



# Scalable lattice-strain in preferentially oriented acceptor-doped cerium oxide film and its impact on oxygen ion transport kinetics



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## ABSTRACT

Fast ionic conduction through strain engineered heteroepitaxial film have been demonstrated well. However, this effect in the preferentially orientated film remains to be unexplored. Here, we report the effect of interatomic distance between cation-oxygen bonds on the oxygen ionic transport in preferentially (111) oriented  $\text{Ce}_{0.80}\text{Sm}_{0.1}\text{M}_{0.1}\text{O}_{2-\delta}$  ( $\text{M} = \text{Gd}, \text{Nd}, \text{Pr}, \text{La}$ ) film over an amorphous quartz substrate. With the increase in ionic radii of dopant cation, the films exhibited a substantial increase in tensile strain with a change in lattice constant ( $\Delta a$ ) in the order of  $\sim 1.14\%$  ( $\Delta a: 1.14\% (\text{Sm}^{3+} + \text{La}^{3+}) > 1.04\% (\text{Sm}^{3+} + \text{Pr}^{3+}) > 0.69\% (\text{Sm}^{3+} + \text{Nd}^{3+}) > 0.14\% (\text{Sm}^{3+}) > 0.08\% (\text{Sm}^{3+} + \text{Gd}^{3+})$ ) has strong influence on defect association enthalpy ( $\Delta H_a$ ) leading to the change in migration energy of oxygen ion during conduction process. Highest conductivity was observed from  $\text{Ce}_{0.85}\text{Sm}_{0.1}\text{Nd}_{0.1}\text{O}_{2-\delta}$ , which is four times greater than that of  $\text{Ce}_{0.85}\text{Sm}_{0.2}\text{O}_{2-\delta}$ . As a consequence, it is clear that optimum co-dopant is needed to attain the critical ionic radii/tensile strain to achieve the maximum ionic conductivity in the preferentially oriented ceria-based thin film. This work demonstrates the importance of tuning the ionic radii of dopant cation, which can effectively facilitate the optimum expansion of lattice to attain the fast ionic conduction process in (111) oriented thin film based solid electrolyte.

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## 1. Introduction

Reduction in the dimension of the electrolyte has attracted greater attention due to its fast ionic conduction process at reduced operating temperature for energy devices such as solid oxide fuel cell (SOFC) [1–5]. Among various ionic conducting oxides, doped ceria has a broad set of interest in fuel cell application [6,7]. The bulk ceria has been extensively studied, both experimentally and computationally [8–10]. Ceria has relatively higher ionic conductivity, therefore, much effort has been taken to optimise this property. The key strategy to enhance the ionic conductivity is to dope ceria with lower valent cation that results in the formation of oxygen vacancy to maintain the charge neutrality. These oxygen vacancies increase the oxygen ion transport and thereby increase the conductivity. Based on the dopant nature, the local defect arrangement and migration barrier for ion diffusion vary, thereby

the conductivity of doped ceria depends on the nature of the dopant cation and its concentration [11]. In general, if the dopant radii are equal or little larger than host ion  $\text{Ce}^{4+}$  results in maximum ionic conductivity.  $\text{Sm}^{3+}$  and  $\text{Gd}^{3+}$  are well reported to be optimistic dopant to exhibit maximum ionic conduction [12–15]. In ceria, the lattice parameter changes linearly with the concentration/radii of dopant cation, in accordance with the Vegard rule [12]. Higher doping concentration or radii lead to the association of vacancy, for example, the  $\text{Gd}^{3+}$  concentration more than 25% leads to the double fluorite phase with oxygen vacancies residing around the host Ce cation [16]. The combined change in the defect concentration and its association has great impact on thermally activated ionic conduction process, as given by activation energy (equation (1)),

$$\sigma = A \exp\left(-\frac{E}{kT}\right) \quad (1)$$

where E is the activation energy, k is the Boltzmann constant, T is

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the temperature, and  $A$  is the pre-exponential factor proportional to the defect concentration. The activation energy for the ionic conduction depends on the defect association enthalpy ( $\Delta H_a$ ) and migration enthalpy ( $\Delta H_m$ )

$$E = \Delta H_a + \Delta H_m \quad (2)$$

Though higher defect concentration reduces the migration enthalpy, it facilitates the defect association, thereby, increasing the activation energy. Several computational studies along with experimental work have been carried out on defect association enthalpy on oxygen ion migration. Minervini et al. observed that the cation-vacancy association preferentially resides over the smaller dopant cation, which was also confirmed by density functional theory calculation [17]. Also, many studies were carried out to understand the behavior of vacancy-vacancy association, which has a significant effect on the ionic conduction process [18,19]. The impact of defect association can be varied by tuning the dopant type (radii) along with optimisation of concentration to lower the migration enthalpy as well as activation energy during oxygen ion migration [20]. Though several researchers have well demonstrated the potential of bulk ceria electrolyte, conversion of bulk structures to thin films influences the defect energy as well as migration properties of oxygen ion [21]. Depending on the thin film processing route, the activation energy for oxygen ion transport can be engineered, for example, variation in the thickness of the doped ceria in physical vapor deposition technique (PVD) resulted in the modification of activation energy from 0.8 eV to 1.0 eV [22]. On the other hand, independent of processing condition, bulk doped ceria exhibits an activation energy of 0.7 eV [12]. The changes in transport phenomenon in film differing from that of bulk highlights the importance of engineering the film to achieve maximum ionic conductivity. This variation in mobile properties of oxygen ion in the film dictates the performance of energy devices at an optimum level. The major change in transport property of oxygen ions in a thin film as compared to bulk arises from the change in interfacial properties [23]. Lattice strain and grain boundaries are one of the major interfacial properties of the films which vary the oxygen ion migration as a function of processing parameter. In general, the barrier to oxygen ion mobility increases at the grain boundary due to the space charge effect near its vicinity [24]. The grain boundary area is effectively decreased by orienting the film through biaxial (epitaxial) or uniaxial (out-of plane orientation) direction. For example, samarium (20 mol%) doped cerium oxide film oriented in (100) direction exhibits a conductivity of  $0.07 \text{ Scm}^{-1}$  at  $700^\circ\text{C}$ , which is much greater than polycrystalline SDC film ( $0.02 \text{ Scm}^{-1}$ ) [25]. Thus deleterious grain boundary effect on ionic conductivity is significantly reduced by orienting the film in the defined direction. The other interfacial factor called lattice strain either arises from the lattice mismatch between the film and the substrate or the lattice disorder induced by dopant cation ionic radius mismatch. The experimental and computational studies suggest that lattice strain has a major influence on facilitating the ionic conducting process of oxygen ion in doped ceria thin film [26–29]. The effective lattice constant, significantly varied as a function of dopant cation ionic radii [30,31]. Through density functional theory (DFT), it was observed that the lattice with optimum tensile strain lowers the migration energy barrier for the oxygen ion transport [18,30]. Thus dopant dependent lattice strain, associated with the preferential oriented film has a great impact on the diffusion of oxygen ion.

The objective of this present work is to quantitatively investigate the effect of change in residual lattice strain on transport properties of oxygen ion in doped ceria thin film. In this paper, Sm was taken as a primary dopant in ceria since it has exhibited a highest ionic conductivity [14,32,33] and lanthanides like Gd, La,

Nd, and Pr were chosen as a secondary dopant to vary the lattice parameter. The (111) oriented film with the variation in the magnitude of strain was prepared by Electron Beam Evaporation Technique (EBPVD). The dopant percentage was maintained at 20 mol% for all the compositions in order to study the influence of secondary dopant cation radii on the atomic structure of the film. The lattice constant and the distance between oxygen-cation bond length as a function of dopant cation was investigated using High resolution x-ray diffraction (HR-XRD) and Raman spectroscopy. In particular, the lattice strain evaluated through  $\sin^2 \Psi$  method using HR-XRD, which is a powerful tool to derive the strain quantitatively. Oxygen ion conductivity studies were carried out using electrochemical impedance spectroscopy. The impact of strain on oxygen ion migration barrier was discussed as a function of the change in ionic radii of dopant cation in a thin film. To the best of our knowledge, this is the first report on the direct analysis of ionic conductivity as a function of residual stress with different dopant radii in the preferentially oriented thin film, which provides the insight mechanism behind the enhanced ionic conductivity.

## 2. Experimental section

### 2.1. Target preparation

$\text{CeO}_2$ ,  $\text{Ce}_{0.80}\text{Sm}_{0.2}\text{O}_{2-\delta}$  and  $\text{Ce}_{0.80}\text{Sm}_{0.1}\text{M}_{0.1}\text{O}_{2-\delta}$  ( $M = \text{Gd, Nd, Pr, La}$ ) nanocrystalline powder was synthesized by co-precipitation technique. The precursor metal cation (nitrates) was taken in the required stoichiometry with respect to the metal dopant and dissolved in the distilled water. 1 N of ammonium hydroxide (Merck 30%) was used as a precipitating agent and added dropwise to the above-prepared solution to adjust the pH between 9 and 10. The solution was stirred continuously for 4 h at room temperature to obtain the precipitate and subsequently dried at  $80^\circ\text{C}$  overnight to obtain the powder. The target for the deposition in EBPVD was prepared by uniaxial pressing (5 ton, 3 min) the synthesized powder and subsequently annealing at  $800^\circ\text{C}$  for 6 h. The X-ray diffraction analysis was carried out on the target material to identify the crystal structure (discussed in the supplementary section). Also, X-ray fluorescence spectroscopy analysis was carried out over target material, which nominally matches with the calculated elemental composition.

### 2.2. Thin film deposition

The cerium oxide-based thin films were deposited on amorphous quartz (Ant labs, 99.99%) substrate by EBPVD technique (BC-300 Vacuum box coater, Hind High Vacuum). After reaching the base pressure of  $\sim 1 \times 10^{-6}$  mbar, the deposition was established at  $\sim 2 \times 10^{-5}$  mbar. The deposition rate was maintained around  $4 \text{ \AA/s}$  at a substrate temperature of  $300^\circ\text{C}$ . The film thickness was carefully controlled by the *in-situ* digital thickness monitor under constant deposition rate and the substrate temperature to reach around  $\sim 1.5 \text{ \mu m}$ . After completing the deposition, the deposited film allowed to cool at a reduced pressure of  $1 \times 10^{-3}$  mbar. The post-annealing of the film was carried out at  $800^\circ\text{C}$  for 2 h under ambient condition. The thickness of the film was measured by a profilometer (Dektak 6, Veeco, USA) which resulted in an average thickness of  $\sim 1.4 \text{ \mu m}$ .

### 2.3. Structural characterization

The phase identification of thin film was carried out using Rigaku SmartLab High Resolution X-ray diffractometer (HR-XRD) system with Cu  $K\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ), equipped with a Scintillation counter and a high-speed 2D detector (Pilatus). Pole figure

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