High pressure structural study of Samarium doped CeO_2 oxygen vacancy conductor - Insight into the dopant concentration relationship to the strain effect in thin film ionic conductors

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Abstract

The bulk modulus of nanocrystalline, fluorite-structured samarium doped ceria, $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$, has been investigated using synchrotron-based high-pressure x-ray diffraction technique. Experiments were carried out under both quasi-hydrostatic condition with silicon oil pressure transmitting medium (PTM) and nonhydrostatic conditions without PTM. The high pressure structural results indicate that the highly defected ionic conductor is stable up to 20GPa and has a lower bulk modulus than what has been reported for undoped- CeO_2 . The isothermal bulk modulus of $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ is ~150-190GPa compared to ~210-220GPa for CeO_2 . The collected data experimentally verifies the effect of Sm^{3+} dopant and oxygen vacancy defect formation on bulk modulus in doped CeO_2 . The effect of modulus on misfit dislocation formation and dopant ion segregation is discussed in relation to a fundamental understanding of the strain effect in this important family of fast ionic conductors, with potential application as oxygen vacancy conducting solid state electrolytes.

Graphical Abstract

Key Words

Solid state ionics, nanoionics, solid oxide fuel cells, strain effect, doped-ceria, isothermal bulk modulus

Abbreviations

DAC	Diamond Anvil Cell
SDC20	$\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$
SOFC	Solid Oxide Fuel Cell
PTM	Pressure Transmission Medium
HPXRD	High Pressure XRD

Introduction

In the pursuit to develop fast ionic conductors, a concentrated focus towards interfacial effects on transport has evolved over the previous two decades. Effects at grain boundaries and heterogeneous interfaces, where structure and electrochemical potential deviate significantly from the bulk, are being studied intensively as possible opportunities for dramatically enhancing ionic conductivity in solid state fuel cell and battery electrolytes.^[1-10] The strain effect on ionic conductivity in oxygen anion conductors has been reported to dramatically alter oxygen vacancy transport in thin films. A dilatative strain increases the activation volume for oxygen-vacancy migration, ΔV_{mig} , and reduces the activation energy for defect migration, ΔE_{mig} .^[11] The strain effect is predicted to alter the transport properties of thin films by four orders of magnitude according to computer simulation.^[11] Experimental data documents changes in ionic conductivity of several ionic conductors by one or more orders of magnitude.^[5; 12] Drastic changes in charge carrier transport at strained, heterogeneous interfaces in solid state ionic conductors have been reported in important oxygen ion-conducting materials systems, including Y_2O_3 stabilized ZrO_2 (YSZ)^[1; 3-5], doped CeO_2 ^[10; 13] and doped BaZrO_3 ^[14; 15]. In the reported studies, strain is induced in the crystal lattice by interface mismatch with single crystal substrates by up to 8%. The dramatic variation in transport properties in strained thin films has led to significant interest in the strain effect on transport properties and a pursuit to understand the effect more

fundamentally. However, fundamental study of structural properties at thin film interfaces is difficult and can lead to misinterpretation of the strain effect due to a lack of understanding of the real interface properties gained by transmission electron microscopy (TEM) and X-ray scattering techniques alone. For this reason we will consider the bulk properties of Sm^{3+} doped ceria at high pressure and relate them to the interfacial properties to develop the theoretical understanding of the strain effect in this important oxygen anion conductor.

The bulk elastic properties of a material are directly related to formation of misfit dislocations at semicoherent solid-solid interfaces in thin films by the volume elastic energy of the film^[16]. Additionally, the strain field around a dislocation is responsible for the segregation of dopant ions to the dislocation.^[17] As the modulus of the material decreases, the volume elastic energy decreases, misfit dislocation generation is suppressed and the strain field around the dislocation is relaxed. Recent computational work by Yildiz, Marrocchelli, et al.^[17] suggests that dislocations in doped- CeO_2 slow down ion transport due to defect-defect interactions. Therefore, the bulk elastic properties of doped- CeO_2 will directly affect the transport properties of strained, doped- CeO_2 .

The bulk modulus, which relates the change in volume of a material to the applied pressure, of common heavily doped solid state O^{2-} ionic conductors has not been extensively studied but should be determined to provide critical information for optimizing strain at thin film interfaces for fast ionic conductivity. The Young's Modulus of Gd-doped CeO_2 and undoped CeO_2 has been studied by nanoindentation^[18] and by first principles calculations^[19] as a function of oxygen partial pressure. The incorporation of oxygen vacancies in the CeO_2 lattice at low oxygen partial pressure is known to increase the average bond length of the crystal and reduce the intrinsic elastic modulus of the material.^[18] The bulk modulus of $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SDC20) can be predicted to behave similarly to Gd-doped CeO_2 at low oxygen partial pressure, indicating that the bulk modulus for SDC20 will be different from the bulk modulus of CeO_2 .

The diamond anvil cell (DAC) technique is used in this work to investigate the effect of pressure on the crystal structure of heavily doped nanocrystalline $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SDC20) to determine if structural transitions, which could significantly change transport properties, occur at high pressure (up to ~20GPa) and to determine the isothermal bulk modulus in comparison to pure CeO_2 . The diamond anvil cell (DAC) is a testing device commonly used to achieve high pressures (from few GPa to >100GPa) for geophysical and materials science research.^[20] The DAC is readily combined with synchrotron X-ray diffraction (XRD) analysis of the sample, which provides detailed information about the evolution of crystal structure and pressure-volume data for calculating isothermal bulk modulus and its derivatives over a large pressure range. Additionally, Designer DACs^[21; 22] equipped with embedded electrodes can be applied in the future to directly measure electrical transport properties of solid state ionic conductors at high pressure and large lattice strains.

$\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ is a well-known oxygen vacancy conductor used as an intermediate temperature electrolyte in solid oxide fuel cells (SOFCs). Structure-transport property relationships studied in this material have focused on the effect of dopant radius on ionic conductivity. From detailed study of the doped- CeO_2 systems it has been shown that strain in the lattice critically affects the ionic conductivity. For example, in the $\text{Ln}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ (where $\text{Ln} = \text{La}$, Gd , and Yb) system, when $x=0.2$ and the dopant ion is varied from Yb to Gd the lattice parameter changes from $\sim 5.40 \text{ \AA}$ to $\sim 5.45 \text{ \AA}$ accompanying significant changes in the oxygen vacancy diffusion coefficient.^[23] The correlation between ionic conductivity and lattice strain due to varying dopant radius has also been well documented in the doped BaCeO_3 perovskite ionic conducting electrolytes.^[24]

Unusual compression behavior in nanocrystalline CeO_2 has been recently reported from high pressure experiments when silicon oil is used as pressure transmission medium (PTM).^[25] The unit cell is reported to slightly expand at $\sim 15 \text{ GPa}$. The anomalous compressibility behavior has been reported in 4.7 nm , 5.2 nm and 12 nm CeO_2 nanoparticles.^[25] In the current work nanocrystalline (35 nm) $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ will be used and the compressibility behavior will be compared to the nanocrystalline CeO_2 data to extend our investigation into the effect of crystal sizes.

In this study the cell volume data calculated from the XRD data will be used to determine the bulk modulus of $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$, and the result will be compared to the reported bulk modulus of undoped CeO_2 . An implication will be discussed about a relationship between the change in bulk modulus of doped- CeO_2 and the oxygen vacancy transport properties at strained interfaces. The information gained from this study will enhance the understanding of the structure-property relationships in these important solid state ionic conductors.

2. Materials and Methods

$\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ was fabricated by a co-precipitation method. Cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Alfa Aesar, 99.5%) and samarium nitrate hexahydrate ($\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Alfa Aesar, 99.9%) aqueous solution was prepared with cation concentration of 0.1 mol/L and molar ratio of $\text{Ce}^{3+}:\text{Sm}^{3+}$ equal to 4:1. Ammonia dicarbonate (NH_4HCO_3 , Fluka, 99.9%) aqueous solution with concentration of 0.1 mol/L was prepared with molar ratio of ammonium bicarbonate to cation equal to 2. The metal nitrate solution was added to the ammonia bicarbonate solution slowly (10 mL/min) while stirring. White precipitates were collected and rinsed with distilled water (2x) and ethanol (2x) and then dried and calcined at 600°C for 2h. The cubic fluorite phase (Fm3m) was confirmed with ambient temperature and pressure XRD. The average particle size is estimated to be 35 nm from Figure 1B, a scanning electron microscope image of the agglomerated particles collected after pre-firing at 600°C . The XRD pattern shows the pure phase and the Rietveld refinement of the pattern with lattice parameter, $a=5.433 \text{ \AA}$.

Figure 1 (A) Scanning electron microscope (SEM) image of ~35nm nanocrystalline SDC20 used in all high pressure experiments. (B) Ambient pressure XRD pattern of SDC20 powder ($P=0.25$ GPa, $\lambda=0.4246$ Å).

High pressure was applied to the sample using a diamond anvil cell (DAC) with a stainless steel gasket with inner diameter of 100 μ m. Pressure was applied to the SDC20 nanocrystalline samples in two separate runs with no pressure transmitting medium (PTM) and with silicon oil PTM. Silicon oil PTM was used to enhance the hydrostaticity of the applied pressure and will provide the most accurate pressure-volume data for evaluation of the elastic properties of SDC20. For comparison, the SDC20 nanocrystalline samples have been measured without PTM which produced differential and shear stresses on the sample. Pressure was loaded onto the sample using a gas diaphragm in steps of ~1 GPa up to approximately 20GPa.

Structural characterization of the SDC20 powders at high pressure was conducted using high pressure X-ray diffraction (HPXRD) at HPCAT 16-BM-D beamline^[26] of the Advanced Photon Source, Argonne National Laboratory. The X-ray wavelength was 0.4246 Å, and the fluorescence of a ruby ball was used for pressure calibration. The 2D diffraction patterns at each pressure were integrated using Dioptas.^[27] The 2-theta vs. intensity curves were analyzed and refined using the FullProf software.^[28]

3. Results

Figure 2 displays high pressure x-ray diffraction spectra taken up to ~20GPa for the nanocrystalline SDC20 with (A) silicon oil as PTM and (B) no PTM. Rietveld refinement of the highest and lowest pressure spectra are included. In both spectra no structural transition is observed and the cubic fluorite-type structure remains up to ~20 GPa. Peak shifting to higher two-theta is consistent with volumetric contraction of the SDC20 lattice.

Peak depression and broadening as a function of pressure is observed in both sets of patterns but most noticeably in the SDC20 sample measured with no PTM (Figure 2B). While the (222) Bragg diffraction peak is distinguishable up to ~13 GPa in the SDC20 sample measured with silicon oil PTM, its intensity decreases drastically above ~5 GPa for the SDC20 measured without PTM. Similar peak intensity decrease and peak broadening is observed in the higher two-theta peaks. The peak depression and broadening, with most significance in the SDC20 without PTM sample, is consistent with quasi- and non-hydrostatic conditions due to silicon oil PTM^[29] and no PTM used for the measurements. In non-hydrostatic and quasi-hydrostatic compression conditions a pressure gradient with sample distribution can form causing orientation-texture development as the sample tries to reorient in order to minimize internal energy during the applied stress. It is noted that the raw pressure measurements for the SDC20 with silicon oil PTM sample, calibrated by ruby fluorescence, have been adjusted by 3 GPa so that the ambient pressure unit cell volume of SDC20 in silicon oil coincides with the known ambient pressure unit cell volume of SDC20.

Figure 2 XRD patterns for SDC20 up to 20 GPa with (A) Silicon oil PTM and (B) no PTM. The red trace is the difference between the measured and fitted spectra.

To quantify the peak broadening as a function of pressure in the diffraction data the full width half maximum (FWHM) values for the (220) Bragg diffraction peak in both PTM conditions is given in Table 1. The (220) FWHM value for the sample measured with no PTM is 54.1% wider than that of SDC20 measured with silicon oil PTM at ~3.5 GPa. The (220) FWHM

value for the sample measured at 15.75 GPa with no PTM is 31.6% wider than that of SDC20 measured with silicon oil PTM at 17 GPa.

Table 1 FWHM comparison of SDC (220) Bragg reflection with silicon oil PTM and without PTM

	Pressure (GPa)	FWHM (2-theta)
SDC20 w/ silicon oil PTM	3.43	0.266
	17	0.38
SDC20 w/o PTM	3.55	0.41
	15.75	0.5

Figure 3 displays the variation in unit cell volume for SDC20, refined from the XRD data, with and without silicon oil PTM up to ~20GPa. Volumetric strain up to 5% is observed in both measurements. The P-V curve is linear up to ~13GPa for both conditions. However, an apparent compressibility disruption is observed in the P-V curve around 15 GPa for the SDC20 data with silicon oil PTM. The observation is consistent with the reported effect of silicon oil as PTM^[29] on the high-pressure compressibility of nanocrystalline CeO₂ by Wang et al.^[25] and will be discussed in more detail in the following section.

Figure 3 Pressure-Volume curves for nanocrystalline 35nm SDC20 with silicon oil PTM and without PTM. It is noted that the in-situ pressure calibration for the SDC20 with silicon oil PTM had an obvious error (in its zero pressure reference) so that has been re-adjusted by 3 GPa to match with $V/V_0 = 1.0$ at $P = 0$ GPa condition.

In order to determine the relative effects of pressure on individual atomic plane compression, d-spacings for the (111), (200), (220), and (311) Bragg peaks were analyzed and relative d-spacings (d/d_0) are plotted in Figure 4. Interestingly, the (200) d-spacing shift is the most significant both for silicon oil PTM and without PTM. This relative d-spacing data is again consistent with the recently reported data on nanocrystalline CeO_2 by Wang et al.^[25] The anomalous compressibility behavior around 15 GPa is found in (111), (200), (220), and (311) Bragg peaks of SDC20 in the silicon oil PTM sample. The effect is also observed in the (220) peak of the SDC20 sample measured without PTM.

Figure 4 Variation of relative d-spacing (d/d_0) for 35 nm SDC20 at (111), (200), (220) and (311) Bragg reflections as a function of pressure with (A) Silicon oil PTM, and (B) No PTM

In Figure 5, the pressure-volume data from both data sets are fit to the Birch-Murnaghan equation of state to determine the isothermal bulk modulus of the nanocrystalline SDC20 and the results are listed in Table 2 where V_0 is the ambient pressure unit cell volume, K_T is the isothermal bulk modulus, K_T' is the pressure derivative of the isothermal bulk modulus, and K_T'' is the second pressure derivative of the isothermal bulk modulus. The ambient pressure unit cell volume for the SDC20 powders is fixed to $V_0=160.41 \text{ \AA}^3$. The bulk modulus of SDC20 with silicon oil PTM is $K_T=156.92 \text{ GPa}$. It is noted that the anomalous compression behavior of nanocrystalline SDC20 above 13 GPa is not included in the fitting for the bulk modulus determination. The bulk modulus of SDC20 without PTM is $K_T=188.67 \text{ GPa}$.

Figure 5 (A) EOS fit of SDC20 Silicon Oil PTM P-V data, (B) EOS fit of SDC20 with no PTM P-V data

Table 2 EOS data for SDC20 with and without silicon oil PTM

EOS Parameters for 35nm SDC20		
	Silicon Oil	No Pressure medium
$V_o (\text{\AA}^3)$	160.41	160.41
$K_T (\text{GPa})$	156.92	188.67
K_T'	28.76	38.95
K_T''	-4.09	-6.68

4. Discussion

The highly defected nanocrystalline Sm-doped CeO_2 shows no structural phase transition up to 5% compressive lattice strain (~ 20 GPa). In comparison to reported P-V curves in the literature for CeO_2 , our data is consistent.^[25] Significant peak broadening and intensity reduction of the Bragg peaks with increasing pressure was observed. The broadening and intensity reduction can be attributed to a strain distribution within the sample in non- and quasi-hydrostatic conditions.

The bulk modulus of SDC20 has been calculated from high pressure diamond anvil cell measurements when tested with and without PTM. The bulk modulus value calculated from the SDC20 sample measurements with silicon oil PTM (156.92 GPa) is the most accurate experimental data due to the near-hydrostatic pressure acting on the sample during measurements. The effect of differential stress and shear stress on the SDC20 sample without PTM is most likely the cause of the significantly higher bulk modulus (188.67 GPa) calculated from the experimental data for this sample.

The observed compressibility anomaly of the nanocrystalline SDC20 sample observed above ~ 15 GPa is partially attributed to the nonhomogeneity of silicon oil PTM above ~ 13 GPa as

reported by Klotz.^[29] We report that our results replicate and are consistent with those reported by Wang et al.^[25] At this time additional measurements (Raman, etc.) are needed to resolve the mechanism leading to the negative pressure effect observed. The data for ~35nm SDC20 presented in this work extends the previous data interpretation of 4.7nm, 5.2nm and 12nm CeO₂ data presented by Wang et al..

The relative d-spacing (d/d_0) data reveals the change in packing density of specific planes in the SDC structure, (111), (200), (220), and (311) as a function of pressure. Differences in compression and evidence of nonhydrosticity (spread of the relative d-spacing data) for each atomic plane is noticeable in the silicon oil PTM sample and the sample with no PTM. The (200) plane consistently shows the highest compressibility of all planes and the compressibility anomaly of nanocrystalline SDC20 is observed in all planes but most dramatically in the (111) plane.

The effect of defect concentration on elastic properties of SOFC electrolyte ionic conductors is important for understanding the effect of strain on transport properties and for the mechanical robustness of the high temperature energy conversion device. Wang, Y. et al. describe the effect of oxygen vacancy concentration on elastic properties^[30] and predict that the elastic modulus of doped-CeO₂ decreases as oxygen vacancy concentration increases. The reduction in bulk modulus of Sm_{0.2}Ce_{0.8}O_{1.9} observed in our measurements by high pressure XRD is in agreement with preliminary results by Wang, Y. et al.^[18] Samarium, Sm³⁺, doping in the Ce site of CeO₂ creates oxygen vacancies, V_O^{••}, which is responsible for the decrease of the bulk modulus of the material. The bulk modulus determined by fitting a Birch-Murnaghan EOS curve to the data in this work is consistently lower for nanocrystalline SDC20 in comparison to the bulk CeO₂ properties reported (~210-220GPa)^[31; 32], for both PTM conditions tested.

Theoretical model development of the strain effect on ion transport in ionic conducting films has been developed by Schichtel, Korte, Janek et al.^[12; 33; 34] Biaxial elastic strain at a coherent interface of two phases with similar symmetry but mismatched d-spacing is defined as ϵ_{12} where each phase d-spacing is represented by $d_{hkl,1}$ and $d_{hkl,2}$.^[34] If isotropic mechanical properties are assumed, the isotropic pressure of the phase 1 thin film is related to the Young's modulus, Y_1 , Poisson ratio, ν_1 , and the biaxial elastic strain, ϵ_{12} , by Equation 1.

$$P = -\frac{2}{3} \frac{Y_1}{1-\nu_1} \epsilon_{12} \quad (1)$$

Additionally, the bulk modulus is related to Young's modulus by equation 2, where K_1 is the bulk modulus of phase 1.

$$Y_1 = 3K_1(1 - 2\nu_1) \quad (2)$$

Combining equation 1 and 2 yields the biaxial elastic strain relationship to the pressure, poisson's ratio and bulk modulus, given in Equation 3. The biaxial elastic strain is inversely dependent on the bulk modulus of phase 1.

$$\varepsilon_{12} = -\frac{3}{6} \frac{P(1-\nu_1)}{K_1(1-2\nu_1)} \quad (3)$$

In order to create maximum strain in the thin film ionic conductor without misfit dislocation generation, which have been shown to decrease ion transport^[17; 35], a material with low elastic modulus is most desirable to reduce the volume elastic energy of the film.^[16] The volume elastic energy of the film is given by Equation 4.^[16] As the modulus of the material decreases the film volume elastic energy decreases and misfit dislocation formation decreases.

$$\text{Film volume elastic energy} = \text{Young's modulus} * \text{film thickness} * \text{coherency strain} \quad (4)$$

As bulk modulus of the material decreases (increasing elasticity of the material) a larger strain can be accommodated in the lattice (before misfit dislocation generation) causing enhanced lattice expansion and faster ionic transport through the lattice. This result could effect the optimum dopant ratio to achieve the highest ionic conduction for common ionic conductors when fabricated as epitaxial thin films. For example, the optimum dopant concentration of 20% in bulk doped-ceria may not be the optimum dopant concentration for fast ionic transport at strained interfaces. This insight might prove to be crucially important for the optimization of ionic conductivity in strained ionic conductors. The effect of decreasing bulk modulus on misfit dislocation formation is summarized in Figure 6.

Figure 6 Schematic representation of bulk modulus dependent misfit dislocation formation in doped CeO_2 thin film on a single crystal substrate with $d_{\text{substrate}} > d_{\text{CeO}_2}$ as a function of dopant concentration. As dopant concentration increases in CeO_2 , bulk modulus decreases and misfit dislocation decreases. The change in strain field and dislocation concentration are expected to have significant effects on ionic conductivity at the strained interface.

The presented experimental data is expected to be useful to compliment calculations of the effect of strain on energy barriers to ionic conductivity and advance the integrity of the calculation by providing experimental data on a relevant intermediate temperature SOFC electrolyte material. A computational simulation work on the strain effect by De Souza et al^[11] uses the undoped-CeO₂ high pressure diamond anvil cell data of Duculos et al^[36] to verify the computed lattice volume, V_{latt} , of CeO₂ with pressure. The P-V data of Sm_{0.2}Ce_{0.8}O_{1.9} presented in this work will benefit further strain-effect computations by providing the P-V curve of the doped material, which is importantly shown to have different elastic properties from undoped-CeO₂. Also, the structural stability of Sm_{0.2}Ce_{0.8}O_{1.9} has been experimentally verified up to 20 GPa. The experimental confirmation of reduced bulk modulus in heavily doped-CeO₂ provides new information about the interdependence of dopant concentration in doped CeO₂, misfit dislocation formation and the strain effect on ionic conductivity.

The intent of the data collection in this work is to prove that oxygen vacancy formation in doped-CeO₂ does lead to softening of the elastic properties. After concluding that the doped-CeO₂ bulk modulus is lower than the pure CeO₂ modulus, the finding is related to the strain effect on ionic conductivity. The soft, doped crystal will be more sensitive to strain at heterogeneous interfaces which will alter the ionic transport in the material.

Conclusions

The high pressure structure and bulk modulus of heavily doped Sm_{0.2}Ce_{0.8}O_{1.9} (SDC) was studied by the diamond anvil technique and high pressure synchrotron XRD.

Highly defected SDC20 does not show structural phase transitions up to 20GPa.

The relative d-spacing for SDC20 with both silicon oil and no PTM are consistent with previous literature reports.^[25]

The bulk modulus of the highly defected SDC20 structure is less than the bulk modulus for pure CeO₂, which is consistent with “softening” of the structure due to oxygen vacancy defect concentration.

The decrease in bulk modulus of SDC20 due to cation doping is expected to alter the volume elastic energy of thin film SDC20 and allow the film to accommodate more strain before misfit dislocation generation occurs. Currently, the maximization of strain but prevention of dislocation formation is expected to provide the largest enhancement in ionic conductivity in strained ionic conductors. This result indicates that the optimum dopant concentration for fast ionic conductivity in bulk doped-CeO₂ will not necessarily be the same optimum concentration for strained thin film doped-CeO₂.

The current work is a foundation for guiding dopant concentration optimization for maximum ionic conductivity in strained ionic conductors.

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