_2 , Ga_2O_3 , and Fe_2O_3 on the sintering behavior of ceria material. Chen et al [10] investigated effect of different aliovalent and heterovalent dopants on the grain boundary mobility of CeO_2 , and found that among all, Y^{3+} exhibits the most effective suppression of grain growth. According to Ruiz-Trejo et al [11], Y^{3+} -doped CeO_2 is also a serious candidate for variety of high-temperature electrochemical devices. However, there have been just a few studies [12, 13] on the sintering behavior of Y_2O_3 (yttria)-doped CeO_2 . The first part

of this study investigates the sintering behavior of Y₂O₃-doped CeO₂, and aims to enhance the sinterability while prohibiting grain growth by adding various amounts of Y₂O₃ mater. It is noteworthy that in this study, the high temperature calcination of mixed powders is avoided in order to keep yttria as a second phase (not as a solute) in the ceria matrix. This enables yttria to be more effective to suppress the grain growth.

CeO₂-based electrolytes have higher low temperature electrical conductivity compared to ZrO₂-based materials [14], which are most commonly used in the SOFCs applications. However, the inferior mechanical properties of CeO₂ have restricted its industrial applicability. There have been some studies on the mechanical properties of CeO₂-based materials [14, 15], but just a few studies on the mechanical properties of ceria obtained via nano indentation technique [16, 17]. This work also evaluates the nano indentation (nano hardness and elastic modulus) and micro indentation (Vickers hardness and toughness) properties of undoped and Y₂O₃-doped CeO₂. The objectives are to improve the mechanical properties and to reveal the effects of various parameters, such as density, grain size, and yttria doping on the nano/micro indentation behavior of ceria material.

2. Experimental Procedure

Micro size ceria powder (CeO₂, 99.9%, from SIGMA-ALDRICH) with an average grain size of 0.38 μm was used as a raw material in the present study. To make the yttria-doped ceria powder, the desired amounts (0.25, 0.5, 1.5, and 8 mol%) of yttria (Y₂O₃, 99.9%, from SIGMA-ALDRICH) and ceria were dispersed in ethanol, stirred in the ultrasonic bath for 2 hr, and finally dried in the oven at 50°C. Deagglomeration of powder was done by grinding the dried precipitates in the pistol and mortar for approximately 30 min.

Cylindrical pellets (green density = 57%) of 10 mm diameter and 6 mm height were prepared by cold uniaxial pressing. Yttria-doped ceria (henceforth named YC, for example 0.25YC for 0.25 mol% yttria-doped ceria) green bodies were heated up with the rate of 5 deg/min, and sintered at the various temperatures (Ts) of 1550°C and 1700 °C without applying any sintering dwell time (t_s). The undoped samples (for example pure ceria, henceforth named PC) were sintered at 1550°C, and kept for the various sintering times of 0 to 14 hr. The density (ρ) of the sintered samples (average of 5 runs) was determined by the Archimedes method using distilled water as a displacement liquid. To measure the relative density, theoretical densities of 7.132 and 5.013 g/cm³ were used for the ceria and yttria, respectively. In the case of yttria-doped samples, the theoretical densities were calculated according to the rule of mixtures [18]. The microstructures of the ceramics were investigated using the scanning electron microscopy (SEM, JSM-5600LV). The average grain size was determined by SEM micrograph of surface using the linear intercept technique [19].

The elastic modulus (E) and nano hardness (H_n) of samples at the room temperature were measured from the load-displacement nano indentation data using the widely accepted Oliver and Pharr method [20]. The samples were mechanically polished down to 1 μm diamond paste prior to the indentation test. The nano indentation was carried out using XP nano indenter with a three-

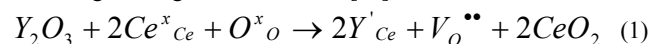
sided pyramidal Berkovich diamond indenter. The samples were loaded at 2 and 50 mN, held for 2 sec then unloaded. At least 20 indentations were made, and the average E and H_n were determined.

In order to measure the micro indentation properties, the specimens were indented with Vickers indenter (FM-300e) for an indentation time of 5 sec. At least 10 indentations were done, and the Vickers hardness and fracture toughness of samples were calculated [21] by measuring the average indentation diagonal half-length and crack length emanating from the indentation corner at the indentation loads (P) of 0.25 and 20 N, respectively.

3. Results and Discussion

3.1. Grain size and sintering behaviour

Effect of yttria concentration on the sinterability of ceria powders sintered at 1550°C and 1700°C is shown in Figure 1. The relative density of samples sintered at 1550°C increased with the increase of yttria concentration up to 0.5 mol%, and then decreased for the higher additive concentrations. According to the XRD results [22] of Y₂O₃-doped samples sintered at 1550°C, Y₂O₃ with the concentrations lesser than 0.5 mol% entirely dissolved in the CeO₂ matrix. Dissolution of Y³⁺ ions in the ceria crystal structure would result in the formation of oxygen vacancy according to Kroger-Vink notation [23],



Since interstitial cation diffusion is a rate limiting mechanism in the ceria-based materials, increase of oxygen vacancy (V_o^{''}) would result in the formation of interstitial cerium (Ce_i^{''}) (Equation 2) [10], and enhancement of ionic diffusivity and sinterability of samples as a result.

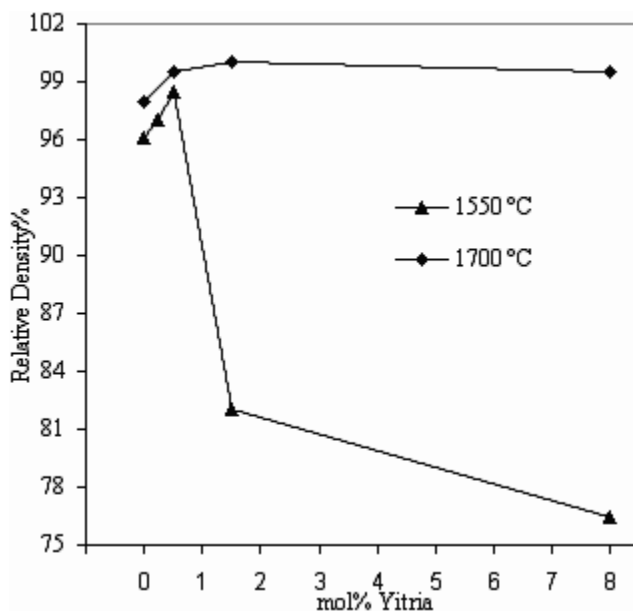


Fig. 1. Relative density of Y₂O₃-doped CeO₂ as a function of dopant concentration

$$[Ce_i \dots] = [V^{..}_o]^p \frac{k_F}{k_S} \exp\left(-\frac{\Delta G_F - \Delta G_S}{kT}\right) \quad (2)$$

where k_F and k_S are the temperature-independent constant, ΔG_F and ΔG_S refer to Frenkel and Schottky defect formation, k is Boltzmann constant, and T is temperature.

The sharp decrease in the relative densities at the higher yttria concentrations e.g., samples 1.5YC (82.00%) and 8YC (76.50%) sintered at 1550°C can be attributed to the distortion of ceria lattice structure due to exceeding the solubility limit, and precipitation of larger amount of yttria in the ceria matrix [24].

The relative density of YC samples sintered at 1700°C increased consistently with the increase of Y_2O_3 concentration. This can be attributed to the dissolution of yttria molecules or the faster atomic diffusion at the higher temperatures, which can supersede the deteriorating effect of lattice distortion at the higher yttria concentrations. However increase of yttria concentration up to 8 mol% resulted in the presence of micro cracks and a slight decrease in the relative density at this temperature. Nearly full density of 99.99% was obtained for the 1.5YC sample sintered at 1700°C.

Figure 2 shows the effect of yttria concentration on the grain size of samples sintered at 1550°C and 1700°C. At the both of sintering temperatures, the grain size of YC samples consistently decreased with the yttria concentration. This can be attributed to the solute drag effect [10] or Zener effect [25] of second phase, which suppresses grain boundary mobility and grain growth of samples as a result. The effect of yttria doping to suppress the grain growth is obvious from the SEM images of samples PC (98.00%, 26.4 μm) and 1.5YC (99.99%, 10.7 μm) sintered at 1700°C (Figs. 3a and b). A slight increment in the grain size of 0.5YC sample sintered at 1700°C can be attributed to the higher solubility of yttria at the higher temperature, which would result in the formation of oxygen vacancies and increase of diffusion rate [10] and grain size of sample as well.

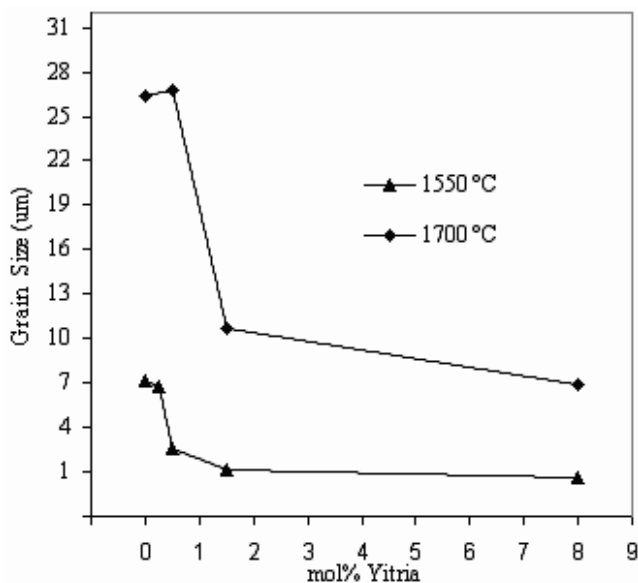


Fig. 2. Post-sintering grain size of Y_2O_3 -doped CeO_2 as a function of dopant concentration

Considering the results in Figures 1 and 2; it can be deduced that, higher amounts of yttria doping are preferential at the higher sintering temperatures due to the significant effect of yttria on suppressing the grain growth while not deteriorating the relative density at the same time; whereas at the lower sintering temperatures an optimum amount of yttria should be defined to obtain both advantages of small grain size and high degree of relative density. However, the formation of macro cracks at the higher amounts of yttria doping needs further study.

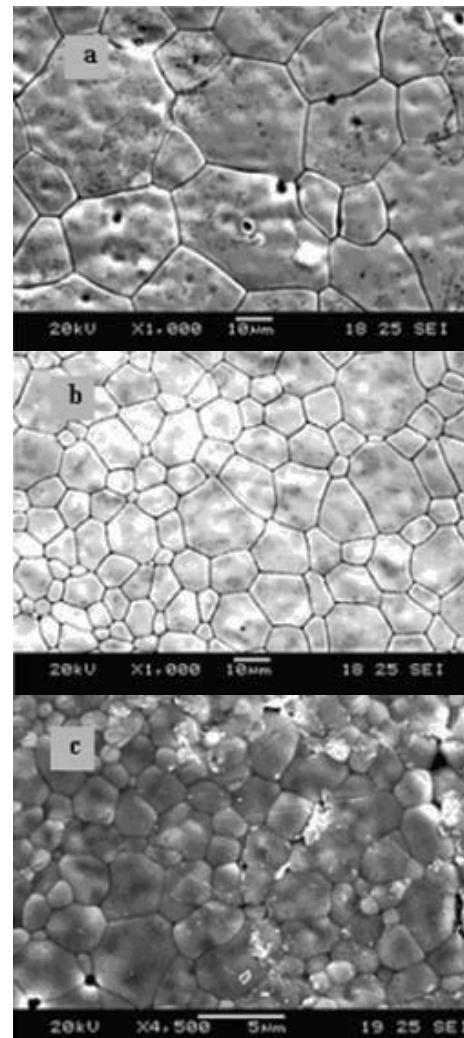


Fig. 3. SEM images of (a) undoped CeO_2 sintered at 1700°C (grain size = 26.4 μm , density = 98.00%); (b) 1.5 mol% Y_2O_3 -doped CeO_2 sintered at 1700°C (grain size = 10.7 μm , density = 99.99%); and (c) 0.5 mol% Y_2O_3 -doped CeO_2 sintered at 1550°C (grain size = 2.5 μm , density = 98.50%)

In the optimum condition, high relative densities of 98.50 and 99.99% with the grain sizes of 2.5 and 10.7 μm were obtained for the 0.5YC and 1.5YC samples sintered at 1550°C and 1700°C, respectively. The grain size obtained for sample 0.5YC was smaller than a reported value of 6 μm [12] for the 3 mol% yttria-doped ceria

with the same relative density of 98.5%. Avoiding ball milling of admixture of primary powders in order to keep yttria as a second phase (to enhance Zener effect [25]) -not as a solute- in the ceria matrix may be responsible for the smaller grain size obtained here. However, these two samples had large grain size distributions (Figures 3b and c) for example, the grain size of 1.5YC sample sintered at 1700°C ranged from 3.2 to 14.7 μm.

3.2. Nano and micro hardness

It is generally accepted that the indentation hardness increases with decrease of indentation force (indentation size effect (ISE)) [26]. In order to obtain a complete understanding of indentation phenomena over a wider range of applied test load, and also to compare the present results with the other literatures, the indentation properties of samples were investigated at the various loads of 2 and 50 mN (nano range), and 0.25 N (micro range). As it is expected, the nano hardness results were larger than the micro hardness. The main reason can be explained as the analysis of the nano indentation hardness using the projected contact area at the peak load instead of the projected area, as well as the purely elastic contact assumption describing the elastic/plastic indentation process [27].

The effect of yttria doping on the nano and Vickers hardness of YC samples sintered at 1550°C is shown in Figure 4. In general, both nano and Vickers hardness increased with the increase of yttria doping up to 0.5 mol%, and then decreased for further amounts of doping irrespective of the various loads were used to measure the hardness. This can be attributed to the superseding effect of density (Figure 1) than yttria doping on the hardness (Figure 4) of samples. Sample 8YC sintered at 1550°C with a lowest relative density of 76.50% had the minimum H_V of 2.0 GPa, and H_n of 10.3 and 3.8 GPa at 2 and 50 mN loading respectively, whereas in the same condition, a larger H_V of 5.9, and H_n of 24.7 and 11.6 GPa were obtained for 0.5YC sample which had a maximum relative density of 98.50%.

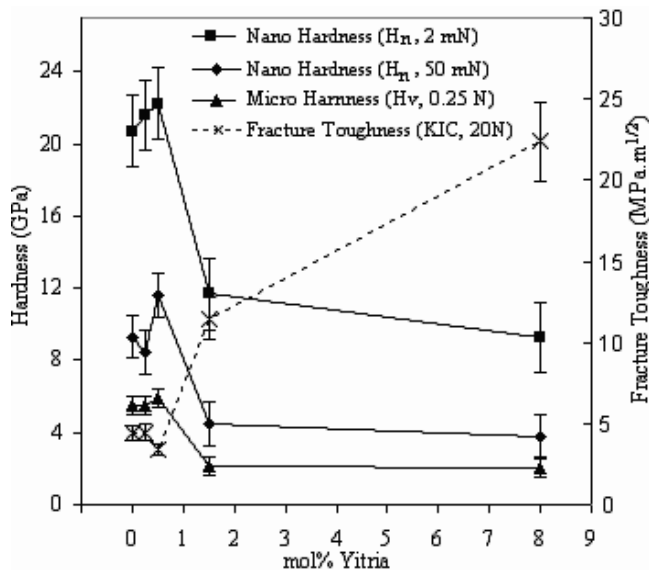


Fig. 4. Effect of Y_2O_3 doping on the Nano and Micro hardness, and fracture toughness of CeO_2 samples sintered at 1550°C

Samples sintered at 1700°C had larger hardness values than the ones sintered at 1550°C due to their higher values of relative densities (Table 1). The 1.5YC sample ($\rho = 99.99\%$) sintered at 1700°C revealed the largest H_V of 8.9, and H_n of 55.0 and 15.7 GPa at the various loads of 2 and 50 mN, respectively. These results are higher than the H_n of 9 GPa [17] ($\rho = 94\%$) at 5 mN loading and H_V of 3.9 GPa [28] ($\rho = 94\%$) at 20 N loading, which have been reported for undoped ceria. H_n value of 55.0 obtained for 1.5YC sample ($T_s = 1700^\circ C$) at 2 mN loading is also much higher than the reported H_n of 18.3 GPa [20] for yttria-doped zirconia at 1 mN loading. Effect of density on the hardness results was also obvious from the result of PC samples sintered at 1550°C for 0, 8, and 14 hr (Table 1). In general, these samples were harder when compared to the lower densified 1.5 YC, 1550°C sample and 8YC, 1550°C sample.

To study effects of second phase or solid solution strengthening on the hardness of ceria, the yttria concentration was sharply increased to 8 mol%, but as it is seen from Figure 4, the hardness decreased for the 8YC sample sintered at 1550°C. According to the literatures [4, 29], grain size is the other important factor that can affect hardness of both cubic and non-cubic ceramic materials. However, due to the superseding effect of density on the hardness, this trend was not very obvious here. The direct effect of density on the hardness of ceramics also has been reported by some others [30].

3.3. Fracture toughness

The fracture toughness (K_{IC}) results obtained by applying Vickers indentation at 20 N loading are shown in Figure 4 and Table 1. In general, K_{IC} decreased with the increase of hardness and density e.g., sample 1.5YC, 1700°C with the maximum values of hardness and density revealed the lowest K_{IC} of 3.4 $MPa.m^{1/2}$. In the optimum condition, the K_{IC} of 5.1 $MPa.m^{1/2}$, H_V of 7.7 GPa, and H_n of 13.0 GPa (at 50 mN loading) were obtained for the PC sample ($\rho = 98\%$) sintered at 1700°C. The K_{IC} value obtained here was larger than the reported K_{IC} of 1 to 2 $MPa.m^{1/2}$ for the undoped ceria [28, 31]. This can be attributed to the different methods or different values of E used to measure K_{IC} . In other hand, this higher value can also be attributed to the lower processing defects of samples produced here.

Effect of density on the fracture toughness of samples can be explained by considering the basic equation (Equation 3) for the fracture toughness of ceramics,

$$K_{IC} = \sqrt{EG_C} \quad (3)$$

where E is the elastic modulus and G_C is known as a critical elastic energy release rate. Density would affect the value of fracture toughness by activating micro crack formation and extension, or deflection toughening (in the case of larger fraction of porosity) mechanisms [15]. Briefly, these mechanisms explain that, presence of any micro crack, defect, or porosity inside the material would result in the increase of G_C or strain energy release rate by extension of micro cracks and redistribution of stress ahead of the crack tip or by modifying the crack path. In summary, decrease of density, which results in the increase of porosities or defects fraction inside the material will increase the G_C and K_{IC} of samples as a result.

Table 1.

Mechanical properties of undoped and yttria-doped ceria samples sintered at 1550°C and 1700°C

Sample Name	Relative Density %	Modulus (GPa)		Nano Hardness (GPa)		Vickers Hardness (GPa) 0.25 N	Toughness MPa.m ^{1/2}	Remarks
		2 mN	50 mN	2 mN	50 mN			
PC	98.00	686.7	371.5	39.7	13.0	7.7	5.1	T _s = 1700°C
1.5YC	99.99	964.0	389.0	55.0	15.7	8.9	3.4	t _s = 0 hr
PC 0 hr	96.13	451.0	252.0	23.0	9.3	5.5	3.9	T _s = 1550°C
PC 8 hr	97.50	464.3	287.3	23.8	10.3	5.2	3.7	t _s = 0, 8 & 14 hr
PC 14 hr	98.30	390.5	284.2	19.1	10.4	4.6	4.2	hr

The effect of crack deflection mechanism to improve the fracture toughness of samples is evident from the micro indentation image (Figures 5a and b) of samples YC0.5 (98.50%) and YC8 (76.50%) sintered at 1550°C. The crack observed at the corner of YC8 projection (Figure 5b) is quite sharp and straight, whereas the crack exhibits in the YC8 indentation (Figure 5a) is propagated and deflected multiple times due to the interaction of micro crack with the porosity inside the sample with the smaller relative density.

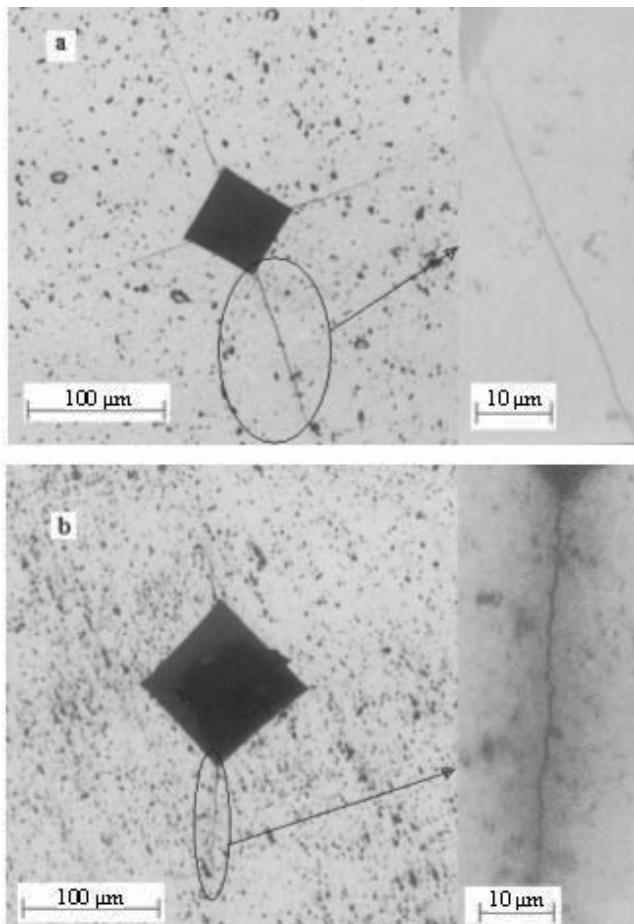


Fig. 5. Vickers indentation images of samples (a) YC0.5, 1550°C (density = 98.50%) showing sharp crack; and (b) YC8, 1550°C (density = 76.50%) showing deflected crack

3.4. Elastic modulus

The same effect of density on the hardness results was observed for the elastic modulus (E) of samples sintered at 1550°C and 1700°C (Table 1 and Figure 6). Sample 1.5YC sintered at 1700°C with a nearly full density of 99.99% had the highest E value of 964.0 and 389.0 GPa at 2 and 50 mN loading, respectively. These results are higher than the E value of 270.0 GPa at 5 mN loading which was reported by Wang et al¹⁷ for ceria with a relative density of 94%. Wang also revealed E value of 264 GPa for the undoped ceria using the four-point method. This result is near to the E values obtained here for the samples with the lower relative densities of 96.00 to 98.00% (Table 1).

There is not any good explanation that clarifies effect of density on the elastic modulus of samples; this is because the elastic modulus mostly depends on the intrinsic atomic bonding energy rather than the atomic movement. However, the E values were measured from the indentation load curve, and the density effect, as it is also reported by Atkinson et al³², can be applied again to explain the different values of E obtained for the various yttria concentrations.

Wang et al [33] have reported the reciprocal effect of oxygen vacancy on the elastic modulus of ceria due to the expansion of Ce-O bond length. However, as it is obvious from Figure 6 and Table 1, the elastic modulus of YC samples sintered at 1550 (up to 0.5 mol %) and 1700°C increased with the increase of yttria concentration (increase of oxygen vacancy (Equation 1)). So the effect of yttria doping to decrease the elastic modulus of samples seems to be superseded by the density effect in this work.

4. Conclusions

This work investigated sinterability, post-sintering grain size, and nano/micro indentation properties of Y₂O₃-doped CeO₂ material. The main conclusions are:

- In general, increase of yttria concentration enhanced the sinterability slightly, but it significantly suppressed the grain growth of samples. In the optimum condition, high relative densities of 98.50 and 99.99% with the grain sizes of 2.5 and 10.7 μm were obtained for the 0.5 mol% and 1.5% yttria-doped samples sintered at 1550°C and 1700°C, respectively.
- Relative density rather than the yttria concentration or grain size was the most important factor that affected mechanical properties of ceria. Increase of density resulted in the larger nano and Vickers hardness and the larger elastic modulus as well. Smaller values of density resulted in the larger amounts

of fracture toughness (K_{IC}) due to activation of crack deflection mechanism at the smaller densities. In the optimum condition, the of $5.1 \text{ MPa}\cdot\text{m}^{1/2}$, nano hardness of 13.0 GPa, and elastic modulus of 371.5 GPa were obtained for PC sample ($\rho = 98.00\%$) sintered at 1700°C .

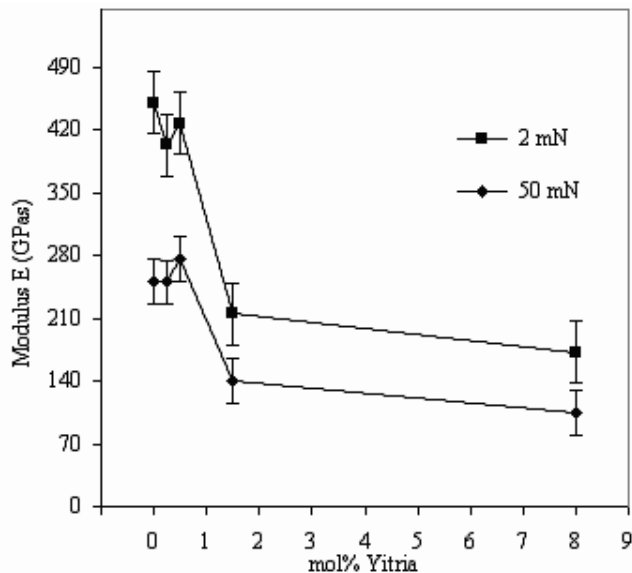


Fig. 6. Elastic modulus of Y₂O₃-doped CeO₂ sintered at 1550°C as a function of dopant concentration

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