



Structural interpretation of optical properties and ion transport mechanism in mixed valent Pr containing nanoceria



Sk. Anirban^{a,b}, Abhigyan Dutta^{a,*}

^a Department of Physics, The University of Burdwan, Golapbag, Burdwan, 713104, India

^b Department of Physics, Govt. General Degree College, Singur, Hooghly, 712409, India

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ABSTRACT

Microstructure, optical and ionic transport properties of chemically derived $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}$ ($0.05 \leq x \leq 0.2$) has been investigated in this work. Rietveld analyses of the X-ray diffraction patterns showed that, microstructural parameters depend on Pr content as well as sintering temperature. The High Resolution-Transmission Electron Microscopy together with Rietveld analyses confirmed the cubic fluorite structure of the samples. The Scanning Electron Microscope images showed gradual grain growth due to sintering. The Energy Dispersive X-ray spectra showed decrease of oxygen content with Pr concentration. The direct optical band gap was found to show a red shift with dopant concentration and sintering temperature. The conductivity has been found to have strong dependency on the oxidation of Pr^{3+} to Pr^{4+} , impurity, oxygen vacancy concentration, defect association and charge carrier concentration and found to obey Variable Range Hopping phenomenon. The ion dynamics has been correlated with the structural changes due to Pr doping.

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1. Introduction

Doped cubic fluorite structured ceria have attracted great deal of interests due to its properties like high oxygen ion conductivity, mixed electronic and ionic conduction, defect association and dissociation reaction, chemical expansion at reduced partial pressure etc. [1–4]. These made doped ceria as one of the promising candidates for various applications like solid electrolyte in solid oxide fuel cells (SOFCs) [5], oxygen storage material in gas reformation catalysis [6], oxygen sensor [7], UV absorbent and UV filter materials [8] etc. In general, pure ceria is not a good ionic conductor. However, when ceria is doped with rare earth elements, the substitution of Ce^{4+} by the rare-earth cation distorts the lattice structure and generates oxygen vacancies that permit high oxygen ion conduction [9]. Among the various rare earth elements, Praseodymium (Pr) draws more attention due to its analogous fluorite structure that of ceria and near ionic radius of the Ce^{4+} ions. Therefore, Pr is expected to be one of the appropriate rare earth cation for dissolution into the ceria lattice to form a solid solution [4]. Again, Pr is interesting because it produces coloured

nanoparticles ranging from pink-orange to red-brown depending on the doping concentration, sintering temperature, synthesis process etc. [10]. Recently, Pr containing oxides, like $\text{Pr}_2\text{Zr}_2\text{O}_7$, $\text{Pr}_2\text{Ti}_2\text{O}_7$, Pr_2O_3 and in particular Pr doped CeO_2 have attracted much more attention in different applications. $\text{Pr}_2\text{Ti}_2\text{O}_7$ is a good candidate for high temperature piezoelectric application because of its high Curie point [11]. Recently, Alam et al. [12] investigated different magnetic properties of the pyrochlore $\text{Pr}_2\text{Zr}_2\text{O}_7$ and found that these properties significantly depend on the presence of Pr^{3+} ions. Patwe et al. [13] investigated the electrical properties of $\text{Pr}_2\text{Ti}_2\text{O}_7$ by ac impedance spectroscopic studies and reported that an appreciable contribution of ionic conductivity in $\text{Pr}_2\text{Ti}_2\text{O}_7$ is observed at higher temperature ($\approx 700\text{K}$). Again, Pr_2O_3 is an attractive material to be considered as promising gate dielectrics because it offers a combination of high dielectric constants, large band gaps and high conduction band offsets on Si [14,15]. Using XPS studies, Borchert et al. [16] investigated the quantification of Pr^{3+} and Pr^{4+} and possible existence of Ce^{3+} in Pr doped ceria. They found that in the composition $\text{Ce}_{0.8}\text{Pr}_{0.2}\text{O}_{2-\delta}$ only about 6% of the cerium ions are in +3 state and about 51% of the praseodymium ions are in +3 state after treatment with O_2 . They also found that after treatment with CH_4 about 10% of the cerium ions are in +3 state and about 63% of the praseodymium ions are in +3 state. Laramendi [17] also reported that only 7% of the cerium ions are in +3 state in $\text{Ce}_{0.8}\text{Pr}_{0.2}\text{O}_2$ prepared by sol-gel method. The

* Corresponding author at: Department of Physics, The University of Burdwan, Golapbag, Burdwan, 713104, India.

E-mail addresses: sk.anirban@gmail.com (S. Anirban), adutta@phys.buruniv.ac.in (A. Dutta).

multivalent Pr ion ($\text{Pr}^{3+}/\text{Pr}^{4+}$) in the doped ceria leads to the pronounced mixed ionic and electronic conductivity at high oxygen partial pressures [18]. The most common oxide form of praseodymium is Pr_6O_{11} in which the referential oxidation state of Pr is +4. Ahn et al. [19] reported that among the incorporated multivalent Pr ions in Pr-doped ceria, Pr^{3+} have been incorporated as majority ions. Therefore, it is expected that the ionic conductivity is much higher than electronic conductivity in Pr doped ceria. Here, the ionic conductivity arises due to the formation of oxygen vacancies and electronic conductivity arises due to small polaron hopping of electrons between Pr^{3+} and Pr^{4+} cations [20]. These mixed conductivity materials are very much useful as electrodes in SOFCs because they render the entire electrode surface active for the reduction and oxidation of oxygen, as they oppose to being limited to the triple phase boundaries [21]. The oxygen storage capacity of multivalent Pr doped ceria approaches to that of ceria-zirconia materials due to the enhancement of formation and migration of oxygen vacancies [22]. The oxygen defects accompanied with the valence charge can be achieved due to the conceivable valency change of Pr from 3+ to 4+ or vice-versa [19]. However, a recent study [23] showed that Pr doped ceria exhibit high ionic conductivity which only somewhat lower than those of Gd and Sm doped ceria. Dholabhai et al. [24] investigated the oxygen vacancy migration in Pr-doped ceria using DFT study and reported that the presence of Pr in ceria significantly affects vacancy formation and migration. Bishop et al. [4] calculated the transference number of $\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ and found its value is approximately 0.5 in air which makes it a potential candidate for SOFC cathodes. Again, according to Chiba et al. [2] the composition $\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ is favorable for the active layer material of an SOFC cathode, because of the high conductivity and high concentration of oxygen vacancies. However, in literature the mixed conductivity of Pr doped ceria was discussed more than the ionic conductivity [2,18,24] and structure property correlation study is limited. Therefore, there is a scope to study the ionic conductivity corroborated with structure in details for Pr doped ceria.

In our present study, Pr doped ceria nanoparticles $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}$ ($0.05 \leq x \leq 0.2$) were prepared using citrate auto-ignition method [25,26] and calcinated at different temperatures. The detailed microstructures, optical and electrical properties of these nanoparticles were investigated. The effect of Pr doping into ceria and effect of sintering temperature on the microstructure, optical properties and ionic conductivity are discussed and correlated.

2. Experimental

For the synthesis of $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}$ ($0.05 \leq x \leq 0.2$) nanoparticles, using low temperature citrate auto-ignition method, Cerium nitrate hexahydrate [$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%)] and Praseodymium Oxide [Pr_6O_{11} (99.9%)] were chosen as precursors. First, stoichiometric amount of Pr_6O_{11} was dissolved in de-ionized water and nitric acid. The solution was stirred vigorously at about 60 °C using magnetic stirrer for 2 h until the solution becomes transparent. After that, proper amount of weighted $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was mixed with the solution and anhydrous citric acid ($\text{C}_6\text{H}_8\text{O}_7$), was added at 1:1 molar ratio with the cations. The solution was stirred for 6 h at temperature 80–85 °C. Due to evaporation, the solution became brownish and gel/foam was formed. The auto-ignition process completed within a minute and produced nanopowder. It was then grounded in an agate motor and sintered at temperatures $T_s = 400$ °C, $T_s = 600$ °C, $T_s = 800$ °C, $T_s = 1000$ °C and $T_s = 1200$ °C for 6 h in a muffle furnace in air at atmospheric pressure. During heating, the rise in temperature was at rate 5 °Cmin⁻¹ and the cooling rate was 2 °Cmin⁻¹. As the redox properties of mixed valent Pr doped ceria very much depend on the pressure and

atmosphere of sintering [27], hence the sintering condition was maintained unaltered throughout the synthesis process for all the compositions. The thermogravimetric (TG) measurements of the as prepared powders were performed with a Netzsch TG 209 F3 Tarsus system at a heating rate of 10 °Cmin⁻¹ and the samples were scanned from room temperature to 1000 °C under a nitrogen atmosphere. To identify the crystal structure and phase purity of the sintered nanopowders, X-ray diffraction profiles were recorded with a powder X-ray diffractometer (BRUKER, Model D8 Advance-AXS) using CuK_α radiation [$\lambda = 1.5418$ Å] from $2\theta = 20^\circ$ to 80° with step size 0.02°. The morphology and grain growth of the sintered powders were examined using scanning electron microscopy (SEM) (Carl Zeiss SMT Ltd. SUPRA™ 40). The microstructural analysis of the sintered nanopowders at high magnification were performed by placing the particles in a formvar-carbon coated 300 mesh copper grid with the help of transmission electron microscope (JEOL, Model JEM- 2010) operated at 200 kV. The compositions of the samples were evaluated from energy dispersive X-ray analysis (Hitachi S-3500). The ultraviolet-visible (UV-vis) absorption spectra were taken at room temperature using Shimadzu spectro-photometer (Model-1800) in the wavelength range 200–900 nm. In order to form a homogeneous suspension, the particles were well dispersed in de-ionized water by sonicating in ultrasound bath for 1 h at room temperature. De-ionized water was used as reference during the absorption measurement. For electrical measurements, cylindrical pellets were prepared from sintered powder by uniaxial pressing in a 10 mm diameter stainless steel die. The pellets were covered on both sides with conductive graphite paste (Alfa-Aesar) to make the electrodes. The electrical measurements were performed in tube furnace using two probe methods in air with temperature stabilization of 1/2 h. An LCR meter (HIOKI, Model 3532-50) interfaced with computer was used to collect the electrical data in the frequency range 42 Hz–5 MHz and in the temperature range 250–550 °C. The relative density of the sintered pellets was measured using Archimedes's principle and found to be in between 92%–97%.

3. Results and discussion

3.1. Thermogravimetric analysis

The as prepared Pr doped ceria was subjected to TG analysis before sintering. The obtained thermograms between 30 °C and 1000 °C are shown in Fig. 1(a). All the samples show a continuous weight loss in the entire temperature range. To clearly observe the weight loss of the samples differential thermogravimetric (DTG) curves are shown in Fig. 1(b). There are significant peaks at temperature around 100 °C, 200 °C and 340 °C which correspond to the removal of residual water and decomposition of residual organic materials [28]. The weight losses for the samples $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}$ ($0.05 \leq x \leq 0.2$) in the temperature range 400–1000 °C are 1.9%, 6.2%, 8.2% and 14.1%. Therefore, weight loss increases with Pr content into the ceria which is also supported by earlier studies [19]. This indicates that the instability of the compositions increases with the doping concentration [29]. The significant weight loss observed at temperatures around 500 °C, 590 °C, 725 °C, 785 °C, 860 °C and 940 °C. These gradual weight loss are mainly due to the loss of lattice oxygen [30] which results the creation of oxygen vacancies [31]. These oxygen vacancies associate with Pr^{3+} and form dopant vacancy associate [9]. This reduces the concentration of Pr^{3+} ions. According to Matovic et al. [32], at higher temperature, the valency change from Pr^{3+} to Pr^{4+} is high due to higher thermodynamic stability of Pr^{4+} at higher temperature in ambient atmosphere. Thus, the major weight loss observed at around 785 °C for the samples $0.05 \leq x \leq 0.15$ and at around 860 °C for the samples $x = 0.2$ are may be due to the

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