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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, $Sm_{0.2}Ce_{0.8}O_{1.9}$, 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 20 GPa and has a lower bulk modulus than what has been reported for undoped-CeO_2. The isothermal bulk modulus of $Sm_{0.2}Ce_{0.8}O_{1.9}$ is ~150–190 GPa compared to ~210–220 GPa 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.

1. 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

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Abbreviations: DAC, diamond anvil cell; SDC20, $Sm_{0.2}Ce_{0.8}O_{1.9}$; SOFC, solid oxide fuel cell; PTM, pressure transmission medium; HPXRD, high pressure XRD.

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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 $Sm_{0.2}Ce_{0.8}O_{1.9}$ (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 $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC20) to determine if structural transitions, which could significantly change transport properties, occur at high pressure (up to ~20 GPa) 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 >100 GPa) 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 evolvement 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.

$Sm_{0.2}Ce_{0.8}O_{1.9}$ 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 $Ln_xCe_{1-x}O_{2-\delta}$ (where Ln = La, Gd, and Yb) system, when x = 0.2 and the dopant ion is varied from Yb to Gd the lattice parameter changes from ~5.40 Å to ~5.45 Å 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 ~15 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) $Sm_{0.2}Ce_{0.8}O_{1.9}$ 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 $Sm_{0.2}Ce_{0.8}O_{1.9}$, 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

$Sm_{0.2}Ce_{0.8}O_{1.9}$ was fabricated by a co-precipitation method. Cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$, Alfa Aesar, 99.5%) and samarium nitrate hexahydrate ($Sm(NO_3)_3 \cdot 6H_2O$, Alfa Aesar, 99.9%) aqueous solution was prepared with cation concentration of 0.1 mol/L and molar ratio of Ce^{3+}: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 (2×) and ethanol (2×) and then dried and calcined at 600 °C for 2 h. The cubic fluorite phase (Fm3m) was confirmed with ambient temperature and pressure XRD. The average particle size is estimated to be 35 nm from Fig. 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 Å.

High pressure was applied to the sample using a diamond anvil cell (DAC) with a stainless steel gasket with inner diameter of 100 μm.

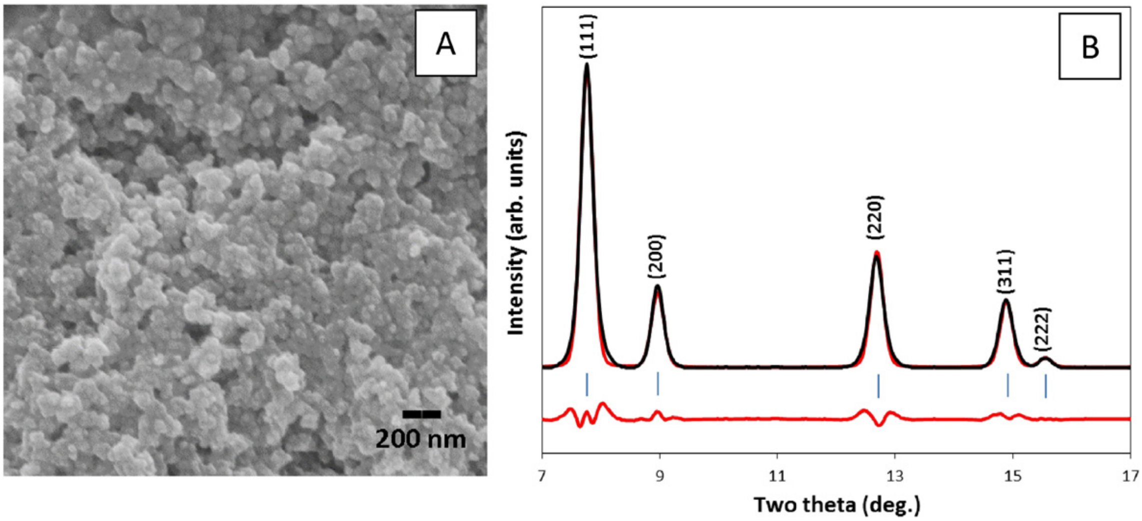

Fig. 1. (A) Scanning electron microscope (SEM) image of ~35 nm nanocrystalline SDC20 used in all high pressure experiments. (B) Ambient pressure XRD pattern of SDC20 powder (P = 0.25 GPa, λ = 0.4246 Å).