Investigation of structural, optical and electronic properties of (Co, Ni) codoped CeO\textsubscript{2} nanoparticles

Saurabh Tiwari\textsuperscript{a}, Nivedha Balasubramanian\textsuperscript{b}, Sajal Biring\textsuperscript{c}, Somaditya Sen\textsuperscript{a,}\textsuperscript{*}

\textsuperscript{a}Metallurgical Engineering and Material Sciences, Indian Institute of Technology, Indore, India

\textsuperscript{b}Department of Physics, PSG College of Arts and Science, Coimbatore, India

\textsuperscript{c}Electronic Engg., Ming Chi University of Technology, New Taipei City, Taiwan

E-mail: sens@iiti.ac.in

Abstract. Cerium oxide co-doped with cobalt and nickel, is synthesized using sol-gel method. The phase purity and crystal structure are confirmed using x-ray powder diffraction (XRD). Rietveld analysis of XRD data confirms cubic fluorite structure of undoped and (Co, Ni) co-doped CeO\textsubscript{2}. Lattice strain increases with codoping which results in reduction of crystallite size, lattice disorder and defects. UV-vis absorption analysis shows that co-doping leads to huge reduction in bandgap from 3.05 eV to 2.31 eV; this is due to the presence of defects and disorder as confirmed by Urbach energy calculation. Raman and Photoluminescence (PL) analysis shows that oxygen vacancies related defects are increasing with codoping. These defects leads to lattice disorder and shifts the bandgap from UV region to visible region by modifying its electronic levels.

1. Introduction

Nanocrystalline materials with crystallite size less than 100 nm has attracted a lot of interest of researchers by its better mechanical, electrical, optical, catalytic and thermal properties that notably differ from their bulk form. In recent times, CeO\textsubscript{2} nanostructures have received significant attention because of its novel properties i.e. hardness, UV absorption, high temperature stability, ability for reacting [1]. These properties leads to its wide application in sunscreens [2], degradation of dyes [3], in solid oxide fuel cells [4] etc.. It has cubic fluorite structure with each cerium is surrounded by 8 oxygen sites and each oxygen with 4 cerium sites. Recently, lots of work has been done on transition element doped CeO\textsubscript{2} such as enhancement in its photocatalytic activity, ferromagnetism and anticancer properties [5–7]. Oxygen vacancies related defects play crucial role in versatile application of CeO\textsubscript{2} as mentioned above.

But very less work has been done on transition element co-doped CeO\textsubscript{2}. In the present study undoped and (Co, Ni) co-doped CeO\textsubscript{2} samples were synthesized by sol-gel method. We have applied different characterization techniques such as X-ray diffraction, Raman spectroscopy, UV-visible
spectroscopy and Photoluminescence spectroscopy for understanding the effect of (Co, Ni) co-doping on structural, optical and electronic properties of CeO$_2$.

2. Experimental

Starting material used for synthesizing CeO$_2$ and Ce$_{0.95}$Co$_{0.025}$Ni$_{0.025}$O$_2$, were (Ce(NO$_3$)$_3$.6H$_2$O), (Co(NO$_3$)$_2$.6H$_2$O) and (Ni(NO$_3$)$_2$.6H$_2$O), all were obtained from Alfa Aesar. The precursors were dissolved in double distilled de-ionized water in separate beakers. These precursors were mixed together and final solution is stirred for 2 h. For formation of the chelating chains and burning of gel, citric acid and glycerol were used. The resulted solution was maintained at constant temperature (80°C) which in the end gives a black powder. For denitrification and decarburization, the samples were calcined at 450°C for 6 h. The calcined samples were used for further characterization and the different compositions were referred as C1 for undoped CeO$_2$ and C2 for Ce$_{0.95}$Co$_{0.025}$Ni$_{0.025}$O$_2$ respectively.

For identification of the crystal structure X-ray diffraction (XRD) having Cu K$_{α}$, wavelength 1.54 Å (Bruker D$_2$ Phaser) was used. UV-visible spectroscopy (Shimadzu (UV-2600)) has been used for determining the optical bandgap. Photoluminescence (PL) measurement was done using fluorescence spectrometer (Perkin Elmer LS55, 340nm). Raman spectra were recorded using LabRAM HR ((HORIBA Scientific, He-Ne laser (632.8 nm)) having spectral resolution of 0.4 cm$^{-1}$.

3. Result and discussion

![XRD patterns](image)

Fig.1. (a) XRD patterns of undoped and (Co, Ni) codoped CeO$_2$ (-inset shows peak shifting) (b) Variation of lattice parameter with cooping (-inset shows Rietveld refinement).

XRD patterns for CeO$_2$ (C1) and Ce$_{0.95}$Co$_{0.025}$Ni$_{0.025}$O$_2$ (C2) were shown in Fig. 1. (a), which shows the typical cubic fluorite structure having characteristic (111), (200), (220), (311), (222), (400), (331) and (420) planes (CIF file-4343161, Crystallography open database). No impurity phases were detected. The lattice parameter was determined using Rietveld analysis using Fullprof suite software, found decreasing from 5.4148 Å to 5.4099 Å [Fig. 1 (b)]. The lattice parameters were decreased because of lower ionic radii of Co$^{2+/3+}$ (0.75-0.9 Å), Ni$^{2+/3+}$ (0.7-0.83 Å) than Ce$^{4+}$ (0.97 Å). This was inferred from Figure 1 (a-inset) peak which shift to higher angle that hints reduction in lattice parameter. The mean crystallite size (D) were evaluated from Scherer’s formulae; $D = \frac{k\lambda}{\beta \cos \theta}$, using X-ray line broadening, where k (0.9) is a constant, $\theta$ is angle of diffraction, $\beta$ is full width at half maxima FWHM and $\lambda$ is X-ray wavelength. The crystallite sizes was found to be 6.7 nm for undoped
and 4.9 for (Co, Ni) codoped CeO$_2$ samples [Fig. 2]. Decrease in crystallite size and lattice parameter lead to lattice distortion and strain. Strain was evaluated by Williamson-Hall equation [8]; $\beta \cos \theta / \lambda = 1/D + \eta \sin \theta / \lambda$, where $\eta$ is strain. Co-doping of (Co, Ni) increase the strain in CeO$_2$ lattice [Fig. 2].

![Graph](image1.png)

**Fig. 2.** Change in crystallite size and strain with composition.

The UV-visible absorption spectra of the C1 and C2 samples were shown in Figure 3 (a). An intense absorption below 400 nm was observed for both the samples, owing to charge transition from O 2p band to Ce 4f band [9]. For estimating bandgap, absorption data has been fitted with indirect transition relationship and by extrapolating linear part of the plot to zero absorption; $(\alpha h\nu)^{1/n} = A(h\nu - E_g)$, where A is a constant, $h\nu$ is photon energy, $E_g$ is bandgap, $\alpha$ is absorption coefficient and $n$ is a constant ($n = 2$ for indirect and $n=1/2$ for direct transition) [10].

![Graph](image2.png)

**Fig. 3.** (a) Optical absorption spectra of C1 and C2 (-inset shows plot of $(\alpha h\nu)^{1/2}$ vs energy); (b) Changes in bandgap and Urbach energy with composition (-inset shows Urbach fitting).

The bandgap of undoped CeO$_2$ is red shifted from UV region to visible region with (Co, Ni) co-doping from 3.05 eV to 2.31 eV [Fig. 3 (b)]. This red shifting of bandgap is due to the formation of
some localized band between valance band (VB) and conduction band (CB) [11]. To confirm this Urbach energy is calculated \( \alpha = \alpha_0 \exp \left( \frac{E}{E_U} \right) \), where \( E_U \) is Urbach energy (eV) and \( E \) is photon energy.

![Graph showing room-temperature PL spectra of C1 and C2 samples.]

**Fig. 4.** Room-temperature PL spectra of C1 and C2 samples.

The plot between \( \ln \alpha \) and \( E \) has been plotted and the inverse of the slope gives Urbach energy [12]. Increase in Urbach energy with (Co, Ni) co-doping in CeO\(_2\) [Fig. 3 (b)] pointing out increase in defect states between VB and CB. These defect states forms new band between VB and CB and thereby reduces its bandgap.

Photoluminescence spectra of undoped and (Co, Ni) co-doped samples were obtained at room temperature using excitation wavelength of 340 nm are shown in Figure 4. Cerium oxide (CeO\(_2\)) reversibly takes and release oxygen and form oxygen vacancies while maintaining the cubic fluorite structure [13].

![Graph showing Raman spectra of monocrystalline samples.]

**Fig. 5.** (a, b) Raman spectra of monocrystalline samples (-inset shows oxygen vacancies related peak).
Oxygen vacancies related defects were present just below the Ce 4f band which is situated ~3 eV from VB. During electronic transition, excited electron goes to Ce 4f band and also to the bands that were related to oxygen vacancies related defects. The spectra of undoped and (Co, Ni) co-doped CeO₂ were almost similar. It has peaks at pale blue ~ 424 nm due to surface related defects, blue ~ 457 nm, blue-green ~485 nm due to dislocation or oxygen vacancies, and green ~ 528 nm due oxygen vacancies related defects [14]. Reduction in PL emission occurs due to increase in oxygen vacancies related defects which cause nonradiative recombination [15] of charge carriers.

Figure 5 (a, b) shows Raman spectra of undoped and (Co, Ni) co-doped CeO₂ nanoparticles. The cubic fluorite structure of prepared samples were confirmed by characteristic Raman active F₂g mode at 460.8 cm⁻¹ [16]. It was a symmetrical stretching mode of Ce-O8 vibrational unit. The peak intensity of undoped CeO₂ decreases and become asymmetric with (Co, Ni) co-doping. This occurs due to increased strain and decreased phonon lifetime. The broad peak ~ 540-640 cm⁻¹ has been attributed to oxygen vacancies [17]. Raman analysis confirmed the Urbach and PL study which hints the generation of defects related to oxygen which cause quenching of PL emission and reduction of bandgap.

4. Conclusion

Pure and cobalt, nickel co-doped CeO₂ nanoparticles were successfully synthesized using sol-gel method. Rietveld refinement of XRD data confirms cubic fluorite structure for CeO₂ (C1) and Ce₀.95Co₀.025Ni₀.025O₂ (C2) nanoparticles. Lattice parameter decreases owing to lesser ionic radii of cobalt and nickel than that of cerium. This lattice contraction increases the strain ~ 93%, which has been reflected in reduced crystallite size. Lattice strain and disorder increases with cobalt, nickel co-doping. It were reflected in notable band tail and increase in Urbach energy (0.15 eV−→0.60 eV). Co-doping lead to shifting of bandgap from UV region (3.05 eV; C1) to visible region (2.33 eV; C2) which enhances its utility for photocatalytic and other solar energy applications. The PL analysis shows that the emission intensity decreases with Co, Ni co-doping in CeO₂ due to increase in non-radiative centers which are oxygen vacancy related defects. The oxygen vacancy related defects were increasing and it has been confirmed by Raman analysis (~ 540-640 cm⁻¹).

Acknowledgements

The authors would like to thank IIT Indore for the funding, Dr. V. K. Jain (Amity University, Noida, India) for UV-Vis measurement facility, Dr. Manoj kumar (IISER, Bhopal, India) for Raman spectroscopy of the samples.

References

[1] Maensiri S, Masingboon C, Laokul P, Jareonboon W, Promarak V, Anderson P L and Seraphin S 2007 Egg White Synthesis and Photoluminescence of Platelike Clusters of CeO2 Nanoparticles Cryst. Growth Des. 7 950–5
[2] Yabe S and Sato T 2003 Cerium oxide for sunscreen cosmetics J. Solid State Chem. 171 7–11
[3] Channei D, Incesungvorn B, Wetchakun N, Ukritnukun S, Nattestad A, Chen J and Phanichphant S 2014 Photocatalytic Degradation of Methyl Orange by CeO2 and Fe–doped CeO2 Films under Visible Light Irradiation Sci. Rep. 4 5757
[4] Steele B C H 2000 Appraisal of Ce1–yGdyO2–y/2 electrolytes for IT-SOFC operation at 500°C Solid State Ion. 129 95–110
[5] Mansingh S, Padhi D K and Parida K M 2016 Enhanced photocatalytic activity of nanostructured Fe doped CeO2 for hydrogen production under visible light irradiation Int. J. Hydrog. Energy 41 14133–46

[6] Ranjith K S, Saravanan P, Chen S-H, Dong C-L, Chen C L, Chen S-Y, Asokan K and Rajendra Kumar R T 2014 Enhanced Room-Temperature Ferromagnetism on Co-Doped CeO2 Nanoparticles: Mechanism and Electronic and Optical Properties J. Phys. Chem. C 118 27039–47

[7] Abbas F, Jan T, Iqbal J, Ahmad I, Naqvi M S H and Malik M 2015 Facile synthesis of ferromagnetic Ni doped CeO2 nanoparticles with enhanced anticancer activity Appl. Surf. Sci. 357 931–6

[8] Kuriakose S, Satpati B and Mohapatra S 2014 Enhanced photocatalytic activity of Co doped ZnO nanodisks and nanorods prepared by a facile wet chemical method Phys. Chem. Chem. Phys. 16 12741–9

[9] Soni S, Kumar S, Meena R S, Vats V S and Dalela S 2015 Interplay of structural, optical and magnetic properties in Gd doped CeO2 AIP Conf. Proc. 1665 130029

[10] Khatun N, Rini E G, Shirage P, Rajput P, Jha S N and Sen S 2016 Effect of lattice distortion on bandgap decrement due to vanadium substitution in TiO2 nanoparticles Mater. Sci. Semicond. Process. 50 7–13

[11] Veis M, Kucera M, Zahradnik M, Antos R, Mistrik J, Bi L, Kim H-S, Dionne G F and Ross C A 20140507 Optical and magneto-optical properties of Co-doped CeO2−δ films in the 0.5 to 4 eV range J. Appl. Phys.

[12] Tiwari S, Bajpai G, Srivastava T, Viswakarma S, Shirage P, Sen S and Biring S 2017 Effect of strain due to Ni substitution in CeO2 nanoparticles on optical and mechanical properties Scr. Mater. 129 84–7

[13] Masui T, Fujikawa K, Machida K, Adachi G, Sakata T and Mori H 1997 Characterization of Cerium(IV) Oxide Ultrafine Particles Prepared Using Reversed Micelles Chem. Mater. 9 2197–204

[14] Wang G, Mu Q, Chen T and Wang Y 2010 Synthesis, characterization and photoluminescence of CeO2 nanoparticles by a facile method at room temperature J. Alloys Compd. 493 202–7

[15] Alla S K, Mandal R K and Prasad N K 2016 Optical and magnetic properties of Mg2+ doped CeO2 nanoparticles RSC Adv. 6 103491–8

[16] Weber W H, Hass K C and McBride J R 1993 Raman study of \( \text{CeO}_2 \) \( \text{Co}_2 \)\( \text{S}_2 \): Second-order scattering, lattice dynamics, and particle-size effects Phys. Rev. B 48 178–85

[17] Bernardi M I B, Mesquita A, Béron F, Priota K R, Zevallos A O de, Dorigueto A C and Carvalho H B de 2015 The role of oxygen vacancies and their location in the magnetic properties of Ce1−xCuxO2−δ nanorods Phys. Chem. Chem. Phys. 17 3072–80