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Elastic moduli of pure and gadolinium doped ceria revisited: Sound velocity measurements

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ABSTRACT

The Young's, shear and bulk moduli of dense (>95%) Gd-doped ceria ($Ce_{1-x}Gd_xO_{2-x/2}$) ceramics were determined as a function of Gd content using the ultrasonic pulse-echo method and corrected for porosity according to both static and dynamic models. With increasing defect concentration (0–20 mol% Gd), the Young's and shear moduli decrease linearly by 10% while for 29 mol%, the values lie above the linear fit; the bulk modulus decreases linearly within the complete range. We conclude that structural changes, induced by oxygen vacancy ordering for x > 0.2, may influence the uniaxial and shear moduli, leaving the bulk modulus unaffected.

Pure and doped ceria are among the most technologically important materials for diverse industrial applications such as automobile exhaust catalysts, oxygen sensors and fuel cells. In addition to such practical interest, ceria has also attracted considerable attention in basic materials research due to the richness of its chemical and mechanical properties. The oxygen ion conductivity of Gd^{3+}-doped ceria ($Ce_{1-x}Gd_xO_{2-x/2}$; GDC) has been studied extensively, while characterization of its complex mechanical properties is particularly important for practical applications, especially in the case of microscopic fuel cells. Both experimental [1–3] and theoretical investigations [4,5] have suggested that there is an inverse relationship between the elastic (Young's) modulus and Gd content. However, despite the availability of a considerable volume of data [1,2,4,6–15] this question remains a subject of heated discussion. Certainly, more accurate data would contribute to improved theoretical understanding of the defect structure [16–18]. In 2012, Korobko *et al.* used nanoindentation of large grain size ceramics to determine the Young's modulus of Gd-doped and also of Pr^{3+}, Pr^{4+} and Lu^{3+} doped ceria [19]. The Young's modulus of Gd^{3+}-doped ceria was found to be in the range of 204–228 GPa for dopant concentration 0–20 mol%, and that of Pr^{3+}-doped ceria, 208–230 GPa within the same concentration range [20]. Since no trend could be detected within the observed range, either the Young's modulus does not depend on dopant content, or the magnitude of the dependence on doping is ≤11%. However, reducing the uncertainty in the nanoindentation measurements is challenging. Although nanoindentation probes the elastic properties of a single grain and is not affected by porosity, Gd-doped ceria is strongly anelastic [19,20]. This requires that the measurements be made rapidly (<2 s), which adversely affects their possible accuracy. On the other hand, bulk measurement techniques (impulse excitation [9], flat punch [1], forced resonance [3]) can produce highly accurate values for elastic moduli when sample density is > 95% theoretical. However, such dense Gd-doped ceria ceramics are difficult to prepare. Consequently, elastic moduli values determined for these materials by the bulk methods must be corrected for high levels of porosity and this reduces their reliability.

In the current work, we provide experimental evidence that the elastic moduli of Gd-doped ceria display a small, but readily detectable, decrease as the Gd content increases from 0 to 29 mol%. In order to reach this conclusion, we succeeded in preparing ceramics of Gd-doped ceria with density > 95% theoretical and determined their elastic properties by the ultrasonic pulse-echo method of measuring sound velocity. The moduli of the pore-free compounds were determined by correcting the measured values for the relatively low levels of porosity.

Powders of pure and Gd-doped ceria were prepared by a co-precipitation method similar to that described in ref. [19]. The resulting powders were calcined at 500 °C for 3 h to remove residual water, ammonium ions, carbonates and nitrates. Powders were pressed uniaxially (~1 MPa) in either 10 mm or 18 mm dies followed by isostatic pressing at 300 MPa for 5 min to form a green body. The green body was sintered in a two-step sintering procedure [21], with

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the maximum temperatures in the first and second stage 1450 °C and 1275 °C respectively, with subsequent cooling at a rate of 5 °C/min. The density, ρ, of the resulting pellets was measured by the Archimedes technique using deionized water (18 MΩ cm) as the working liquid. The densities of the >30 samples measured were >95% theoretical (Fig. 1a). For the highly dense samples (>98% theoretical), no visible porosity was observed in scanning electron microscopy images (Supra 55 FEG Zeiss HRSEM)(Fig. 1b,c) and grain sizes were within the range of 0.3–1.5 μm. According to the X-ray powder diffraction data (XRD, Rigaku Ultima III) samples with $0 \le x \le 0.2$ were in a pure fluorite (Fm-3m) phase (Fig. 2a) with the lattice parameter increasing linearly with Gd content (Fig. 2c). The lattice expansion is 1.2% per mole Gd, which matches the values reported previously in ref. [19,22] and is close to the value reported in ref. [23]. A slow-scan XRD pattern of a sample with $x = 0.27$ showed diffraction peaks characteristic of the Ia-3 (double fluorite) phase, as expected for this composition [22] (Fig. 2b). The large linewidth and relative integrated intensity of the Ia-3 peaks are consistent with the presence of anti-phase domains, observed previously for both Gd and Y doped ceria [24,25]. The composition of each sample was verified with energy dispersive spectroscopy (EDS) at 25 kV acceleration voltage (Bruker XFlash 6–60).

The shear (transverse) and longitudinal sound velocities ($V_s = d/\tau_s$, $V_L = d/\tau_L$) were determined with accuracy better than 0.25% from the sample thickness, d, measured with uncertainty ≤0.15% and the ultrasound reflection time, τ, as described in ref. [26]. The reflection time was measured using an appropriate transducer coupled directly to the sample using a thin film of high viscosity, commercial honey without the application of external force. The elastic constants C_{11} and C_{44} (shear modulus, G), Young's modulus, E, Poisson's ratio, ν, and bulk modulus, B, were evaluated from the sound velocities as [27]:

$$\begin{aligned} C_{11} &= \rho \cdot V_L^2; \\ G &= \rho \cdot V_s^2; \\ E &= C_{44} \cdot \frac{3 \cdot V_L^2 - 4 \cdot V_S^2}{V_L^2 - V_S^2}; \\ \nu &= (E/(2 \cdot G)) - 1; \\ B &= \frac{E \cdot G}{3 \cdot (3 \cdot G - E)} \end{aligned} \quad (1)$$

The shear and longitudinal sound velocities, presented as a function of Gd content, display strong scatter, (Fig. 3a) and the elastic constants derived from these data, uncorrected for sample porosity, show a similarly large spread. Consequently, no conclusion regarding a possible correlation between Gd content and elastic properties can be drawn. Correction for porosity was performed using both static and dynamic models. The static model considers a porous solid as a composite material [28–30], and as summarized by Pal (see ref. [31] and references cited therein), correction factors for Young's modulus and shear modulus are:

$$E_S = E_0/(1-23p/12) \;\; and \;\; G_S = G_0/(1-5p/3), \quad (2)$$

where p is the relative volume of the pores. The subscript "0" denotes the values of the elastic moduli before correction for porosity as deduced from Eq. (1), while the subscript "S" denotes the values corrected for porosity according to the static model. The second (dynamic) model was developed specifically for the case of elastic moduli determined *via* sound velocity measurements as performed here. This model [32], treats scattering of sound waves by the pores, considered as inclusions. The resulting correction factors are [33]:

$$\begin{aligned} G_D &= \left[-F + \left(F^2 - 4 \cdot A \cdot C \right)^{1/2} \right] \Big/ (2A), \\ B_D &= 4G_D \cdot B_0 / [4(1-p)G_D - 3p \cdot B_0]. \end{aligned} \quad (3)$$

where the subscript "D" denotes the values corrected for porosity according to the dynamic model and

$$\begin{aligned} A &= 8(1-p)/3; \\ C &= -3(1+p)B_0 \cdot G_0; \\ F &= (3-2p)B_0 - (8/3 + 4p)G_0 \end{aligned} \quad (4)$$

Correction according to each of the two models gives similar values for both the Young's and shear moduli (Fig. 3c-f).

Ultrasonic pulse echo measurements of the longitudinal and transverse velocities of sound in the ceramic pellets of $Ce_{1-x}Gd_xO_{2-x/2}$ are shown here to be accurate, reproducible and not affected by the material's known anelastic properties [19,20]. Analysis of the sound velocity data leads to conclusions concerning the elastic properties of GDC, which are of practical importance. **i**) Over the complete doping range of interest, the porosity corrections for the Young's and shear moduli do not depend strongly on whether the static or dynamic theory is used. However, for the bulk modulus, corrections according to the dynamic and static theories do diverge moderately for samples with porosity >3%, with the static theory predicting somewhat larger values. This can be attributed to the fact that both the bulk modulus and the Poisson's ratio are derived from the Young's and shear moduli (Eq. 1) with the attendant small differences between the two correction protocols (Fig. 3 c,d). **ii**) After correction for porosity, all three elastic moduli of GDC display a small but clearly detectable decrease with increasing Gd content from 0 to 29 mol%. Because the anelastic properties of GDC reduce the accuracy of the room temperature nanoindentation measurements, the decrease in the Young's modulus (~10% at $x = 0.2$) could not be detected by the nanoindentation technique used in ref. [19]. Recent work has shown that nanoindentation measurements at 600 °C on thin films of 20 mol% Pr doped ceria under reducing conditions do reveal a decrease in the Young's modulus [34] as do acoustic resonance measurements on 10 mol% GDC pellets at temperatures above 900 °C and under reducing conditions [3]. **iii)** The decrease in the Young's modulus is in qualitative agreement with theoretical predictions [4,5] for reduced ceria and reduced 10 mol% GDC: a scaling law relationship between the Young's modulus and the lattice constant, both normalized to vacancy-free values, showed that an increase in the

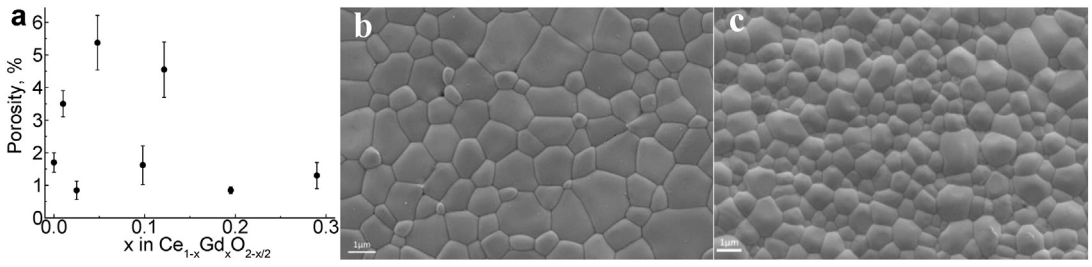

Fig. 1. a) Porosity of ceria pellets with Gd doping 0 to 29 mol%, prepared as described in the text, and measured by the Archimedes method; b) and c) SEM images of pure ceria and 10% Gd-doped ceria, respectively. The density of both samples is 98.3% theoretical. The scale bar corresponds to 1 μm.