Effect of transition elements substitution on structural, optoelectronic, magnetic and mechanical properties of CeO₂

Ph.D. Thesis

By

SAURABH TIWARI



DISCIPLINE OF METALLURGY ENGINEERING AND MATERIALS SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE April,2019

Effect of transition elements substitution on structural, optoelectronic, magnetic and mechanical properties of CeO₂

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Submitted in partial fulfillment of therequirements for the award of the degree **of**

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By

SAURABH TIWARI



DISCIPLINE OF METALLURGY ENGINEERING AND MATERIALS SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE April, 2019



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "Effect of transition elements substitution on structural, optoelectronic, magnetic and mechanical properties of CeO₂"in thepartial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY and submitted in the DISCIPLINE OF METALLURGY ENGINEERING AND MATERIALS SCIENCE, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from March, 2015to April, 2019under the supervision of Dr. Somaditya Sen, Associate professor, and Dr. Parasharam M. Shirage, Associate Professor, IIT Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Signature of the student with date (Saurabh Tiwari)

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

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SAURABH TIWARI has successfully given his Ph.D. Oral Examination held on 21st August 2019.				
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			То		
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	Me	All	my Teachers		
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- Saurabh Tiwari, Sajal Biring, Somaditya Sen, Effect of Co/Ni codoping in CeO₂ on structural, optical and vibrational properties; Material Today Proceeding, 5, 17641 (2018).
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Abbreviations

Cerium oxide	CeO_2
Bandgap	E_g
Urbach Energy	E_U
Oxygen Vacancies	Vo
Photoluminescence	PL
Full Width at Half Maxima	FWHM
Ultra Violet	UV
Visible	Vis
Diffuse reflectance spectroscopy	DRS
X-ray absorption near edge structure	XANES
Extended X-ray absorption fine structure	EXAFS
X-ray Diffraction	XRD
Physical property measurement system	PPMS

Chapter 1

Introduction

1.1 Basis and Motivation

1.1.1 Cerium Oxide (CeO₂): Importance and History

Cerium is the most abundant rare earth metal in the earth's crust (66.5 ppm).It is more abundant than copper (60 ppm) [1].Metallic cerium is available in various minerals i.e. Allanite/Orthite, Monazite, Bastnasite, Cerite, and Samarskite [Figure 1.1] [2].



Figure 1.1 *Allanite/Orthite, Monazite, Bastnasite, Cerite, and Samarskite* (Adapted with permission from www.iRocks.com)

The increasing mention of cerium oxide (CeO₂) is observed in catalysis [1], solid oxide fuel cells (SOFC) [3] and in some cases, it is irreplaceable. CeO₂ has strong redox and intrinsic structural properties which makes it special. Catalytic properties of CeO₂ are highly influenced as one approaches nanoscale size [4]. Production of CeO₂ with controlled size and morphology using new synthesis techniques leads to different functionalities [5]. The present principal global source of energy (fossil fuel) is on the verge of extinction. Hence, new sources of energy are being explored globally. It has indeed become a prime concern of the scientific community. This has led to an exponential rate of new technological development.Sustainable and environment friendly technologies are of specific interest. Renewable sources are the only reliable option for a consistent supply of energy in the future. CeO₂, having all these properties, is increasingly becoming more important [4,6-8]. CeO₂ has been consistently cited as a primary energy and environmental applications material since 1980. In three-way catalysis and photo-catalysis the role of cerium oxide is unique [9]. It is used in environmental applications for controlling toxic auto exhaust gas emissions. It is also used in major energy applications such as hydrogen production, dye-sensitized solar cell, solid oxide fuel cells (SOFC) and so on; with cerium-based compounds playing an important role. CeO₂-based compounds have led to breakthroughs in treating various diseases such as cancer, cardiac, inflammableetc [10,11]. It is also interesting that the multifunctional behavior of CeO₂ relies on decreasing dimensions of the materials to the nano-domain. Its wide applications are due to its high abundance and unique properties such as oxygen storage capacity, oxygen ion conductivity, high hardness, stability at high temperature and reactivity. Ce based materials have important industrial applications [3,9,12].

 CeO_2 has various applications in catalysis, bio-medical, solid oxide fuel cells (SOFC), UV-absorbent, polishing, gas sensor etc. This is used as three-way catalysis (TWC) for reducing pollutant emissions (mounted on exhaust of automobiles) and as fuel additives in diesel engines. It has major applications in catalysis i.e. in oxidation of cooking waste (hydrocarbons) for self-cleaning of ovens, in photocatalysis for degradation of dye pollutants. It is also used in sunscreens and cosmetics because it is UV-absorbent. The inclusive lists of present and potential applications of CeO₂ are discussed below. Ceria has excellent hardness properties hence it has found applications in glass polishing (chemical mechanical planarization (CMP) and removing SiO₂ films.

The catalytic properties of ceria come from its oxygen storage capacity (OSC) which helps in oxidation of lethal pollutants i.e. carbon monoxide (CO) and hydrocarbons to less harmful carbon dioxide (CO₂) as in TWC [92,95]. It is used in industries for de-nitrification and de-sulfurification of the waste from flue gases i.e. $NO_x \rightarrow NO_2$ and $SO_x \rightarrow SO_3$ [13].In oil refineries in fuel catalytic cracking (FCC), CeO₂ helps in de-sulfurification which in turn helps in the conversion of hydrocarbon present in crude oil to useful gasoline and olefinic gases. It is used in many industries in processing very harmful volatile organic compounds which are released as by-products. The catalytic application of CeO₂ is not only limited to gases since it has also successfully treated lethal pollutants present in waste water. Ceria also plays a crucial role in photocatalysis for degradation of dye pollutants.

The CH₄ (methane) \rightarrow H₂/CO₂ (synthesis gas) conversion with an H₂/CO₂ ratio '2' is achieved by CeO₂ which acts as recoverable oxidizing

agent [14]. This also has an application as a catalyst in the production of chemicals such as ethyl carbonate from ethanol, carbon dioxide and butylene. In present scenario, CeO₂-based catalysts have demonstrated great potential for photocatalysis and in SOFC. CeO₂ based materials shows high ionic conductivity and is hence used in SOFC as electrolyte and anode. These multifunctional applications of ceria-based materials are due to its OSC, which because of its nature of formation of oxygen vacancies is, reversible at the surface. This in turn depends upon the ability of ceria to reversibly change its oxidation state (Ce⁴⁺ \rightarrow Ce³⁺) as per the availability of oxygen partial pressure.

The property of changing valence state reversibly, also helps in designing long lasting and fast gas sensors. The oxygen and CO sensor have been developed by making a film of ceria ~100 nm by mist pyrolysis process. It is observed that time response depends on nanoparticle size which can be controlled by varying the firing temperature [15]. Its combination with other metals like Pt/Ce_{0.8}Gd_{0.2}O_{1.9}/Au also results in a CO sensor [16].

Ceria-based materials are also useful in anti-corrosion applications, owing to its redox ($Ce^{4+} \rightarrow Ce^{3+}$) properties. For guarding aluminum and steel alloys from corrosion, a thin coating ~100 nm is deposited on them using cathodic electrolytic deposition method [17]. The deposition of thin layer of CeO₂ nanoparticles (~5 nm) on alloys of steel prevents its oxidation even at high temperatures. The dielectric constant (k) and refractive index (n) of ceria can be tailored by varying the thickness of film growing epitaxially on Sisubstrate. This resulting film is used in CMOS technology as ultra-thin gate oxide [18]. Along with this, it also suppresses the gate leakage current. The epitaxial growth of ceria is performed on Si (111). This helps in the miniaturization of microelectronic devices for future electronic applications. If CeO₂ film (~3 nm) is grown on Si substrate epitaxially, it works as buffer layer when it is followed by the growth of tin–doped indium oxide (ITO) on it. In solar cells this system has got application [19].

CeO₂ has been cited as a UV absorbing material owing to its electronic properties. It protects substrate from UV radiation which are used in outdoor applications by screening them. Hence it is widely used in sunscreens and cosmetics [20] and in varnishes for forming clear coatings with improved UV protection [21,22].

Ceria nanoparticles are also used in various biomedical applications mainly for diseases which are related to reactive oxygen species (ROS) i.e. cardiac, Alzheimers and cancer [10]. The ROS scavenging properties of ceria nanoparticles makes it a potential candidate for treating oxidative stress and various diseases and disorders.

Recently, cerium-based compounds have found great application in photocatalysis in degradation of dye pollutants. CeO_2 has a high bandgap ~ 3.1 eV which allows the material to absorb only ultra violet (UV) radiation, thereby transmitting all the visible light. In solar radiation, UV light is only 2-3% of the entire spectra, whereas, in visible light it is ~ 45% [8]. Hence, to maximize the efficiency of CeO_2 , one needs to tune the bandgap so that it may absorb a major portion of the visible light.

1.1.2 Cerium: The element and its compounds

Cerium is a member of the Lanthanide Rare Earth elements with an atomic number 58 and electronic configuration [Xe] $4f^45d^1 6s^2$. It has two oxidation states, 3+ and 4+. Among the simple anions it can bond with F, O, Cl, Br. The electronegativity of these elements is in descending order i.e F>O>Cl>Br. Hence, a weaker electropositive Ce³⁺, can bond with weaker electronegative elements like Cl or Br by losing three electrons. On the other hand, the strongly electropositive Ce⁴⁺ bond only with two of the most electronegative O and F, because of high shielding of *f*-electron. However, oxygen being more abundant in nature than fluorine, cerium oxides are more common than fluorides. The most common oxide of Cerium, CeO₂ is discussed. However, cerium may also form Ce₂O₃ and a mixed valence compound CeO_{2-x} ($0 \le x \le 0.5$) due to both valence states of Ce [23]. Being a member of the lanthanide group Ce should be stable in Ce³⁺ state. But when it combines with 'O' or 'F' it shows a more stable Ce^{4+} state. The energy of 4f and 5d orbitals of Ce is like a large extent. This facilitates the changing of oxidation states as per the availability of oxygen in the neighborhood.


Figure 1.2 *Cubic fluorite structure of* Ce^{4+} *and* O^{2-} *of* CeO_2 *Crystal Structure*

Cerium oxide has a cubic fluorite structure with lattice parameter 5.4110 \pm 0.0005 Å and belongs to Fm3m space group in its perfect stoichiometry [Figure 1.2]. The structure remains stable with temperature up to the melting point ~2400°C. Ce⁴⁺ ions are surrounded by 8 O²⁻ ions; on the other hand, each O²⁻ is surrounded by 4 Ce⁴⁺ ions. The Wyckoff position of Ce is 4*a* 0,0,0 and of O is 8*c* 1/4, 1/4.

Imperfections in Ceria

In an ideal crystalline solid, atoms are arranged in a regular symmetric structure, which is periodic. This crystal structure can be obtained by the combination of a basis and infinite space lattice. This space lattice can be broken down to unit cells, where the entire crystalline structure can be built from the combination of these identical cells. However, in nature there are no perfect crystal structures; disorder is always present. Disorder in crystal structures occurs when atoms are displaced from their lattice positions and hence, the symmetry of the perfect periodic crystal lattice is broken. The disorder is also known as imperfections or defects. The types of defects are categorized with respect to their geometrical shape and include point defects, line defects and surface defects. Point defects dominate in ceria.

a) **Vacancies:** lattice positions that are unoccupied (vacant) due to a missing atom. Formation is stimulated by thermal vibrations.

b) **Substitutional**: When an impurity is present within the crystal.

c) **Interstitials**: Positions within the lattice are occupied where there are usually no atoms.

d) **Anti-sites:** When atoms of different types exchange positions in the crystal.

Morphology

Morphology and shape of CeO_2 can be tailored. These may result in different applicability of materials (Figure 1.3) Morphology and shape can be tailored. The precursor can determine these properties of the final sample maintain the same during the entire conversion to CeO_2 . The precursors may also impede the growth of specific lattice planes which results in anisotropic growth. There are various factors such as temperature, pressure, solvent, pH, etc. which affect morphology [25].

Creative shapes/structures like cluster formation or aggregation of small nanoparticles leading to formation of hollow spheres or raspberry-

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like aggregates are also obtained [8]. Morphology of ceria nanostructure can also be tailored by using templates of silicates or polymers which may be removed later leaving behind CeO_2 hollow structures. Preparing nanostructures from vapor phase is the most common amongst other synthesis techniques. However, different morphologies are generally obtained from wet chemical technique, hydrothermal, co-precipitation etc. Depending on the requirements of a specific application different techniques may be employed for synthesizing ceria at nanoscale.



Figure 1.3 shows morphologies of CeO_2 like (a) nanroads (b) flowers and (c) sphere Adapted with permission from ref 1. Copyright © 2016 American Chemical Society.

1.2 Properties:

1.2.1 Physical properties:

Cerium oxide is white or pale yellow in colour. It is also known by other names such as ceria and ceric oxide. CeO_2 is not soluble in water but commonly soluble in hard mineral acids. It is odourless, hygroscopic and tends to absorb moisture and CO_2 . Its molecular weight is 172.11 g/mol, density 7.65 g/cm³ and refractive index is 2.3. It has a high hardness of 6

(Mohr's hardness) and melting point ~2500°C. However, with a change in pressure and environment, the melting point may change.

1.2.2 Optoelectronic properties

In an ideal situation where all Ce ions are in Ce^{4+} state, the CeO₂ bandgap is ~6eV. The bandgap is formed due to O2p (valence band, VB) and Ce 5d, 6s (conduction band, CB) [26].



Figure 1.4 Left: Band tails due to impurities (C.B: Conduction band, V.B: Valence band, E_g : Bandgap, E_g' : Reduced bandgap, and DOS: Density of states), Right: Energy band for CeO₂, where cerium is in the Ce⁴⁺ state, and the trap level associated with cerium is in the Ce³⁺ state [26].

A narrow sub-band ~1eV is formed due to the presence of empty $Ce^{4+} 4f^{0}$ states [27]. This effectively reduces the bandgap to ~4.58eV (above VB) (Figure 1.4). However, in presence of Ce^{3+} ions, a $Ce^{3+}4f^{4}$ sub-band is formed ~1.2-1.5eV above the VB and 3.3eV below the CB [27].

This band behaves as a hole trap in the bandgap. This creates an energy gap of ~3.1-3.3eV between available electrons in $Ce^{3+}4f^{4}$ and the empty $Ce^{4+}4f^{0}$ sub-band.

The bandgap varies from $\sim 3eV-3.7eV$. The value depends upon various factors i.e. synthesis technique, growth and post-growth process temperatures, and the size of the particles. Addition of doping elements or impurities in a semiconductor modifies the effective bandgap due to bandto-impurity level transitions. The dopant creates traps within the forbidden bandgap or due to local variations in the bandgap owing to formation Ce₂O₃. The other phenomenon is the formation of Urbach tail near the bands. Since impurities scatter arbitrarily and are grouped unevenly in lattice, they cause differences in local interactions which lead to such local variances in bond lengths and therefore the energy gap. The density of states (DOS) associated with tails extend into the bandgap. This is shown schematically in Fig. 1.4. Hence, CeO₂ nanostructures are vital for future solar applications.

On the other hand, presence of oxygen vacancies, V_0 , may create states inside the bandgap. Generally, a V_0 can trap two electrons. The trapped state is generally represented in the academic literature as F or F⁰ state. The F⁰ state may lose one electron and become F⁺ state and further lose two electrons to become F⁺⁺ state [28].Theoretical calculations show that F⁺ states are closer to VB compared to F⁰ states [29]. However, F^{++} centers are located at about ~0.15-0.2eV below the CB [29]. F^{++} states act as electron traps [29]. There is a fundamental difference between the F^{++} state and the F^+ or F^0 states. While F^{++} have no localized electrons, F^+ and F^0 states have electrons and are partially and fully occupied states [30]. The F^+ and F^0 states are ~1.7eV and ~2.1eV above the VB and ~3eV and ~2.74eV below CB [30,31]. However, excited states of F^+ and F^0 states are also empty states and are located near the CB and are denoted as F^{+*} and F^{0*} respectively. The excited states of F^+ and F^{0*} are ~0.4eV below CB.The difference between F^0 and F^{0*} is ~2.1eV; while, that of F^{+*} and F^+ is 2.4-2.5eV. Various complex defects like Ce³⁺–Vo–Ce³⁺may also exist. Such complex defect states have been explained as accidental recombination sites of a hole due to Ce³⁺ and an electron at the V₀ site. Such defects show a Stokes-shifted broad luminescence.

Hence, defects are located everywhere in the bandgap. Therefore, it was found logical to fit a wide band PL data with multiple peaks to not only observe major contributions involving well known defects states but also gather knowledge on the distribution of complex defects in the lattice. It is also to be noted that a $Ce^{3+}4f^{-1}$ electron is not actually located at a single location but can in fact travel from one Ce atom to another. Thereby, depending on the availability of V₀ sites in the near vicinity and the distortions in the lattice, the respective energy levels are supposed to behave as multiple defect possibility in the lattice, forming simple and complex defect states all along the bandgap.

1.2.4 Electrical properties

CeO₂ has been scientifically established as a good oxide ion conductor [32]. It is used as a reference material for the analysis of electrolytic properties of fluorite structured metal oxides [33]. It shows ionic conductivity when doped with acceptor ions. It is even superior to ZrO_2 at fixed doping amount and concentration in solid oxide fuel cells (SOFC) [34]. But at elevated temperatures and low oxygen partial pressure, it suffers from reduction of $Ce^{4+} \rightarrow Ce^{3+}$ which results in decreased ionic conductivity owing to the emergence of electronic conductivity. It is used as an interfacing material for Si on insulator usages, superior dielectric capacitors and as a buffer material [35]. Nanoscale ceria, at lower temperatures show higher oxide conductivity than at microscale. Oxygen ion conduction in nanoscale material is considered more efficient through surface or interface than crystal interior. It is observed that at nanoscale, this material has higher DC conductivity than at microscale. The activation energy for polycrystalline CeO₂ is reported as 0.4 eV (electronic activated hopping) to 0.7 eV (ionic transport). On the other hand, in redox regulated electronic conduction it is observed to be between 1.7 and 2.7 eV (acceptor-dominance in defect region). Hence, this makes CeO₂ a prominent material for investigation for future electrical applications.

1.2.5 Magnetic properties

In future spintronic applications, oxide based diluted magnetic semiconductor (DMS) will attain a greater importance. They show room temperature ferromagnetism (RTFM) with curie point higher than RT and are also optically transparent [23,36,37]. The ferromagnetic properties of oxide based DMS is described by carrier induced ferromagnetism. However, sometimes defects (especially Vo) play an important role in RTFM in oxide based DMS along with carrier. It is reported that Co doped CeO₂ shows high magnetic moment of 5.8 μ B/Co and 560 Oe coercivity [38].This not only depends upon the transition element doping but also on crystallization, defect concentration like Vo as well. These defects play a significant role in magnetic coupling. RTFM observed in CeO₂ is caused by oxygen vacancies, while substitution of transition element increases it further. Hence, it can be concluded that Vo along with doping result in RTFM in CeO₂.

1.2.6 Mechanical properties

Ceria has excellent hardness properties. It is applied in glass polishing (chemical mechanical planarization (CMP)) and removing SiO₂ films [39,40]. SOFC electrolytes should have high chemical stability along with good mechanical properties. Despite having high chemical stability, ceria has inferior mechanical properties in contrast to ZrO₂. Hence, one needs to improve the mechanical properties of ceria. The oxidation state of CeO₂ varies with the oxygen partial pressure. This leads to volume expansion and compression, thereby causing stress in the electrolyte and affecting ceria's performance as an electrolyte in a SOFC. This may be rectified by layering the electrolyte with yttria stabilized zirconia (YSZ) and by decreasing operating temperature ($<750^{\circ}$ C).

1.3 Method of Synthesis:

Ceria nanostructures are mainly synthesized by solid state reaction method [41,42]and Wet-chemical methods. Wet-chemical methods include hydrothermal [43–45], solvothermal [46,47], chemical vapor deposition [48,49], sol-gel [50–52]etc. A selected few are discussed in the following section.

1.3.1 Solid State Reaction Method

Conventional mixed oxide method may also be named as solid-state method. In a solid-state reaction method, individual oxides are mixed in stoichiometric quantities and are ground well to obtain a homogeneous mixture (Figure 1.5). The grinding is done by different methods such as ball milling, mortar and pestle (ceramic) etc.



Figure 1.5 Synthesis of nanostructures by solid state reaction method

The ground powder is subjected to annealing, usually at elevated temperatures, for long periods of time. This results in a large particle size with a wide particle size distribution. It also improves the compaction and thermal reactivity of the powder by reducing particle size and creating defects inside the powder crystallites. The wet milling (i.e. grinding in some alcoholic or aqueous medium) is preferable than dry milling which adversely affects the particle size. Although this conventional process is dated, it is continued as to meet the massive demands of the soft ferrite industry. Some disadvantages of Solid-state routes are: High temperatures are generally required (500-2000°C) because it takes a significant amount of energy to overcome the lattice energy, so that a cation or anion can diffuse into a different site. The desired compound may decompose at higher temperatures. The reaction may proceed very slowly, but increasing the temperature speeds up the reaction since it increases the diffusion rate. Generally, solids are not raised to their melting point, so reactions take place in the solid state (subsolidus).

1.3.2 Hydrothermal Method

It is the technique used to crystallize a material by using aqueous solution at high temperature and pressure. Hydrothermal synthesis takes place in a closed container in which water is used as solvent. When this container is heated, a very high pressure is induced in the container and the reaction which takes place at such an elevated pressure is known as a hydrothermal reaction (Figure 1.6). When the temperature of a liquid increases from its critical point, the liquid is said to be supercritical and the fluid demonstrates the properties of a liquid as well as a gas. The surface tension of the liquid becomes negligible and dissolves the compound easily.





The critical temperature and pressure of water is 374 °C and 218 atm respectively. But the reaction rate is slow and to increase the reaction rate; ultrasonic, electric field or microwaves are used which increases their cost. The hydrothermal system in which ultrasonic methods are used for heat treatment is called ultrasonic-hydrothermal. Similarly, the hydrothermal system using microwaves and electric fields for heating are called microwave-hydrothermal and electrochemical-hydrothermal respectively.

There are other techniques for synthesizing ceria nanoparticles. Amongst several other synthesis methods; sol-gel is economic, easy and less time consuming. It also provides homogeneous samples of high purity and can be used for bulk production of nanoparticles.

1.3.3 Sol-gel synthesis route:

The synthesis of materials using sol-gel method dates to the late-18th century. However, it became widely used only in the late-19th century, when glass was made using sol-gel technique. The use of elevated temperature for melting was avoided. A solution (sol) of required precursors was prepared. By applying heat, evaporation of liquid phase takes place and a complex polymeric chain forms, known as gel. Polymeric chains are formed with a combination of oxo (-O-) or hydroxo (-OH-) groups with dissolved metal ions which leads to the formation of M-O-M/M-OH-M. Parameters such as pH, precursor type, polymerization agent, etc. are varied from case to case. Sol-gel ceramics or polymers are prepared in this way.

The important features of the sol-gel method are: a) Better homogeneity b) High purity c) Lower processing temperature d) Better size and morphological control e) More uniform phase distribution in multi component systems like ferrites.

Citrate Method:

Citrate $(C_3H_5O (COO)^{3-3})$ sol-gel method is widely used. Citric acid $(C_3H_5O(COOH)_3)$ is an excellent polymerization agent. It is one of the best economic and effective binders for metal ions. Hence, in sol-gel it is used as a binder for forming polymeric chains of metal ions. Different

chemicals can be used for preparing gel, but the citrate method is the most common. Metal oxides are easily formed from gel by pyrolysis in air. Different types of metal oxides simple or complex can be easily synthesized in either amorphous or crystalline form. Calcining at ~450°C, all unwanted compounds (organic and nitrous compound) are eliminated, so that the pure and homogenous metal oxide powder of different morphologies can be obtained. In the present work citrate sol-gel method is used for synthesis of cerium oxide.

Citric acid easily dissolves in water @ RT

$$CA + H_2O \leftarrow [CA]^- + [H_3O]^+$$

Negative citrate species \rightarrow complexes with metal ions

 \rightarrow stronger complex \rightarrow better homogeneity

 \rightarrow Generally, stability.

 \rightarrow trapping the randomness of homogeneous metal ion solution

Glycerol \rightarrow added (not for pH adjustment)

 \rightarrow facilitates multiple condensation reaction to form polyester

 \rightarrow gel formation results from poly-ester

Polymeric network \rightarrow a fishing net, traps the metal-citrate complexes \rightarrow homogeneity/ randomness polyester \rightarrow highly thermoplastic \rightarrow enormous swelling on heating

Metal-citrates are usually bi-or tridentate. Hence, they are less stable compared to EDTA-Metal complexes.

1.4 Scope and Goals of Thesis

The main objective of this thesis is to study the structural, optical, photoluminescence, magnetic and mechanical properties of modified single phase CeO₂ nanostructures. The CeO₂ nanostructures are synthesized using a normal sol-gel process and then systematically studied using XRD, HRTEM, EXAFS, XANES, Raman spectroscopy, UV-vis spectroscopy, PL spectroscopy, PPMS, and Vickers's hardness tester. The properties being extensively studied, are then proposed for diverse applications including, solar, biomedical, and catalysis.

1.4.1 The precise objectives of the research work plan are categorized as follows:

- Synthesis of pure and Mn/Co/Ni modified CeO₂nanopowders using modified sol-gel process.
- Study of structural changes with substitution using XAS/XRD/HRTEM and Raman spectroscopy.
- In-depth analysis of structure-property relationship and reporting mechanism/phenomenon for unique behavior observed in modified CeO₂ nanostructures.
- 4. Proposing transition elements doped and co-substituted CeO₂ based material for prospective multifunctional applications.

1.4.2. The current work is performed in a planned manner as:

(i) Synthesizing pure and substituted/co- substituted CeO₂ samples.

- (ii) Analyzing the effect of Co substitution on structural, optoelectronic and mechanical properties of CeO₂.
- (iii) Analyzing the effect of Ni substitution on structural, optical, vibrational, photoluminescence and mechanical properties of CeO₂.
- (iv) Analyzing the effect of Co-Ni substitution on structural, optical, vibrational, and photoluminescence mechanical properties of CeO₂.
- (v) Analyzing the effect of Mn, Co-Mn and Mn-Ni substitution on structural, optical, vibrational, magnetic and mechanical properties of CeO₂.

The remaining chapters of the thesis are summarized as follows:

Chapter 2: Experimental Details

This chapter discuss the synthesis method of undoped and doped CeO₂ along with a brief explanation of instruments used and their working principle.

The instruments used include: X-ray diffraction (XRD), Extended X-ray absorption fine structure (EXAFS), X-ray absorption near edge structure (XANES), Raman spectroscopy, High resolution transmission electron microscope (HRTEM), Field emission scanning electron microscope (FESEM), UV-Vis spectroscopy, Photoluminescence spectroscopy (PL), Physical Property measurement system (PPMS) Vickers's micro-hardness tester, etc.

Chapter 3: Effect of Co substitution on structural, optical and

mechanical properties of CeO₂

- XRD pattern, HRTEM and Raman spectra are used to confirm the exact phase of CeO₂ and lattice distortion.
- Rietveld refinement of XRD data is done using Fullprof software to see the effect of Co substitution on crystal structure of CeO₂.
- Valence states of elements, oxygen vacancies, and modification in structure are confirmed by XANES and EXAFS analysis.
- HRTEM images are used to see particle size, morphology, chemical composition and distribution of the element in the samples.
- Effect of Co substitution on bandgap and mechanical properties of CeO₂ is analyzed by DRS measurement and Vickers's Micro-hardness tester respectively.

Chapter 4: Effect of Ni substitution on structural, optoelectronic and

mechanical properties of CeO₂

- Phase formation of the samples is confirmed by XRD pattern, HRTEM and Raman spectra.
- Structural distortion due to Ni substitution and valence states of elements is analyzed by XANES and EXAFS study.

- HRTEM images are used to see particle size, morphology, chemical composition and distribution of the element in the samples.
- DRS study is performed to observe the change in absorption spectra and modification of bandgap of CeO₂ by Ni substitution.
- Photoluminescence and Vickers's hardness testing study is performed to observe the change in emission spectra and hardness of CeO₂ by Ni substitution.

Chapter 5: Effect of Co-Ni substitution on structural, optical,

vibrational and photoluminescence properties of CeO2

- XRD pattern is used to see the effect of Co-Ni cosubstitution on structural modification of CeO₂.
- Phase formation of the samples is confirmed by XRD, HRTEM and Raman spectra.
- Structural distortion due to Co-Ni substitution and valence states of elements is analyzed by XANES and EXAFS study.
- HRTEM images are used to see particle size, morphology, chemical composition and distribution of the element in the samples.
- DRS study is performed to observe the change in absorption spectra and tuning of bandgap of CeO₂ by Co-Ni substitution.
- Photoluminescence study is performed to observe the change in emission spectra CeO₂ by Co-Ni co-substitution.

<u>Chapter 6: Effect of Mn, Co-Mn and Mn-Ni substitution on</u> structural, optical, magnetic and mechanical properties of CeO₂.

- XRD pattern is used to see the effect of Mn, Co-Mn and Mn-Ni co-substitution on structural modification of CeO₂.
- Phase formation of the samples are confirmed by XRD, HRTEM and Raman spectra.
- Structural distortion due to Mn, Co-Mn and Mn-Ni substitution and valence states of elements is analyzed by XANES and EXAFS study.
- HRTEM images are used to see particle size, morphology, chemical composition and distribution of the element in the samples.
- DRS study is performed to observe the change in absorption spectra and modification in bandgap of CeO₂ by Mn, Co-Mn and Mn-Ni substitution.
- PPMS and Vickers's hardness testing study is performed to observe the change in magnetic properties and hardness of CeO₂ by Mn, Co-Mn and Mn-Nico-substitution.

Chapter-7: Conclusions and Future Research Scope

- Summary of present research work
- Concluding remarks
- Future scope of the present study

Chapter 2

Experimental Details

This chapter includes the sample specifications, detailing the sol-gel technique used for synthesis and instrumental setup used for characterization and analysis of the properties. The samples were analyzed by the following techniques:

- (i) X-ray diffraction (XRD)→ to ensure crystal structure and phase purity
- (ii) Raman spectroscopy→ to analyses vibrational modes of pure and Mn/Co/Ni doped CeO₂
- (iii) High resolution transmission electron microscope (HRTEM)→
 to investigate crystal structure and microscopic phase
 individuality
- (iv) Field Emission Scanning Electron Microscopy (FESEM)→ to study the morphology
- (v) Energy Dispersive X-ray spectroscopy (EDX) to study elemental composition
- (vi) UV-Visible spectroscopy (UV-Vis)→ to investigate variations in bandgap
- (vii) Photoluminescence spectroscopy (PL)→ to observe defect states in the bandgap
- (viii) X-ray absorption spectroscopy (EXAFS/XANES)→ to analyze variations in CeO₂ local structure and estimate oxidation states of Ce, Mn, Co and Ni
- (ix) Vickers's hardness test \rightarrow to estimate micro-hardness
- (x) Physical property measurement system (PPMS)→to investigate variations in magnetic properties

A brief discussion on the field of study including the importance of the material and these properties is also presented in this chapter.

2.1 Synthesis process

Today, ceramics are an integrated part of human life. It constitutes a vital part of investigation in material science and thrives to find better usage. There are various synthesis techniques for synthesizing ceramic materials; some of them include: co-precipitation, sol-gel, solid state reaction and hydrothermal technique, etc.

In this work CeO₂-based ceramic materials were synthesized using standard Pechini sol-gel method followed by calcination at elevated temperatures [Figure 2.1].

2.1.1 Sol-gel method

Polycrystalline CeO₂ nanopowders were prepared using cerium (III) nitrate hexa-hydrate (99.99 %, Alfa Aesar, Puratronic).



Figure 2.1 Schematic diagram of Sol-gel method

It was dissolved in doubly deionized (DDI) water of low conductivity ~ 0.055 $\mu \Omega^{-1}/cm$. Solutions of nitrates of dopant elements Co, Ni and Mn with high purity (discussed later) in DDI water were used

as dopant precursors. The required precursors were mixed together and stirred for 2h to ensure homogeneous mixing of the component ions. A solution of citric acid and glycerol was heated at 80°C for 2h in a different beaker to form a polymeric solution which can act as a binder for gel formation when added to precursor solution containing Ce and other dopant ions. This polymeric solution causes homogenous attachment of Ce ions to its chains.

This final solution was stirred and heated at ~80°C on a magnetic stirrer to dehydrate the solution. A yellowish black powder was formed which was ground and heated in air at 450°C for 6h to denitrify and decarburize. Off-white powders of different tints of yellow were formed for different substitution concentrations in CeO₂. For structural, electrical and mechanical analysis, pellets were prepared at uni-axially applied 4 tons pressure and thereafter sintered in muffle furnace.

 $Ce(NO_3)_3.6H_2O + C_6H_8O_7 + C_3H_8O_3 \rightarrow$

 $-(C_2H_5 - O - Ce - O - C_2H_5)_n \rightarrow$

 $CeO_2 + H_2O + N_2\uparrow + CO_2\uparrow$

2.2 Substituted sample preparations

All the substituted samples were synthesized using the same procedure as discussed in the previous section. All the precursors were used in stoichiometric ratio and mixed in a similar way as discussed in the previous section. The details of preparing these solutions are discussed in the following sections.

i. Ni substituted CeO₂ synthesis:

 $Ce_{(1-x)}NixO_2$ samples were prepared for x = 0, 0.025, 0.05 and 0.10 compositions using sol-gel method and named as CNO0, CNO2, CNO5 and CNO10 respectively. These samples were prepared using high purity

precursors of Cerium (III) nitrate (Ce(NO₃)₃ .6H₂O) and Nickel nitrate (Ni(NO₃)₂.6H₂O) with purity > 99.99 % (Alfa Aesar, Puratronic grade). The equation for synthesis is as follows:

$$Ce(NO_{3})_{3.6}H_{2}O + Ni(NO_{3})_{2.6}H_{2}O + C_{6}H_{8}O_{7} + C_{3}H_{8}O_{3} \rightarrow$$

-(C_{2}H_{5}-O-Ce-O-C_{2}H_{5}-O-Ni-O-C_{2}H_{5})_{n} \rightarrow
$$Ce_{1-x}Ni_{x}O_{2} + H_{2}O + N_{2}\uparrow + CO_{2}\uparrow$$

Ce(NO₃)₃ and Ni(NO₃)₂ were dissolved in double distilled water in separate beakers. Ni solution was mixed with Ce solution and stirred for 1h. In a different beaker a solution of citric acid and glycerol in 1:1 molar ratio was prepared as gel former and later added to this solution. The resultant solution was vigorously stirred and heated at ~ 80 °C on a hot plate to form gels. The resultant gels were heated to form a black powder thereby heated for de-carburization and de-nitrification at 450 °C for 6h. The well grinded powder pressed into Pellets (diameter ~10 mm; thickness ~1.5 mm) by pressing uniaxially. For making these pellets mechanically dense, they were sintered at 1400 °C for 12 h.

ii. Co substituted CeO₂ synthesis:

Nano-crystalline powder of $Ce_{(1-x)}Co_xO_2$ for x = 0,0.025, 0.05 and 0.10 compositions were taken and named as CCO0, CCO2, CCO5 and CCO10. Samples were synthesized using sol-gel process with using precursors: Cerium (III)nitrate hexa hydrate (99.99 %, Alfa Aesar) and Cobalt (II) nitrate hexa-hydrate (99.99 %, AlfaAesar).Ce(NO3)3 and Co(NO3)2 were dissolved in double distilled water in separate beakers. Co solution was mixed with Ce solution and stirred for 1h. In a different beaker a solution of citric acid and glycerol in 1:1 molar ratio was prepared as gel former and later added to this solution. The resultant solution was vigorously stirred and heated at ~ 80 °C on a hot plate to form gels.

The equation for synthesis is as follows:

$$Ce(NO_{3})_{3.}6H_{2}O + Co(NO_{3})_{2.}6H_{2}O + C_{6}H_{8}O_{7} + C_{3}H_{8}O_{3} \rightarrow$$

--(C_{2}H_{5}-O-Ce-O-C_{2}H_{5}-O-Co-O-C_{2}H_{5})_{n} \rightarrow
$$Ce_{1-x}Co_{x}O_{2} + H_{2}O + N_{2}\uparrow + CO_{2}\uparrow$$

The resultant gels were heated to form a black powder thereby heated for de-carburization and de-nitrification at 450 °C for 6h. The well grinded powder pressed into Pellets (diameter ~10 mm; thickness ~1.5 mm) by pressing uniaxially. For making these pellets mechanically dense, they were sintered at 1400 °C for 12 h.

iii. Co-Ni co-substituted CeO₂ synthesis:

nanoparticles The polycrystalline of $Ce_{0.9}(Co_xNi_{1-})$ $_{x}$)_{0.1}O₂samples were prepared for x = 0 (CNO), 0.5 (CCNO) and 1 (CCO)using sol-gel method. These samples were prepared using high purity precursors of Cerium (III) nitrate (Ce(NO₃)₃.6H₂O), Nickel nitrate (Ni(NO3)₂.6H₂O) and Cobalt nitrate (Co(NO3)₂.6H₂O) with purity > 99.99 % (Alfa Aesar, Puratronic grade). Ce(NO₃)₃, Ni(NO₃)₂and Co(NO₃)₂ were dissolved in double distilled water in separate beakers. Ni and Co solution were mixed with Ce solution and stirred for 1h. The equation for singly substituted samples synthesis is previously discussed and for co-substituted samples is as follows:

 $Ce(NO_3)_{3.}6H_2O + Co(NO_3)_{2.}6H_2O + Ni(NO_3)_{2.}6H_2O + C_6H_8O_7 + C_3H_8O_3 \rightarrow -(C_2H_5 - O - C_2H_5 - O - C_2O - C_2H_5 - O - Ni - O - C_2H_5)_n \rightarrow$

 $Ce_{0.9}(Co_xNi_{1-x})_{0.1}O_2 + H_2O + N_2\uparrow + CO_2\uparrow$

The resultant gels were heated to form a black powder thereby heated for de-carburization and de-nitrification at 450 $^{\circ}$ C for 6h.

iv. Mn substituted CeO₂ synthesis:

The polycrystalline nanoparticles of $Ce_{(1-x)}Mn_xO_2$ samples were prepared for x=0, 0.025, 0.05 and 0.10 compositions using sol-gel method and named as CMO0, CMO2, CMO5 and CMO10 respectively. These samples were prepared using high purity precursors of Cerium (III) nitrate (Ce(NO₃)₃.6H₂O) and Manganese nitrate (Mn(NO₃)₂.4H₂O). Ce(NO₃)₃ and Mn(NO₃)₂ were dissolved in double distilled water in separate beakers. Mn solution was mixed with Ce solution and stirred for 1h. The resultant gels were heated to form a black powder thereby heated for de-carburization and de-nitrification at 450 °C for 6h. The well grinded powder pressed into Pellets (diameter ~10 mm; thickness ~1.5 mm) by pressing uniaxially. For making these pellets mechanically dense, they were sintered at 1100 °C for 12 h.The equation for singly substituted samples' synthesis is previously discussed and for substituted samples is as follows:

$$Ce(NO_{3})_{3.}6H_{2}O + Mn(NO_{3})_{2.}4H_{2}O + C_{6}H_{8}O_{7} + C_{3}H_{8}O_{3} \rightarrow$$

-(C_{2}H_{5}-O-Ce-O-C_{2}H_{5}-O-Mn-O-C_{2}H_{5})_{n} \rightarrow
$$Ce_{1-x}Mn_{x}O_{2} + H_{2}O + N_{2}\uparrow + CO_{2}\uparrow$$

The resultant gels were heated to form a black powder thereby heated for de-carburization and de-nitrification at 450 °C for 6h. The well grinded powder pressed into Pellets (diameter ~10 mm; thickness ~1.5 mm) by pressing uniaxially. For making these pellets mechanically dense, they were sintered at 1100 °C for 12 h.

v. Mn and Co substituted CeO₂ synthesis:

The polycrystalline nanoparticles of $Ce_{0.9}(Co_xMn_{1-x})_{0.1}O_2$ samples were prepared for x = 0 (CMO), 0.5 (CCMO) and 1 (CCO) using sol-gel method. These samples were prepared using high purity precursors of Cerium (III) nitrate $(Ce(NO_3)_3)$.6H₂O), Manganese nitrate $(Mn(NO_3)_2.4H_2O)$ and Cobalt nitrate $(Co(NO3)_2.6H_2O)$ with purity > 99.99 % (Alfa Aesar, Puratronic grade). Ce(NO₃)₃, Mn(NO₃)₂ and $Co(NO_3)_2$ were dissolved in double distilled water in separate beakers. Mn and Co solution were mixed with Ce solution and stirred for 1h. The resultant gels were heated to form a black powder thereby heated for decarburization and de-nitrification at 450 °C for 6h. The equation for singly substituted samples synthesis is previously discussed and for cosubstituted samples is as follows:

 $Ce(NO_3)_{3.}6H_2O + Co(NO_3)_{2.}6H_2O + Mn(NO_3)_{2.}4H_2O + C_6H_8O_7 + C_3H_8O_3 \rightarrow -(C_2H_5 - O - Ce - O - C_2H_5 - O - Co - O - C_2H_5 - O - Mn - O - C_2H_5)_n \rightarrow$

 $Ce_{0.9}(Co_xMn_{1-x})_{0.1}O_2 + H_2O + N_2\uparrow + CO_2\uparrow$

vi. Mn and Ni substituted CeO2 synthesis:

The polycrystalline nanoparticles of Ce_{0.9}(Mn_xNi_{1-x})_{0.1}O₂ samples were prepared for x = 0 (CNO), 0.5 (CMNO) and 1 (CMO) using sol-gel method.These samples were prepared using high purity precursors of Cerium (III) nitrate (Ce(NO₃)₃.6H₂O), Manganese nitrate (Mn(NO₃)₂.4H₂O) and Nickel nitrate (Ni(NO₃)₂.6H₂O) with purity > 99.99 % (Alfa Aesar, Puratronic grade). Ce(NO₃)₃, Mn(NO₃)₂ and Ni(NO₃)₂ were dissolved in double distilled water in separate beakers. Mn and Ni solution were mixed with Ce solution and stirred for 1h. The equation for singly substituted samples is as follows:

 $Ce(NO_{3})_{3.}6H_{2}O + Mn(NO_{3})_{2.}4H_{2}O + Ni(NO_{3})_{2.}6H_{2}O + C_{6}H_{8}O_{7} + C_{3}H_{8}O_{3} \rightarrow -(C_{2}H_{5}-O-Ce-O-C_{2}H_{5}-O-Ni-O-C_{2}H_{5}-O-Mn-O-C_{2}H_{5})_{n} \longrightarrow Ce_{1-x-y}Mn_{x}Ni_{y}O_{2} + H_{2}O + N_{2}\uparrow + CO_{2}\uparrow$

The resultant gels were heated toform a black powder thereby heated for de-carburization and de-nitrification at 450 °C for 6h.

2.3 Characterizations techniques

2.3.1 X-Ray Diffraction

To inspect the lattice structure and lattice dynamics of a material, X-Ray diffraction (XRD) is one of the most important and reliable tools because of the comparable wavelength of X-rays (it is of the order of Å) and inter-atomic distances. XRD is used to determine the structural properties of materials, etc. Hence, understanding the structural details, such as the shape and symmetry of the unit cell, positions of the ions, nature and distances of the bonds become extremely important. Its nondestructive nature is another advantage of this technique. In XRD, an X-ray falls on the material at some incident angle and get diffracted through different set of atomic planes present in the crystal structure .When, both, d (spacing between successive atomic planes; also called as d-spacing) and θ (the angle of incidence of X-ray), satisfies the Bragg relation $2dsin \ \theta = n \ \lambda$ (here, d is the inter-planer distance, λ is wavelength of incident X-ray and n is an integer), a constructive interference takes place between the diffracted waves. The Bragg condition i.e., the basics of XRD can be understood with help of a schematic ray diagram depicted in Figure 2.2.

According to Figure 2.2, the geometrical path difference between ABC and A'B'C' (say Δ) = N'B'+B'N

= **BB'** Sin θ + **BB'** Sin θ

 $\Delta = 2 \text{ BB' } Sin\theta = 2d Sin\theta$ (2.1)

For the constructive interference, the path difference is always an integer multiple of wavelength, i.e.

$$\Delta = n \lambda \quad (2.2)$$

Now from equations 2.1 and 2.2, the Bragg's condition for constructive interference of diffracted X-rays is $2d Sin\theta = n\lambda$, where n is an integer. The diffracted X-ray photons are then detected, processed and counted. In this way when Bragg's law satisfies, a peak, across the corresponding θ value appears in the intensity versus angle (2 θ) curve. Conversion of the diffraction peaks to d-spacing enables the identification of the material under investigation. Now it's to be noted that the XRD pattern of each element/material is unique and can be considered as a signature of its structural phase. This uniqueness enables the XRD to identify and validate the purity of a structural phase for given a material. XRD pattern depicts almost complete information about the crystal structure like lattice parameters, bond angles, grain size, strain etc.



Figure 2.2 Diffraction of X-rays through lattice/atomic planes of acrystal.

For the studies of structure of elements, the samples in the form of powder/pellet/film can be probed by use of XRD. Here, 2θ is the angle between incident beam and diffracted beam.

Powder diffraction

A single crystal produces only one family of peaks in the diffraction pattern. A polycrystalline sample contains thousands of crystallites. Therefore, all possible diffraction peaks are observed. Powder diffraction is used for characterization of polycrystalline materials. The basic assumption of powder diffraction is that for every set of planes, there are statistically relevant numbers of crystallites that are properly oriented to diffract the incident beam. The diffraction pattern is the fingerprint of any crystalline phase. The position, intensity, shape and width of the diffraction lines give s information on the samples. Powder diffraction data consists of a record of photon intensity versus detector angle 2 Θ . Diffraction data can be reduced to a list of peak positions and intensities. Each d_{hkl} corresponds to a family of atomic planes (*hkl*). However, individual planes cannot be resolved by this method; this is a limitation of powder diffraction versus single crystal diffraction

Applications

The major applications of XRD are discussed below.

1. Phase Identification

The catalysts are generally composed of mixture of several phases. The diffraction pattern for each phase is as unique as a fingerprint. Phases with the same chemical composition can have drastically different diffraction patterns. Phase identification is based on the comparison of the diffraction pattern of the specimen with that of pure reference phases or with a database. Databases such as the Powder Diffraction File (PDF) contain lists for thousands of crystalline phases. The PDF contains over 200,000 diffraction patterns. Modern computer programs can determine the phases present in a sample by quickly comparing the diffraction data to all of the patterns in the database. Various crystalline phases can be quantified based on the fact that each phase of the mixture gives its characteristic

diffractogram independently of the others and the intensity depends on the amount present in the mixture.

2. Determination of average crystallite size

Ideally, a Bragg diffraction peak is a line without width. In reality, diffraction from a crystal specimen produces a peak with a certain width. This is known as peak broadening. The peak width depends on the size of the crystals. Peak width is inversely related to crystal size; that is, peak width increases with decreasing crystal particle size.

The average crystallite size can be determined by Scherrer formula using elementary line broadening analysis. The Scherrer formula assumes that the breadth of the diffraction peak of crystallites (small single crystals) mainly depends on the characteristics of crystallites (size and the defect in the lattice). Elementary analysis of the broadening assumes that lattice deformation is negligible. Crystallite sizes were estimated using Scherer's equation ($D = K\lambda/\beta cos\theta$ (where, K=0.9)), where β is full width at half maxima (FWHM), D is the crystallite size, θ is angle of incidence and λ is wavelength of $K\alpha$ radiation].

The diffraction corresponding to the most intense peak is selected to calculate the average crystallite size using Scherrer relation. The Scherrer formula assumes that crystallite size is the major source leading to line broadening effects of the diffractions peaks, but there is always a broadening can also be due to instrumental factors such as slit width, sample size, imperfect focusing or misalignment of diffractometer.

3. Spacing between atomic planes of a crystal

Based on Bragg's Law, information on spacing between atomic planes can be obtained when constructive interference occurs. Knowing the spacing of crystallographic planes by diffraction methods, the crystal structure of materials can be determined. The plane spacing of cubic crystal is related to the lattice parameter (a) by the following equation.

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

From Braggs Law, $n\lambda = 2d \sin \theta$.

Combining ,

$$\sin^2\theta = \frac{n^2\lambda^2}{4a^2} \left(h^2 + k^2 + l^2\right)$$

2.3.2 X-ray absorption spectroscopy (XAS)

The phenomenon of X-ray Absorption Spectroscopy (XAS) was identified in the early 1920s, However, its application as an analytical equipment started in the 1980s when Synchrotron radiation sources became available. It probes local atomic structure and order of any material, regardless of its chemical state, and long-range ordering is not needed. XAS can probe the interatomic distances (~5 Å from the element of investigation), valence states and the nature and the number of surrounding neighbors of the absorbing atom. Along with this, it differentiates itself and permits investigation of each element of the investigated material due to its selective behavior. For investigation, it requires very less quantity of sample.

XAS consist mainly of two types of study: Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Absorption Near Edge Structure (XANES).X-rays are electromagnetic radiation with energies from 1 to 200 KeV. Interactions of X-rays with material leads to three types of phenomena: elastic scattering, inelastic scattering, and the photoelectric effect. XAS works on the principal of photoelectric effect, where absorption of a photon by atom causes ejection of an electron from the core shells (K, L, etc. shell). This causes the emission of a photoelectron [Figure 2.3].



Figure 2.3 (a) Schematic of X-ray absorption process, and definition of I_0 (incident intensity), I (transmitted and fluorescence intensity) in the measurement. (b) X-ray photoelectric effect; a core level electron is dislodged from the atom due to an x-ray absorption with the appropriate energy. (c) Excited state is declined in x-ray fluorescence and (d) the Auger effect: The possibility of electron and x-ray dependsupon the absorption probability.

The electron which is emitted depending upon the energy of the incident photon, hv, and the binding energy of the electron E_b , may go to bound state within the same atom or an unbound state. The energy of the photoelectron: $E_f = hv - E_b$. Then the absorbing atom relax by various mechanisms which leads to fluorescence X-rays, Auger electrons or secondary electrons [Figure 2.3& 2.4].

In X-ray fluorescence, which is a point of interest, incident photon creates a hole in the inner shell which is filled by an outer shell electron.



Continuum

Figure 2.4 The photoelectric effect; an x-ray is absorbed, and a core level electron is promoted out of the atom. Inset shows schematic for x-ray absorption measurements: An incident beam of monochromatic x-rays of intensity I0 passes through a sample of thickness t, and the transmitted beam has intensity I.

This leads to X-ray fluorescence which is the characteristic of the absorbing material [Figure 2.5]. From a specific atomic state, minimum photon energy required for ejecting an electron, is known as, threshold energy, $E_0 = hv_0$, which represents the binding energy of the electron.

In XAS measurement a range of energy falls on the material which also has the binding energy of core electrons of a specific targeted element. X-rays absorption is described using Beer-Lambert law (transmission experiment):

$$\mu(E)x = ln\frac{I_0}{I_t}$$

where I_0 and I_t are the intensities of incident and transmitted beam respectively. *E* is energy of photon, $\mu(E)$ is absorption coefficient of the sample and *x* is thickness of the sample.





Figure 2.5 Decay of the excited state: (a) x-ray fluorescence and (b) the Auger effect. In both cases, the probability of emission (x-ray or electron) is directly proportional to the absorption probability

X-ray absorption coefficient (μ) varies with incident beam energy. With increase in photon energy, μ decreases till the absorption edge.After this point a sudden jump come in μ . This happens due to ejection of a core electron and then it decreases further as the energy of the photon increases.

The absorption spectrum consists of mainly: Pre-edge, X-Ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine structure (EXAFS) [Figure 2.6].



Figure 2.6 (a) Schematic of EXAFS spectra

- > XANES region is close to the absorption edge but below the threshold energy E_0 (core electron is excited but is not ejected from the atom). XANES gives information of coordination number, electronic configuration, and oxidation state of the absorbing atom. When incident photon energy surpasses ~50 eV above E_0 , core electron ejects from the atom into the continuum. Although, emitted photoelectron has less kinetic energy: its mean free path is relatively high, its wavelength is comparable with interatomic distances. Hence scattering of photoelectron occurs from the surroundings atoms.
- Region 40 to 1000 eV higher than the absorption edge, known as the region of EXAFS. The ejected photoelectron has a high kinetic energy and a low mean free path, which isgenerally implicated in single scattering paths. Photoelectron can be considered as a spherical wavefunction which is backscattered by other neighboring atoms. Interaction of incoming and outgoing

wavefunctions leads to constructive and destructive interferences. This results in the oscillatory nature of μ . Interatomic distances between the neighboring atoms and the absorbing atom is related to the frequency of the oscillations r. However, amplitude of the sinusoidal modulation of μ vs *E* rely upon the type and number of surrounding atoms. This also describes the thermal and structural disorder. Hence, simulation of EXAFS spectra gives essential information of the local environment of the material.

Data analysis and processing

To extract information from XAS spectrum series of numerical treatments since XANES and EXAFS signals are not directly interpretable. The IFFEFIT software package is used for the analysis of the EXAFS spectrum. It has various programs such as ATHENA, a program for XAS (XANES/EXAFS) analysis and ARTEMIS for EXAFS analysis using theoretical models from FEFF.In EXAFS analysis, experimentally obtained raw data is processed first. This comprises of: raw data conversion to spectra, data normalization, background subtraction and Fourier transformation.

Normalization of the data:

For making the experiment independent of the sample details or the detector set-up, data normalization is performed. Using ATHENA subtracting a linear contribution performed before the edge known as "preedge region" and after the edge determine a quadratic polynomial through regression analysis known as "post-edge line".

In ATHENA data is imported and then by defining a background line, $\chi(k)$ signal is extracted. After this threshold energy (E_0) is defined, which is evaluated from the first peak of the first derivative of the $\mu_0(E)$ spectra or else with nearest zero, crossing the second derivative. The evaluation of E_0 is essential since it determines the origin of the k scale. Processing of the data is done after the removal of background and normalization. The normalization is performed by subtracting the curvature of the regression of the quadratic polynomial and the difference between the post-edge and pre-edge polynomial beyond the edge.

The ATHENA and ARTEMIS software package thus meets all requirements for XAS data analysis.

2.3.3 Raman spectroscopy

The vibrational, rotational and other phonon modes of a samples is being investigated with the help of Raman spectroscopy. Sample is irradiated by the transparent medium, then a fraction of radiation is scattered in all directions by the species present in the sample. The change in wavelengths observed for ssmall fraction of the scattered radiation differ from that of the incident beam was discovered by physicist C. V. Raman and K. S. Krishnan in 1928 from India. It is also observed that the shift in the wavelength depends on the structure of the molecules. It is a vibrational spectroscopic technique which probes molecular vibrations and crystal structures. A monochromatic light source (laser) is generally employed for irradiating the sample. After interaction with material, a minute amount of light is scattered inelastically. Since light is an electromagnetic radiation, electric and magnetic fields oscillate perpendicular to each other and perpendicular to the direction of propagation. When light interact with matter it leads to polarization which is responsible for this phenomenon. The motion of two coupled atoms can be assumed as a harmonic oscillator. The inter-atomic force constant k and the reduced mass m governsthe frequency of the participating atoms. However, when identical atom makes a monoatomic chain, it can be defined as $\omega = 2\pi f = \sqrt{k/m}$. When light is incident on a material it interacts with the molecule and distorts the electron cloud which leads to the formation of an unstable "virtual state". Raman spectrum consist of three types of radiations: Stokes (hv_0 -hv), Anti-Stokes (hv_0 +hv) and Rayleigh (hv₀). Raman scatterings consist of Stokes and Anti-Stokes scatterings which are inelastic scattering [Figure 2.7].
However, Rayleigh scattering consists of an excited electron which comes back to the same ground level after excitation, hence energy is conserved and is the dominant process. Raman scattering (inelastic scattering) is very rare, one in $\sim 10^6$ - 10^8 photons. To filter Rayleigh scattering various filters are used i.e. notch, edge and band-pass filters, etc. When an electron excites from Stokes ground level to a virtual state and return to a higher energy level vibration state than the ground state, it is known as Stoke-Raman. Hence this has less energy (longer wavelength) than incident light. However, in anti-Stokes Raman scattering, an electron being excited to a virtual state from the same vibration state, returns to the ground state. The Stokes and anti-Stokes scattered light is detected through a CCD camera which has characteristic signature of a material. Raman spectroscopy is useful to study polymorphs of substances, crystallinity, orientation and stress in the sample. Raman frequencies may be rotational, vibrational or electronic. Stokes to anti-Stokes signal ratio is estimated using the amount of the ground and excited states of the molecule. At room temperature amount of excited vibrational level is smaller than that of the ground level. This leads to less intensity of anti-Stokes signal than Stokes.



Figure 2.7: Experimental set-up of Micro Raman spectroscopy

The ratio of Stokes to anti-Stokes also depends upon temperature and decreases with increase in temperature of the material.Raman spectroscopy is very sensitive to evaluate chemical bonds, crystallographic orientation and symmetry of the structure. Because every material has distinct vibrational properties owing to its chemical composition. This is also useful for estimating preservation of domain structure and structural defects. In this work, Raman analysis is performed to observe substitution effect on phase and Raman mode. Raman spectra were taken with a HORIBA-Scientific spectrometer with spectral resolution of 0.4 cm⁻¹/pixel operating at the spectral range of 200–1050 nm and the source of excitation is 632.8 nm, air cooled He-Ne laser. Origin software is used for analysis of the Raman data. Peaks are mostly fitted with Lorentzian profile and analyzed.

2.3.4 Field Emission Scanning Electron Microscopy (FESEM)

Since light has limited diffraction limit hence it has limited resolution to see nm or lesser size objects. FESEM images the surface of a material using scanning of high-energy beam of electrons over the surface. Due to interaction between incident electrons and atoms of the sample, it produces signals. These signals carry the information about surface topography, composition and other properties. It is a powerful and commonly known tool for imaging the topology of surfaces of almost any material. It has spatial resolution ~1 nm which is quite higher than conventional SEM and optical microscope. The schematic diagram of FESE I shown in [Figure2.8].

For examining elemental composition and uniformity of the material, Energy Dispersive X-ray Spectroscopy (EDX or EDS) is associated with FESEM. This is a comparatively simple, but important technique for the study of elemental composition, non-destructively with a sensitivity of >0.1%. In this high quality and low voltage images are obtained with minute electrical charging in the material. In field emission

technique the emission of electrons occurs due to application of an electrostatic field which leads to the generation of a narrow beam of electrons of low as well as high energy. This improves spatial resolution and minimizes sample charging/damage.

1. FESEM set up.

- 2. Computer system attached with equipment for operating.
- 3. Computer system attached for EDX measurement.
- 4. Gold sputtering unit.
- 5. Enlarged view of gold sputtering system

In the present work, the FESEM images are obtained of powder and pellet surfaces. Supra55 Carl Zeiss FESEM equipment is used for investigation of the samples.



Figure 2.8 Schematic Diagram of FESEM

Since CeO₂ is a nonconductive material hence gold deposition \sim 5nm have been done on the surface. The high-speed electrons which interact with sample surface are known as primary electrons which gives kinetic energy to the surface electrons. Surface electrons, using this energy overcomes the nuclear attraction force and escapes out and are termed as secondary electrons. These electron gives information of the sample surface. Hence secondary electrons give information of surface morphology of the material with a large depth of field. In samples which suffers from more charging, these are best suited since it requires less voltage (< 5 kV). Some electrons of incoming beam are deflected owing to the presence of electrostatic field of the nucleus and are scattered elastically at high angles, these are known as backscattered electrons. These electrons give information about the atomic number of the elements present in the material and is hence used for finding the chemical composition of the sample.

Along with this, there is generation of X-ray photon from the incident electron beam. These are generated due to the ejection of inner shell electrons due to interaction of electron beam. Hence, outer shell electrons fill this inner shell and releases energy, termed as X-ray photon. Since emergence of these X-rays occur fromelements present in the sample which have specific energies, these X-rays are characteristic of the sample and gives analytical information which is termed as EDS/EDX. Thesehave energies between 0.1 and 20 keV. Along with this EDS scan is also possible which is used to study the homogeneity of the constituent elements of the material.

2.3.5 Transmission Electron Microscopy

For material characterization, transmission electron microscope (TEM) is a very important tool. It gives information on the crystal structure, microstructure and micro-chemical state information of each microscopic phase with a high spatial resolution.

In TEM a beam of electrons shines through the sample. TEM works like a slide projector. In the projector, a beam of light shines which transmits through the slide. Only a certain part of the light can pass through the slide according to the patterns painted on the slide. Hence on the slide, replica of the pattern formswhich leads to an enlarged image when it falls on the screen. In place of light high energy electron beam is used. The schematic of electron beam interaction is shown inFigure 2.9.

In TEM, when electron beam shines on sample some high energy electrons transmit while others get scattered from the specimen and part of it is scattered. The electrons which are transmitted from sample does not lose its energy since they do not interact with the sample and gives information about the sample's structure. However, the electrons which are diffracted elastically doesn't lose energy as well and transmits from another region of the sample. Scattered electron follows Bragg's law i.e. they will scatter with same angle from corresponding atomic spacing.

These electrons give information about arrangement of atoms, orientation and phases present in the sample. The transmitted beam gives a bright field image of the specimen. A dark field image is formed when one of the diffracted beams is selected by using a selected area diffraction aperture. The electrons which interact inelastically, loose their energy and transmit from another region of sample. This loss of energy of electron (Electron Energy Loss Spectroscopy or EELS) can be measured which is used for evaluation of elemental composition, chemical bonding and electronic properties of valence and conduction bands.

An advanced TEM consist of a filament, an objective lens system, magnification system, a specimen stage and data recording and chemical analysis system. The preparation of samples in TEM is crucial since electron beam passes through it and hence it should be thin enough. In present work computer-controlled high-resolution transmission electron microscope, JEOL JEM-2100 LaB₆, operated at a voltage of 200KV, is used for characterization.



Figure 2.9 Schematic Diagram of TEM

 CeO_2 nanoparticles are dispersed in propanol solution. This solution is cast on to a copper TEM grid using a micropipette and is allowed to dry for 30-60 minutes inside a heating furnace, such that only CeO_2 samples are left behind. The CeO_2 samples are examined using TEM in the bright field as well as dark field imaging modes.

Advanced HRTEM is a potent equipment for atomic scale and analytical performance. ImageJ software is used for HRTEM images analysis. This Is a public domain Java-based image processing program developed at the National Institutes of Health, USA.

2.3.6 UV-Vis Absorption Spectroscopy and Diffuse Reflectance

Spectroscopy

To find application of different materials, bandgap plays an important role. Bandgap is different for different materials and it also changes according to crystallinity and stoichiometry. Interaction of light with samples leads to various phenomena i.e. reflection, scattering, absorbance, transmittance and fluorescence/phosphorescence. The sum of electronic, rotational and vibrational energies of a material can be represented as total potential energy. The absorption of light occurs when energy of light is equal to the energy required to excite electron from VB to CB. There are two types of electronic transition i.e. direct and indirect. In direct transition excitation of electron needs only photon energy whereas in Indirect transition phonon participation is required along with photon.

The quantitative measure of absorbed light can be done using following equation:

$$A = -\log(\frac{I}{I_0})$$

where, Io and I is intensity of, incident radiation and reflected or transmitted radiation respectively, A is absorbance, T is transmittance. In this tungsten-halogen or deuterium lamp is used as a source with a monochromator which is used to select specific wavelength of incidence. The conversion of UV- visible light \rightarrow electrical signal is achieved with the help of detector [Figure 2.10]. Due to less scattering from thin solid films, bandgap is easy to assess. However, in colloidal samples surface area is increased which leads to high scattering. Since dispersed light does not reach to detector, the detector assumes it to be absorbed light (not able to differentiate between these phenomena). The bandgap estimation for powder samples is done by dispersing in a suitable liquid medium i.e. ethanol, water, methanol etc. However, presence of heavier/bigger particles results in inaccurate measurement since spectrum is mostly due to the liquid.



Figure 2.10 Experimental set up for diffuse reflectance measurement

For estimating bandgap of powder samples unambiguously, diffuse reflectance spectroscopy (DRS) is a potent equipment. This does not require dispersion of powder in liquid hence material is neither contaminated nor consumed. Since in powder samples when light shines, some part of it is regularly reflected while most of the light that enters the sample diffuses.

Bandgap is investigated using diffuse reflectance (DRS) spectra. Reflectance, R, is obtained from DRS spectra, where, $R = R_{sample}/R_{standard}$, R_{sample} and $R_{standard}$ are diffuse reflectance of the sample and a standard (BaSO₄). R is converted into F(R), Kubelka-Munk function using $[F(R) = (1 - R)^2/2R]$, where R denotes the percentage reflectance from the sample [131,132]. A graph between $[F(R).hv]^2$ versus hv (in eV) can provide the Egvalues of a sample with direct bandgap. An indirect bandgap can be obtained from a plot of $[F(R).hv]^{1/2}$ versus hv.

Urbach energy, E_U , was calculated using the following formula $\alpha = \alpha_0$. $exp(E/E_U)$, where α is the absorption coefficient, which is proportional

to F(R) (i.e. $\alpha \propto F(R)$). An inverse of slope of a straight-line fit of a natural logarithm of exponentially decaying F(R) (only tail part) near the absorption edge. This gives estimation of disorder in lattice.

By definition $\alpha \propto \frac{[(h\nu - (E_g)_{eff})]^n}{h\nu}$ [53], where, hv is photon energy, E_gis the bandgap and n is a rational number called power factor. The power factor (n) takes the values of 1/2, 3/2, 2, and 3 for "allowed direct" (DB), "forbidden direct" (FDB), "allowed indirect" (IDB), and "forbidden indirect" (FIDB) optical transitions respectively.From this definition of absorption coefficient, the Tauc relationship is obtained, $(\alpha h\nu)^{\frac{1}{n}} = A[(h\nu - (E_g)_{eff}], where, A is a proportionality constant. This is a$ $straight-line equation of <math>(\alpha h\nu)^{\frac{1}{n}}$ and $h\nu$, where, $(E_g)_{eff}$ is the y-intercept. With the help of integrating sphere detector, diffuse reflectance is measured by UV-Vis spectrometer (Carry 60, Agilent).

2.3.7 PL (Photoluminescence) Spectroscopy

To study the electronic properties of a material, Photoluminescence spectroscopy is a potent tool. It is a versatile optical instrument which probes the material nondestructively. When a light shine on a material, it absorbs light and gives extra energy to material.

This photo-excitation process in which excess energy is released by emission of light or luminescence is termed as photoluminescence. Hence in PL, material excites optically which leads to emission of light. Various properties of material can be assessed by studying this luminescence. In PL, electrons are excited by photons, which causes transition of electrons to excited states within the material. Hence while coming back to their equilibrium state they release energy either radiatively (emission of light) or non-radiatively (Figure. 2.11).



Figure 2.11 Schematic of experimental set up for PL

This emission of light (radiative process) is related to the difference in energy between excited and equilibrium state. In semiconductors, radiative process occurs commonly in states which are present between valence band (VB) and conduction band (CB). The difference between VB and CB is termed as bandgap. In PL, much higher excitation energy is used in comparison to bandgap energy. When electron and holes get excited by photon, they relax at their respective band edge and when they recombine, emits energy as their bandgap. The localized defects or impurity states also plays an important role in radiative or nonradiative transitions. Hence, analysis of PL spectra reveals presence of defects or impurity and their concentration can be estimated by examining the magnitude of PL signals. PL analysis also leads to the understanding of the mechanism of recombination. PL spectra is not like absorption spectra since PL is the measure of excited state \rightarrow ground state transition, on the other hand absorption spectra is ground state \rightarrow excited state transition.

In this present work, PL analysis is done by a Spectro-fluorometer, Horiba Jobin Yuon fluorolog-3 (Xe lamp source (excitation wavelength of 325 nm)).

2.3.8 Micro-Hardness

Factually, hardness signifies the state or properties being hard. How strongly atoms are held together in a material is defined by Hardness. This is the capability of a material to withstand permanent deformation. It has different sense according to implication i.e. for elastomeric materials it is forbearance to elastic deformation while in scratching, it is resistance to groove formation. This imply resistance to bending, abrasion or cutting as well. But in the present scenario, it is defined as quality of a material which facilitates it for withstanding plastic deformation when indented with relatively taut and robust indenter of precise geometry. It is alsodefined as endurance for lattice destruction, while other defined it as ability of solid to withstand permanent deformation. The recognized definition of hardness is to restrict motion of the dislocations in lattice. The intrinsic hardness of a crystal is, resistance offered by the chemical forces to resist mobility of the dislocations since it includes motion of the atoms as well.

Hardness testing is generally termed as macro, micro or nanohardness. These terms are based on applied forces and obtained displacements. Commonly these are referred to as 'micro-hardness' or 'nano-hardness'. These are misnomers since hardness of tested material is neither 'micro' or 'nano'. However, the size of obtained indent are in either micro or nano scale. Hence, for better understanding, terms 'microindentation hardness' or 'nano-indentation hardness' may be better.

Vickers Hardness Test

Vickers hardness test is a nondestructive method and despite different hardness of different surfaces only one kind of diamond indenter can be used with varying loads. Only very small region of indentation can be measured with microscope.



Figure 2.12 (a) Schematic of the Vickers Indentation Process and definitions of d_1 and d_2 (b) A real image of an indented area.

In this only one scale is there for all hardness measurements from smallest to highest, makes hardness analysis simpler. The Vickers hardness test is built on an optical measurement system. Vickers Indenter has apex angle of 136° (Figure 2.12). In Vickers test load range may vary from 5 g to 100 kg, but for measuring micro-hardness, it should be within 5 g to 200 g.

For testing sample should be kept perpendicular to the indenter and a square indentation mark is obtained in microns by application of a definite load generally for 5 s. With the help of an optical microscope diagonals of indentation d_1 and d_2 are measured which is usually an integral part of the Vickers tester and mean arithmetic value d is calculated.

The Vickers micro-hardness number Hv(where H = hardness and subscript V = Vickers) is calculated:

$$H_V = \frac{P}{A} = \frac{2P\sin(\frac{\theta}{2})}{d^2} = \frac{2P\sin 68^o}{d^2} = 1.854 \times \frac{P}{d^2}$$

Where, P is the applied indentation load in kg, A is the pyramidal contact area in sq mm, θ is the angle between the flat faces of the opposite sides of the indentation, which is 136° for Vickers micro-indenter, 1.854 ($\approx 2 \sin 68^\circ$) is a constant geometrical factor for the Vickers diamond type pyramidal indenter, d is the average diagonal length of the indented impressions in mm, and Hv is in kg/mm², conventionally, which can be converted in SI units MPa or GPa.

2.3.9 Physical property measurement system

Physical property measurement system (PPMS) is a multipurpose measurement stage providing flexible and customizable capabilities to find out different physical properties as a function of temperature and magnetic field. A basic PPMS set up consists of dewar with superconducting magnet and a universal 12-pin platform. The PPMS can be used to execute dc magnetization, ac susceptibility magnetic torque, electro-transport, or thermo-electric, heat capacity, magneto-transport *etc*. A classic set up of PPMS, quantum design is shown in Figure 2.13. The sample is mounted to a quartz mounting stick connected to a carbon fibre rod using rubber cement. A linear motor oscillates the sample between the pickup coils placed inside the evacuated sample chamber. An alteration in the magnetic

flux within the pick-up coil induces a current. This induced current is associate with electromotive force (EMF), which is recorded and subsequently gives the magnetic moment of the sample. The quantum design PPMS-VSM instrument offers fast DC magnetization measurements with sensitivity $\sim 10^{-6}$ emu.



Figure 2.13 (Right)A quantum design PPMS and (Left) Schematic of the

VSM Pickup Coil

In the present thesis, field (M–H) and temperature (M–T) dependent magnetic properties of all the samples were measured using a quantum design PPMS equipped with a 9 T magnet at Miami University, USA. The filed dependent magnetization (M–H) of all samples was performed up to 5 or 6 T field.

Chapter3

Effect of Co substitution on structural, optoelectronic and mechanical properties of CeO₂

This chapter aims at studying the influence of Co²⁺ substitution on structural and optical properties of CeO₂. This chapter covers sample preparation followed by characterizations to see properties of materials. We prepared samples using a modified sol-gel combustion process followed by solid-state sintering for crystallization of these samples. After synthesis samples were characterized by XRD and HRTEM to ensure phase purity, crystallinity and crystal structure of these samples. Rietveld refinement was carried out to estimate structural variations with compositions. Vibrational studies were verified by observing variations in phonon modes in Raman spectra of these materials. Local structural properties and oxidation states of samples were investigated using EXAFS and XANES study respectively. Optoelectronic properties were studied by UV-visible and photoluminescence (PL). Lattice disorder and Vo quantities were estimated using X-ray absorption (XAS), UV-vis and Raman spectroscopy. A careful study of oxygen vacancies, strain, bond length and related band structure changes, have been targeted in this study. The possibility of phonon participation in electronic transition has been discussed using Tauc plot. Ce³⁺ forms defects states, between valence and conduction bands. Lattice parameters decrease, but strain increases with substitution.

3.1 Synthesis

Ce_{1-x}Co_xO₂ nanoparticles (hereafter referred as CCO) for x=0, 0.025, 0.05 and 0.1 were synthesized by Pechini sol-gel technique, hereafter referred to as CCO0, CCO2, CCO5 and CCO10 respectively. Cerium (III) nitrate hexahydrate [Ce(NO₃)₃.6H₂O; 99.9%, Alfa Aesar] and Cobalt(II) nitrate hexahydrate [Co(NO₃)₂.6H₂O;99.9%, Alfa Aesar] were dissolved in double distilled de-ionized water (DIW). The detailed synthesis procedure is given in chapter 2. The resultant powders were further calcined at 450° C for 6h to release the trapped carbon particles.

3.2 Structural properties

(I) XRD:

XRD patterns of synthesized CCO0, CCO2, CCO5 and CCO10 (Figure 3.1(a)) shows peaks correspond to (111), (200), (220), (311), (222), (400), (331) and (420) planes, confirming that all samples were crystallized in cubic fluorite structure with space group Fm3m.

No impurity phases of oxides of Co were found. Rietveld refinement was performed using FullProf software to estimate changes in lattice parameter [Figure 3.1(b)]. Lattice parameters reduce with Co substitution (approximately exponentially decaying with substitution) [Figure 3.1(c)]. Note that the size of $\text{Co}^{2+}(\text{VIII})$ is ~1.04 Å, while $\text{Co}^{3+}(\text{VIII})$ is ~0.9Å.Both

are smaller than $Ce^{4+}(VIII)$ (~1.11 Å) and $Ce^{3+}(VIII)$ (~1.28 Å). Hence a proper substitution will lead to contraction and extra strain generated in the lattice. Therefore lattice contraction is a strong hint of substitution of Co in CeO₂[23]. Contraction of lattice was also observed form XANES analysis (discussed later in this work).

From the refined crystallography index files (CIF files), the bond lengths and bond angles were evaluated. It is observed that the bond lengths decrease exponentially with substitution like lattice constant [Figure 3.1(d)].



Figure 3.1 (*a*) XRD data of $Ce_{1-x}Co_xO_2$ samples confirm a cubic fluorite structure with space group Fm3m, b excellent match of experimental data and theoretical fit obtained in Rietveld refinement, c, d variation of lattice parameter and bondlength with x

However, the bond angles did not change much. This indicates an overall proportionate contraction in all three dimensions, maintaining the same crystallographic symmetry. This is expected when proper substitution has taken place in an idealistic manner.

Strain was calculated using Williamson-Hall (WH) method[54,55]: $[\beta Cos\theta = K\lambda/D + \epsilon Sin\theta]$, where β is full width at half maxima (FWHM), θ is angle of incidence of X-ray, λ is wavelength of X-ray (1.5406 Å), D is crystallite size and \mathcal{E} is lattice strain and K(0.9) is a constant dependent on morphology. In general, for spherical crystallites, K is accepted as ~ 0.9 . Note that β in WH equation has two contributions, $\beta = \beta_{size} + \beta_{strain}$, where, β_{size} and β_{strain} are peak width components from strain and size. A linear fit of $\beta Cos\theta$ and $Sin\theta$ results in a positive slope. The slope, m, and y-intercept, c, of the 'Sin θ vs $\beta Cos\theta$ ' plot, were calculated [Figure 3.2(a)]. Both, m and c, were positive for all the samples, implying positive contribution from both size and strain. The slope, m, is an estimation of the strain in the lattice while the estimate of $c/Cos\theta = K\lambda/DCos\theta$ provides the size of the particles. The strain and size have been calculated for all sample and the peak broadening due to size factor was observed to be dominant over the strain factor by an order of magnitude [Figure3.3].

The size decreases, while strain increases with substitution. Crystallite size reduces (approximately following the trend of lattice parameters) from 8.5 nm in CCO0 to 6.7 nm in CCO10 [Figure3.2(b)].Strain is not desirable for long range order and often is instrumental to surface terminations in nanoparticles [56]. Hence, increasing strain due to Co substitution may be responsible for reduction of crystallite size. Crystallite size was also estimated using Debye-Scherer's equation: $D = K\lambda/\beta cos \theta$, (where, K=0.9).



Figure 3.2 (*a*) Variation of strain (*m*) and intercept (*c*) with *x*, obtained from Williamson–Hall analysis, *b* changes in crystallite size with *x*, estimated from Williamson–Hall, Scherrer, Raman and TEM analysis

Note that here the value is that of the combine contribution of size and strain. Hence, without the strain component being deducted this analysis yielded smaller crystallite size. Crystallite size reduces from 6.7 nm in CCO0 to 4.4 nm in CCO10 [Figure3.2(b)]. It has been reported that due to smaller crystallite size there can be a reduction of $Ce^{4+} \rightarrow Ce^{3+}$ [57]. Hence, despite no Co being present in CCO0 we observe reduction of $Ce^{4+} \rightarrow Ce^{3+}$. Ce^{3+} , being larger than Ce^{4+} , results in lattice distortion leading to strain, even in pure CeO₂.



Figure 3.3 (*a*–*d*) β_{size} and β_{strain} variation for CCO0, CCO2, CCO5 and CCO10, respectively. The strain and size have been calculated for all samples and the peak broadening due to size factor was observed to be dominant over the strain factor by an order of magnitude

(II) XANES study:

Valence states of constituent elements were examined using XANES analysis of CCO samples [Figure 3.4 (a, b)]. Ce L₃ edges of pure and Cosubstituted samples consist of two major peaks. All samples have similar shapes, which were fitted by a combination of an arctangent and Gaussian functions. Four peaks, A, B, C and D are observed at 5730.9 eV, 5724.1 eV, 5719.3 eV and 5714.1 eV respectively. A and B represents mixture of multi-electron transitions with final state of $2p4f^05d^*$ and $2p4f^d5d^*L$. For above notations, $2p \rightarrow$ Ce 2p holes, $5d^* \rightarrow$ excited electrons in 5d states and L \rightarrow holes in anion ligand orbital (O 2*p*). Peak C corresponds to Ce in Ce³⁺ valance state. Peak D can be attributed to final states of *O2p-Ce5d* hybridizations due to crystal field splitting of Ce 5*d* states causing delocalization of *d* character at the bottom of conduction band [58,59]. There is shift in peak position, may be due to the high concentration of Ce³⁺ and smaller crystallite size, which may be result of different synthesis method and temperature. In present samples particles are mostly agglomerated. This hints at a higher percentage of Ce³⁺ ions which are uncompensated by The quantification of Ce³⁺ (C) and Ce⁴⁺ (A+B) as [59–61]:

$$Ce^{3+} = \frac{C}{A+B+C} \times 100$$
$$Ce^{4+} = \frac{A+B}{A+B+C} \times 100$$

XANES analysis reveals a major Ce^{4+} state (~75-84%) in pure and modified CeO₂ samples. However, Ce^{3+} states are not negligible (~16-25%).

Concentration of Ce^{3+} increases in Co-substituted samples from ~16% to ~25% for pure and Co doped samples respectively [Figure 3.5]. Note that in CeO₂, Ce is expected to be primarily in Ce⁴⁺ state. Hence, presence of Ce³⁺ hints at O-vacancies, V_O , in lattice. On the other hand, Co is predominantly in Co²⁺ state only [Figure 3.4(b)]. Mathematically, it can be expected that ~16 to ~25% Ce³⁺ can result in ~8 to ~12% O-loss from lattice. Cobalt addition can induce an extra proportionate oxygen loss due

to Co^{2+} valence state. Hence, we expect a lot of oxygen defects in this CCO system, increasing proportionately with amount of substitution.



Figure 3.4 (a) XANES spectra at Ce L_{III} edge; A and B represents mixture of multi-electron transitions with final state of 2p4f05d* and 2p4f15d*L. Peak C corresponds to Ce in Ce³⁺ valance state. Peak D can be attributed to final states of O2p-Ce5d hybridizations. (b) Co K edge; the intense main-edge region located at higher energy results from a dipolar $1s \rightarrow 4p$ transition whereas pre-edge features result from a $1s \rightarrow 3d$ excitation.

 $O^{2-}(IV)$ has a crystal radius of 1.24 Å, comparable to $Ce^{3+}(VIII)$ (crystal radius ~1.28 Å). But both above are larger than $Ce^{4+}(VIII)$ (1.11 Å). We find that similarly $Co^{2+}(VIII)$ has crystal radius 1.04 Å much smaller than all the three above. Lack of oxygen in the pure CeO_2 may be due to oxygen deficit environment during synthesis. Such a symptom is common, similar to other studies involving various types of synthesis [62]. Co^{2+} having a lesser valence state further leads to oxygen removal from lattice. Moreover, Co^{2+} is also smaller in size.



Figure 3.5 (a–d) XANES spectra fitting of CCO0, CCO2, CCO5 and CCO10, respectively, with a combination of an arctangent and four Gaussian peaks using Athena software. Ce^{3+} concentration increases with Co substitution.

Hence, the situation demands space and charge compensation by a larger in size and more charged ion. Hence, an increment in Ce^{3+} concentration is logical.

(III) HRTEM:

HRTEM micrographs also reveal termination planes of the nanocrystals. Well-defined lattice fringes indicate crystalline nature of nanoparticles. A lattice spacing of 0.31 nm is common in most nanoparticles which can be attributed to a (111) reflection plane [57]. Hence, from these micrographs it is revealed that (111) is one important termination plane of these nanocrystals. (200) and (220) are also common termination planes of these crystallites.

SAED patterns of a collection of nanoparticles as well as Fourier transforms of HRTEM images reveal concentric bright rings corresponding to (111), (200), (220) and (311) planes representing Braggreflections of crystalline CeO₂ (inset of Figure 3.6 (a, b)). This confirms that these small nanoparticles are representatives of CCO nanoparticles in discussion and that they have similar structure as the average structure obtained from XRD.



Figure 3.6 (*a*, *b*) *HRTEM images, SAED pattern and EDX spectra of CCO0 and CCO5, respectively, show high crystalline nature of samples*

EDX studies reveal chemical purity and homogeneity of the samples. Regional 2D scans as well as spot scans were performed [Figure

3.6]. Substitutional proportions were estimated and matched with targeted values. Compositional homogeneity was confirmed from these studies. It is also to be mentioned that oxygen deficiency was observed to increase with substitution as was discussed above.

(IV) Raman Analysis:

Raman spectroscopy is a very effective nondestructive tool which provides information on lattice dynamics of materials. Raman spectra of all CCO samples (Figure 3.7 (a)) show a strong peak at 462.7 cm⁻¹ and a broad feature ranging from \sim 520 cm⁻¹ to \sim 660 cm⁻¹.

The strong peak ~462.7 cm⁻¹ corresponds to an F_{2g} triply degenerate mode of CeO₂ fluorite structure. This represents a Ce-O₈ symmetric stretching vibration. This peak red shift, broadens and becomes more asymmetric (lower half widths are larger than higher half width) with substitution [Figure 3.7 (b), (c) and (d)]. Red shift has been reported due to decrease in crystallite size [62]. However, red shift has also been reported due to loss of oxygen which reduces the energy of Ce–O₈ vibrations [63]. Broadening has been reported due to inhomogeneous strain in the lattice [62]. It is also affected by crystallite size (*D*); quantified by $\Gamma(cm^{-1}) = 10 + 124.7/D$ (*nm*) [64]. A crystallite size evaluation using the above equation provided values in agreement with XRD and TEM results [Figure 3.2 (b)]. It is noteworthy that the substituted samples and even the pure sample are lesser than 7–8 nm, the reported Bohr radius for CeO₂ materials. In bulk, defect-free crystalline semiconductor materials one expects perfect symmetry (only q=0 phonons are Raman active) [65]. With crystallite size reduction an increasing volume of reciprocal space is involved. Hence, $q\neq 0$ phonons also starts to contribute as crystallite size < Bohr radius. Hence asymmetry increases and has been related to participation of phonons of other than zone boundary [65–67].



Figure 3.7 (a) Systematic broadening and nominal red shift of F_{2g} phonon mode at ~460 cm⁻¹ in modified $Ce_{1-x}Co_xO_2$; a broad feature in the range 520–660 cm⁻¹ associated with oxygen defects becomesstronger with substitution, (b–d) changes in F_{2g} mode; Peak position, FWHM and intensity with x

In CeO₂, Ce–O lattice vibrations can be of four types depending on the charge state of Ce and the presence of oxygen vacancies, V_0 . Ce exists in an 8–coordination state surrounded by 8 oxygen ions. In the presence/absence of one oxygen vacancy, two scenarios can be observed, Ce–O $_8$ / Ce-[O $_7$ Vo].

For Ce⁴⁺ and Ce³⁺ hence four scenarios are expected [68]. Hence, the frequency, i.e. energy will depend on the scenario. It has been observed that experimentally in a pure CeO₂ lattice oxygen deficit, introduces Ce³⁺ states, which in general leads to a red shift of the frequency. It needs to be mentioned in Ce₂O₃ one expects a prominent phonon mode due to relative vibrations of Ce and O at 409 cm⁻¹[69], instead of O-lattice vibrations at ~ 460 cm⁻¹ [39, 40] in CeO₂. A red-shift is hence a consequence of Ce³⁺ concentration increase. The concentration of Ce³⁺ increases in the sample until x=0.05 but decreases in *x*=0.1. Thus, the samples show a red-shift with substitution, but thereafter for *x*=0.1 a blue shift is observed.

A broad peak at ~ 520–660 cm⁻¹ corresponds to oxygen related defects [72,73]. This feature increases with substitution. As already discussed, Co is in 2+ state. Hence, O-vacancies are created to maintain charge neutrality of lattice. Raman spectroscopy results confirm our speculations from XANES and EDS on enhanced O-vacancies due to substitution. A Ce⁴⁺ \rightarrow Ce³⁺ conversion hence seems logical to compensate excess space created due to smaller size of Co²⁺ and O-vacancies.

3.3 Optical Properties:

Optical properties of the CCO samples were investigated using diffuse reflectance (DRS) spectra. Reflectance, R, is obtained from DRS spectra, where, $R = R_{sample}/R_{standard}$, R_{sample} and $R_{standard}$ are diffuse reflectance of the sample and a standard (BaSO₄). R is converted into F(R), Kubelka-Munk function [20], using [$F(R) = (1 - R)^2/2R$]. In the range, 3.13eV< h ν < 3.54eV (Figure 3.8), F(R) was observed to increase considerably with substitution.

At energies lower than 3.13eV a broad nature of the spectra is observed for all samples and can be interpreted as band-gap smearing due to defect accumulation (i.e., Urbach tail) [53]. The sharpness of the absorption edge in UV-Vis spectra is reduced in substituted samples than pure CeO₂. Urbach tail type profile increases with substitution. This signifies a significant increase of defects states contributing to the electronic properties of the material.



Figure 3.8 Tauc plot of $Ce_{1-x}Co_xO_2$ for an (a) allowed indirect (b) allowed direct (c) forbidden indirect (d) forbidden direct transitions, respectively. The sharpness of the absorption edge in UV-Vis spectra is reduced in substituted samples than pure CeO₂. Bandgap decreases with Co substitution owing to formation of defects states close to the band edges thereby increasing the defect states responsible for band tailing.

Urbach energy, E_U , was calculated using the following formula [32]: $\alpha = \alpha_0 . exp(E/E_U)$, where α is the absorption coefficient, which is proportional to F(R) (i.e. $\alpha \propto F(R)$). An inverse of slope of a straight-line fit of a natural logarithm of exponentially decaying F(R) (only tail part) near the absorption edge represents provided the values of E_U ((Figure 3.9 (a)). E_U increases exponentially with Co substitution from 0.153 eV for x=0 to 0.672 eV for x=0.1((Figure 3.9). Increase in E_U , indicates increased defects in CeO₂ with Co substitution.



Figure 3.9 Urbach energy increases with Co composition in CeO₂ owing to formation of band tails which causes reduction of bandgap.

By definition $\alpha \propto \frac{[(h\nu - (E_g)_{eff})]^n}{h\nu}$ [53], where, hv is photon energy, E_gis the bandgap and n is a rational number called power factor. The power factor (n) takes the values of 1/2, 3/2, 2, and 3 for "allowed direct" (DB), "forbidden direct" (FDB), "allowed indirect" (IDB), and "forbidden indirect" (FIDB) optical transitions respectively [75]. From this definition of absorption coefficient, the Tauc relationship is obtained, $(\alpha h\nu)^{\frac{1}{n}} =$ $A[(h\nu - (E_g)_{eff}]$, where, A is a proportionality constant [76]. This is a straight-line equation of $(\alpha h\nu)^{\frac{1}{n}}$ and $h\nu$, where, $(E_g)_{eff}$ is the y-intercept.

A careful analysis was done with all four values of n, corresponding to four types of transitions. It was found that $(E_g)_{eff}$ reduces

exponentially with substitution for all four types of transitions [Figure 3.10 & 3.11]. (E_g)_{eff}~3.13–3.54 eV has been discussed in literature to arise from direct transitions resulting out of absorption processes from top of the valence band (O 2*p* states) to empty 4*f*–shells of Ce⁴⁺.



Figure 3.10 Band tailing effect on $(E_g)_{eff}$ and $(E_g)_{eff+Eu}$ with increasing substitution owing to formation of impurities bands between valance band and conduction band.

For an allowed direct band transition, n=1/2, the changes in $(E_g)_{eff}$ is the least, and $(E_g)_{eff} \sim 3.36-3.13$ eV. For a forbidden indirect band transition, i.e. n= 3/2, $(E_g)_{eff}$ varies ~2.82–1.78 eV. For an allowed indirect band transition, i.e. n= 2, $(E_g)_{eff} \sim 3.03-2.43$ eV whereas for a forbidden direct band transition, i.e. n= 3, $(E_g)_{eff} \sim 3.09-2.6$ eV. $(E_g)_{eff}$ changes drastically for other values of n other than n=1/2, i.e. a direct bandgap scenario [Figure 3.11 (a)]. Table 3.1. The Bandgap energy, E_g for direct and indirect transitions.

Synthesis/Growth	Crystallite	Direct	Indirect	References
method	Size (nm)	Bandgap	Bandgap	
		(eV)	(eV)	
		n = 1/2	n = 2	
Electron beam	9-24		2.9-3.3	[77]
evaporation				
Pulsed spray-	32.3		3.2	[78]
evaporation CVD				
reactor				
Hydrolysis	9.84	3.28		[79]
Polymer complex	11.6	3.44		[80]
method				
Macroemulsion	8.5	2.92	2.45	[81]
Solvothermal	6.9	3.42	2.70	[82]
Sol-gel	9.1		3.1	[50]
Sol-gel	6.7	3.36	3.03	[Present
				work]
				_

These drastic changes in other types of transitions, raises questions on the feasibility of these processes in a robust structure like CeO₂, especially when the lattice parameter changes are ~a few pm. Also, $(E_g)_{eff}$ values are remarkably low for these types of transitions. The band structure of Co–substituted CeO₂ should be extremely complex due to the following factors; the bond distance reduces, in small amounts ~ a few pm, with substitution. These changes in Ce–O bond length will change the nature and strength of hybridization to a certain reasonable extent but may not be able to justify a drastic change in the extended states [Figure 3.12]. It is expected that the bandgap should increase when bond length decrease [83].



Figure 3.11 (*a*, *b*) $(E_g)_{eff}$ and $(E_g)_{eff+Eu}$ variations with substitution for different types of transitions (c) E_u vs $(E_g)_{eff+Eu}$ variations with x for different types of transitions

Hence, with substitution, the extended states should separate further, as bond length decreases. On top of that the electronic states of

Co, in hybridization with neighboring O 2p ions, are different than that of Ce. The bandgap of CoO is ~ 2.6 eV. Most likely these states in a CeO₂ lattice, will create defect states close to the band edges thereby increasing the defect states responsible for band tailing, i.e. E_U [Figure 3.11]. A detailed theoretical study needs to be performed in this aspect. All these factors play an important role in modifying the effective bandgap. However, for such subtle changes in bond length a drastic change in energy gap between valence band edge and conduction band edge i.e. the extended states are unlikely. The reducing trend in $(E_g)_{eff}$ for all four types of transition does not match with the decreasing trend of bond length. Experimentally, the difference between the extended states should correspond to $(E_g)_{eff} + E_U$. All the four types of transitions were compared, and it is noticed that although E_g decreases, $(E_g)_{eff} + E_U$ increases with substitution in case of direct bandgap [Figure 3.11 (b)]. The increment rates of E_U and $(E_g)_{eff} + E_U$ are also very similar [Figure 3.11 (c)]. In all the other types of transition probabilities, both $(E_g)_{eff}$ and $(E_g)_{eff} + E_U$ decrease with substitution, not agreeing with reduction of bond length.

However, although there is ample strength of claiming direct bandgap in case of these samples, one should not entirely rule out the chances of a phonon assisted indirect bandgap transition in these materials too, as both types of transition have been reported (table 3.1). The present estimated values of $(E_g)_{eff}$ matches well with previous reported values for both types of transitions (table 3.1). The signature of V₀ in substituted

samples from Raman studies hint at increasing Vo-related phonon contribution with increasing substitution. The lesser charge of Co induces $V_{\rm O}$ in the lattice. In presence of $V_{\rm O},$ proportion of $Ce^{3+}(VIII)$ increases. Such changes give rise to localized states in the bandgap. Changes in optical properties may not be only related to bandgap values but also to other interactions of carriers with lattice. Phonon assistance for transitions is an important contribution in deciding the nature of energy levels related to transitions. Lattice changes due to bond length modifications and related strain will affects associated phonon modes. Hence, an electron excitation may be affected by phonon related changes. Thereby, an electronic transition from valence to conduction band may also happen with the aid of a phonon, i.e. an indirect bandgap scenario. Investigating the probabilities of an indirect bandgap, it is observed although E_g reduces quite remarkably, $(E_g)_{eff} + E_U$ fluctuates as 3.203 eV in CCO0, 3.048 eV in CCO2, 3.124 eV in CCO5, and 3.102 eV in CCO10. Hence, the trend is not consistent with the continually decreasing values of bond length. For these reasons most likely a direct bandgap transition is more likely than an indirect bandgap in both pure and substituted CeO₂.

3.4 Microhardness study

Note that it is observed that increasing substitution introduces more strain. The hardness of the materials is related to the bond strength which is correlated with strain and defects of the lattice. To estimate hardness, 1400°C annealed pellets were chosen to avoid ambiguity of the effect of pores. As seen from the SEM images [Figure 3.12] 1400°C sintered pellets have a continuous topography with grains in tight contact with each other without pores or gaps left on the surface. The indentation, d (μ m), increases nonlinearly with the applied load F(N) [Figure 3.12 (a)]. F and d are related by a general equation, given by F=Adⁿ, where, A is standard hardness constant and n refers to Meyer's number.

Indentation Size Effect (ISE) [84]is represented by n<2, where microhardness decreases with increasing applied load. A Reverse Indentation Size Effect (RISE) is represented by n>2, where microhardness increases with increasing load. In between, for n=2, hardness does not depend upon applied load; Kick's law, F=A₁kd². By plotting ln(F) vs. ln(d), the slope and intercept [Figure3.13 (a)] gives the values of n and A_{1k} respectively. Vickers micro-hardness [85] of the 1400°C annealed pellets was estimated by measuring the indent dimension d (µm) for an applied load F(N), using the formula HV = 1854.4 F/d² (GPa). For all samples in this report hardness decreases with increasing applied load [Figure 3.12 (b)], and n<2, the values ranging from 1.96~1.97, which confirm ISE behavior of the samples [Figure 3.13 (e)].
Hardness decreases with increasing substitution in these samples [Fig. 3.12 (c)]. The effective bond strength between modified combinations of Ce/Co ions instead of only Ce ion with O ion may be weaker due to the size and valence state of the effective ions. Microhardness is supposed to decrease due to such weaker bond strengths.



Figure 3.12 (*a*) The indentation $d(\mu)$ variation with the applied load F(N)(b) Hardness variation with applied load (*c*) Hardness variation with *x* (*d*) comparison between experimental hardness (Vickers's hardness) and hardness from different models

With substitution strain was observed to increase. It was also observed that oxygen vacancies increased with substitution. Hence with increased substitution lattice is supposed to be weaker, resulting in lesser hardness of the material. Several models, including Proportional Specimen Resistance (PSR) model, Elastic/Plastic Deformation (EPD) model and Hays-Kendall (H–K) model were used to study the hardness with ISE behavior. In the PSR model, Load is related to indentation, as $F= \alpha d+\beta d^2$. The first term corresponds to the specimen resistance, which is linearly proportional to the indentation size and is an elastic contribution to the equation.



Figure 3.13 (*a*, *b*, *c*, *d*) showing Meyer's plot, PSR model's plot, EPD model's plot, H-K models plot and (e, f, g, h) are showing their slope and intercept respectively

The second term is more a plastic contribution and represents the effective indentation test force and is related to the load independent hardness (i.e. hardness at infinite load), H_{PSR} =1854.4 β .

The slope and intercept of (F/d) vs d plot is used to estimate α and β respectively [Figure 3.13 (b, f)]. The values of α , are positive ~0.0025-0.0019 N/µm while β related to the true hardness values ~0.0031-0.0027 GPa. The load independent hardness value from PSR model does not match the experimental values [Figure 3.12 (d)]. Thereby, it seems PSR model may not be appropriate for the material.

For elastic samples, recovery happens in totality after load is removed. For such materials the true hardness was expressed as the Elastic/Plastic Deformation (EPD) model $F=A(d+de)^2$; where the hardness constant, A= H_{EPD}/1854.4, d is the size of indentation and related to plastic deformation while the elastic de value comes from the yintercept of $F^{1/2}$ -d graph [Figure3.12 (c)]. It is observed that de is positive and increases with substitution [Figure 3.13(g)]. A strong plastic component plays a dominant role in the samples. The estimated values of hardness using the EPD model are lower than the experimental values and matches somewhat with the PSR model [Figure 3.12 (d)]. Hence both PSR and EPD models are not good models for the pure and modified CeO₂ samples. To be noted that in both these models the elastic contribution is related to the indentation. According to the Hays-Kendall (H–K) model, after a preliminary critical load, Fc, is applied, plastic deformation is observed in some materials. The indenter can only penetrate after Fc is applied. Hence the effective load on sample is the difference between the actual force and the critical load and is given by, $F_{eff} = F -Fc$. Therefore, in Hays-Kendall relationship, $F_{eff} = F -Fc = A_{HK} d^2$; where, A_{HK} is a proportionality constant representing hardness $A_{HK} = 1854.4/H_{HK}$. Fc and A_{HK} were estimated from the intercept and slope of the F vs d² plot [Figure3.12 (d)]. The hardness $H_{hk} = 1854.4A_{HK}$, from the Hays-Kendall model decreases with substitution and is in close agreement [Figure3.12 (d)] with the experimental Vickers hardness. Fc is positive and increases showing decrease of hardness with load, i.e. ISE behavior. This model provides the closest explanation of hardness in these materials certifying the presence of both elastic and plastic deformation.

3.5 Conclusions

Single phase nanoparticles Co substituted CeO₂ (Ce_{1-x}Co_xO₂) without the presence of impurity phases were synthesized using sol-gel technique. Rietveld analysis using XRD revealed decreasing lattice parameters and bond length. Increasing strain and decreasing crystallite size with decreasing substitution was revealed from both XRD and Raman analysis. Raman studies confirm increase of V₀. The lower valence states of Co²⁺ induces V₀ which transforms some Ce⁴⁺ to Ce³⁺. XANES study reveals similar implication with the increase of Ce³⁺ population. These defects

form states, between valence and conduction bands. A detailed analysis of Tauc plots with all four values of n, corresponding to four different types of transitions, reveals the possibility of a direct bandgap scenario. The difference between the extended states, estimated from the values of $(E_g)_{eff}$ + E_U increases, with decreasing bondlength in case of direct bandgap only. Possibility of phonons assisted transitions, in case of an indirect bandgap, was considered but the trend of $(E_g)_{eff} + E_U$ was found not to be consistent with the trends of bondlength.Mechanical hardness of highly sintered (1400°C) pellets were tested which was found to be reducing with Co incorporation. Reduced bond strength, increased strain and enhances lattice defects might be reason behind reduction in hardness. ISE behavior is observed in all samples. Theoretical models reveal that the elastic component of deformation is a constant contribution and deformation is mostly plastic in nature, closely obeying Hays-Kendall model.

Chapter 4

Effect of Ni substitution on structural, optoelectronic and mechanical properties of CeO₂

This at studying structural, optical chapter aims and photoluminescence properties of Ni-substituted CeO₂ which has lesser crystal radii and charge state. This chapter covers sample preparation followed by characterizations to see properties of materials. We prepared samples using a modified sol-gel combustion process followed by solidstate sintering for crystallization of these samples. After synthesis samples were characterized by XRD and HRTEM to ensure phase purity, crystallinity and crystal structure of these samples. Rietveld refinement was carried out to estimate structural variations with compositions. Vibrational studies were verified by observing variations in phonon modes in Raman spectra of these materials. Local structural properties and oxidation states of samples were investigated using EXAFS and XANES study respectively. Optoelectronic properties were studied by UV-visible and photoluminescence (PL). Lattice disorder and Vo quantities were estimated using X-ray absorption (XAS), UV-vis and Raman spectroscopy.

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4.1 Synthesis

Pure and Ni-substituted CeO₂, Ce_{1-x}Ni_xO₂ nanoparticles were synthesized by sol-gel technique using cerium nitrate and nickel nitrate (Alfa Aesar, purity 99.99%) as the precursors. The Ce_{1-x}Ni_xO₂ nanoparticles (x=0, 0.025, 0.05 and 0.1) were synthesized and referred as CNO0, CNO2, CNO5 and CNO10 respectively. The detailed synthesis procedure is given in chapter 2. The resultant powders were further calcined at 450°C for 6h to release the trapped carbon particles.

4.2 Structural properties

(I) **XRD**:

XRD patterns of the synthesized CNO0, CNO2, CNO5 and CNO10 samples (Figure 3.1(a)) show (111), (200), (220), (311), (222), (400), (331) and (420) reflection planes belonging to a cubic fluorite (space group Fm3m) structure. No impurity phase of nickel oxides or other complex oxides were found. The absence of any impurity phase even for CNO10 sample with 10% Ni incorporation is a clear indication of proper substitution of Ce by Ni. Ni may exist in Ni²⁺ and Ni³⁺ states. However, irrespective of the valence state, Ni ions are smaller in size than $Ce^{4+}(VIII)$ (1.11 Å). The ionic radii of Ni ions may be estimated as Ni²⁺(VIII) (~0.9 Å) and Ni³⁺(VIII) (~0.76 Å). Changes are noticed in the structure as the XRD peak positions shift towards higher angles reflecting lower *d*-spacings for substituted samples. FullProf software was used to perform Rietveld refinement of the XRD data (Figure 4.1(b)). Lattice parameters reduce with substitution (Figure 4.1(c)). Hence, the unit cell volume decreases. Lattice contraction may be a resultant of a proper substitution of larger Ce ions by smaller Ni ions.



Figure 4.1 (a) XRD data of $Ce_{1-x}Ni_xO_2$ samples confirms a cubic fluorite structure having space group Fm3m (-inset shows reduction of crystallite size with x) (b) Variation of lattice parameter and strain with x.

The XRD peaks were broad enough and the broadness increased with substitution. Due to the broad nature of the XRD peaks, the particle sizes were expected to be small enough. Hence, crystallite sizes were estimated using Scherer's equation ($D = K\lambda/\beta cos\theta$ (where, K=0.9)). Crystallite sizes decreased with Ni substitution from 6.7 nm in CNO0 to

4.3 nm in CNO10 (Figure 4.1(d). Strain was calculated using Williamson-Hall equation [86] [$\beta Cos\theta/\lambda = 1/D + \epsilon Sin\theta/\lambda$; where β is full width at half maxima (FWHM), *D* is the crystallite size, ϵ is lattice strain, θ is angle of incidence and λ is wavelength (1.5406 Å) of *CuKa* radiation]. Strain increases with substitution (Figure 4.1(d)). The increasing strain in the lattice may be an important factor responsible for the decreasing crystallite size with Ni incorporation. It is known that strain and defects impede long-range ordering and is responsible for termination of crystalline growth.

(II) EXAFS and XANES study:

The valence states of Ce and Ni ions were analyzed using Ce L_{III} and Ni *K* edge XANES spectra. The Ce L_{III} edges of pure and Nisubstituted samples have similar shapes and position (Figure 4.2 (a)-inset). The data can be fitted to a combination of an arctangent and four Gaussian peaks (figure 4.2 (b)): two major (A and B) and two minors (C and D).

It was observed that for all the samples, these four peaks, A, B, C and D were invariant at 5730.9 eV, 5724.1 eV, 5719.3 eV and 5714.1 eV respectively. A and B represents electronic transitions involving a final state of $2p4f^{0}5d^{*}$ and $2p4f^{d}5d^{*}L$, respectively, i.e., transitions from Ce2p to Ce4f or Ce5d states. In these notations, 2p stands for \rightarrow Ce 2p holes, $5d^{*}\rightarrow$ excited electrons in Ce5d states and L \rightarrow holes in anion ligand orbital (O 2p). Peak C corresponds to Ce³⁺ valence state. The peak D on the other hand is due to dipole forbidden Ce2p to 4f transition. This transition, which is otherwise not possible, happens due mixing of 5d and 4f orbitals. The splitting of the Ce5d states in the crystal field of O (cubic) can be attributed to final states of O2*p*-Ce5*d* hybridizations due to crystal field splitting of Ce5*d* states.



Figure 4.2 (*a*, *b*) *EXAFS and XANES spectra at Ce-L_{III} edge (b) Ce-L_{III} edge (b) Ce-L_{III} edge XANES spectra of CNO2 sample, fitted using Athena software (c) EXAFS and XANES spectra at Ni-K edges (d) Ni-K edge XANES spectra of CNO2 sample, fitted using Athena software.*

These hybridizations cause delocalization of d character at the bottom of conduction band [59]. The quantification of Ce valance state in

all the samples have been done using area ratio of Ce^{3+} (C) and Ce^{4+} (A+B) as [59–61]:

$$Ce^{3+} = \frac{C}{A+B+C} \times 100$$

$$Ce^{4+} = \frac{A+B}{A+B+C} \times 100$$



Figure 4.3 *EXAFS spectra and fitting at Ce-L_{III}-edge and Ni K-edges for all samples reveal similar local environment with moderate modifications.*

Majority of Ce ions were found to be in Ce^{4+} state (~84-80%) for all the pure and modified CeO₂ samples. However, a considerable amount of Ce^{3+} states (~16-20%) was also observed.

The concentration of Ce^{3+} increases with Ni-substitution from ~16% (CNO0) to ~20% (CNO10) [Table 4.1]. Notably, in CeO₂, Ce is expected to be primarily in Ce⁴⁺ state. However, the presence of Ce³⁺ along with the incorporated Ni^{2+/3+} ions hint at a large V_O content in the samples [Figure 4.2 (d)]. For the pure CeO₂, i.e. CNO0, V_O% was recorded to be ~7.2 %. Nickel has a lower valence state of Ni^{2+/3+}than Ce⁴⁺ (Table 4.1). These lower valence states along with Ce³⁺ are expected to generate oxygen vacancies to maintain charge neutrality of the lattice. Hence, as Ni concentration increases one can expect increasing amount of oxygen vacancies.

Table 4.1: Valance states of Ce, Ni and oxygen vacancy (Vo) calculation from XANES analysis

	Ce4+%	Ce ³⁺ %	Co ²⁺ %	Co ³⁺ %		Ni ⁴⁺ %	
CO	75.6	14.4 (2)	 .	-	_	—	7.2 (1)
CNO	72	18.01 (1)	-	-	86.1 (1)	13.9 (3)	18.31 (3)
ссо	70.2	19.8 (3)	89.7 (2)	10.3 (2)	_	_	19.34 (2)
CCNO	67.5	22.5 (2)	46.35 (1)	3.65 (2)	42.55 (3)	7.45 (2)	20.69 (5)

 $O^{2-}(IV)$ has a crystal radius of 1.24 Å, comparable to $Ce^{3+}(VIII)$ (crystal radius ~1.28 Å). Both are larger than $Ce^{4+}(VIII)$ which has 1.11 Å crystal radius. Similarly, Ni²⁺³⁺(VIII) (~0.76-0.9 Å) is much smaller than all the above three. Lack of oxygen in the pure CeO₂ is a common feature and is observed frequently for samples synthesized with different synthesis processes [62]. The increasing Ce³⁺ concentration may be triggered by Ni substitution. As Ni ions are much smaller than Ce and O ions the lattice will need to shrink due to Ni incorporation. However, Ce³⁺ is larger in size than Ce⁴⁺. Hence, some Ce⁴⁺ ions may get motivated to transit to the Ce³⁺ state under such circumstances.

The local structure of the absorbing atom is obtained from quantitative analysis of Ce L_{III} edge and Ni K edge EXAFS spectra [Figure 4.2 (a, c)]. The absorption function χ (E) is calculated using absorption spectra μ (*E*) as follows [87]:

$$\chi(E) = \frac{\mu(E) - \mu_0(E_0)}{\Delta \mu_0(E_0)}$$
(2)

where, E_0 is absorption edge energy, μ_0 (E_0) is the bare atom background and $\Delta \mu_0$ (E_0) is the step size of $\mu(E)$ at the absorption edge. The wave number (k) dependent absorption coefficient χ (k) is obtained from energy dependent absorption coefficient $\chi(E)$, where k and E can be related as

follows,
$$k^2 = \frac{2m(E-E_0)}{\hbar^2}$$
 (3)

where, m is the mass of electron and h is the Planck's constant. For amplification of oscillation at high k, χ (k) is weighted by k². Thereafter, by Fourier transform of χ (k) k² functions in R-space, χ (R) is generated. A real distances (R) dependent χ (R) plot represents the absorption of the scattered wave from the center of the principal absorbing atom, and hence provides an estimate of the local structure of the material.

The EXAFS data analysis has been performed using a set of analysis programs available from Demeter software package [87]. ATHENA software is used for background correction and normalization of the data for final use. It also does the Fourier transforms to derive χ (R) versus R spectra from the absorption spectra. ARTEMIS software is used to create several scattering paths representing all the coordinated bonds to the atom concerned, in the given crystal structure. By the provision of the crystallographic index file, the program can list several possible bonds at different distances and fit the experimental data to generate theoretical EXAFS spectra. Refinement of the actual bond lengths, coordination numbers and disorder factors of the pure CeO2 structure, leads to an assessment of changes and modifications in the local structure of the modified CeO₂ samples. The theoretical and experimental data of Ce L_{III} edge for all the samples shows good fit [Figure 4]. The available spectrum range at Ni K edge is small. Hence, only first peak fitting is carried out for the Ni K edge EXAFS data. Results of the simulation are shown in Table 4.2.

The first peak of the CeO₂ EXAFS data is a contribution from 8 nearest oxygen atoms of the first coordination shell around Ce at ~2.27 Å. This value is smaller than the reported bond length (2.33 Å) without phase correction. The second peak has contributions of the second coordination shell of 12 Ce atoms at ~ 3.5 Å and the third peak has contribution of the third coordination shell containing 24 oxygen atoms at ~4 Å. Oxygen coordination is found to decrease on substitution. This hints that oxygen vacancies increase with substitution, in agreement with Raman, XANES experiments. The results will also agree with UV and PL results too.

Table 4.2: Bond length, coordination number and disorder factor obtain by EXAFS fitting for CeL_{III}-edge and Ni K-edge.

Path	Parameter s	CNOO	CNO2	CNO5	CNO10
Ce-0 (1)	R (Å)	2.27 (1)	2.25 (2)	2.24 (2)	2.25 (3)
	N	8 (1)	7.92 (2)	7.83 (1)	7.20 (2)
	σ² (Ų)	0.0087 (4)	0.0077 (2)	0.0080 (3)	0.0086 (2)
Ce-Ce	R (Å)	3.78 (2)	3.77 (3)	3.76 (2)	3.77 (1)
	N	12 (3)	11.88 (2)	11.88 (2)	10.80 (3)
	σ² (Ų)	0.0083(2)	0.0013 (3)	0.0010 (3)	0.0011 (3)
Ce-0 (2)	R (Å)	4.40(2)	4.39 (3)	4.39 (2)	4.38 (2)
	N	24 (1)	23.76 (3)	23.76 (2)	21.60 (2)
	σ² (Ų)	0.0076(2)	0.0107 (3)	0.0091 (2)	0.0117 (1)
Ni-0	R (Å)		2.05 (2)	2.02 (2)	2.02 (1)
	N	-	5.25 (1)	5.40 (2)	6.0 (2)
	σ² (Ų)	-	0.0034 (2)	0.0013 (1)	0.0025 (3)

The Ce-O bond length obtained from EXAFS studies decreases with substitution in agreement with XRD results. This leads to increased lattice distortion and strain, which also agrees with XRD and Raman spectroscopic results. Later, this will also show to agree with the Urbach energy calculations in UV-visible spectroscopy studies. The increased disorder factors are present in Ce-O as well as Ce-Ce shells, implying extended results beyond the first shell. The Ni K-edge EXAFS data is like Ce L_{III}-edge data of CeO₂ [Figure 4.3]. This analogous behavior indicates a similar environment of the Ni and Ce ions, thereby suggesting a proper substitution of Ce by Ni. However, the first shell (oxygen shell), i.e., Ni-O bond lengths is at distance of 2.05 Å, much smaller than the Ce-O shell. As the Ni-O bond length is low, it may be inferred that the smaller size of Ni results in smaller Ni-O bond lengths which in turn tries to lessen the bond length of Ce-O. Shorter Ce-O and Ce-Ce bond lengths for the Ni doped samples are observed in comparison to the pure CeO₂.

(III) **HRTEM**: HRTEM studies further confirmed the crystallite size of the samples. Representative images of CNO0 and CNO5 nanocrystals are shown in [Figure 4.4 (a, b)].



Figure 4.4 *HRTEM images revealing average crystallite size of (a) CNOO* ~7.4nm and (b) CNO5 ~5nm with (111) and (200) plane termination for both samples. (Insets) SAED ring patterns show (200), (111), (220) and (311) reflections with d-spacing corresponding to CeO2 structure, (c) EDX patterns of CNO0 and CNO5 showing elemental components of the samples.

Using ImageJ software, the average size of CNO0crystallites was estimated to be ~7.4 (\pm 0.5) nm, while for CNO5 the size reduced to ~5 (\pm 0.5) nm. These results agree with the XRD results. Crystallites were found to be agglomerated. This is a common factor in nanoparticles produced by wet chemical method synthesis. The presence of hydroxyl ions facilitates agglomeration [88]. Agglomeration allows the nanoparticles to achieve more stable energy states. Nanoparticles appear to have thermodynamically stable termination faces of (111) and (200) [57].

SAED studies were performed to verify the structure in the nanoscale. Well-defined lattice fringe patterns confirm the crystalline structure of all the samples. The structures of the synthesized samples match with a fluorite CeO₂ format in agreement with the XRD studies. EDX studies on the nanoparticles were done to verify and estimate Ni incorporation in the samples. Presence of Ce in both samples was observed in major contributions from EDX studies. Ni seems to rise in concentration with increasing substitution.

(IV) Raman Analysis:

All CNO samples show (Figure 4.5(a)) strong phonon modes at 462.5 cm⁻¹ and broad features in the energy range 520~660 cm⁻¹. The strong peak ~462.5 cm⁻¹ is a triply degenerate F_{2g} mode belonging to CeO₂ fluorite structure [27]. This represents a CeO₈ symmetric stretching vibration. The mode is a strong indicator of the vibrations of oxygen around the Ce ion. Hence any changes in the Ce ionic state or the oxygen lattice strongly affects this mode. The F_{2g} peak red shifts, broadens and becomes more asymmetric (lower half widths are larger than higher half width) with substitution [Fig. 4.5 (a, b)]. It was discussed that asymmetry is a consequence of phonon confinement. Red shift was a consequence of an increasing homogeneous strain. However, if the strain was inhomogeneous, the peak was red shifted and symmetrically broadened. A scenario where phonon confinement was associated with an inhomogeneous strain, the peak was red shifted as well as asymmetrically broadened.



Figure 4.5 (a) Systematic broadening and nominal red shift of F_{2g} phonon mode at ~460 cm-1 in modified $Ce_{1-x}Ni_xO_2$; a broad feature in the range 520-660 cm⁻¹ associated with oxygen defects becomes stronger with substitution (-inset shows Raman peak fitting) (b) shows increase in Vo fraction and FWHM with Ni substitution in CeO₂.

The red shifted asymmetrically broadened F_{2g} phonon mode with increasing Ni incorporation, therefore, strongly hints at phonon confinement accompanied with an inhomogeneous strain in CNO samples. Several works have related these effects to factors like defects, strain, phonon confinement, and size distribution [65].

Thus, the increasing asymmetry and broadening nature of the F_{2g} phonon modes matches well with the increasing strain (Williamson-Hall analysis) and decreasing size (Scherer's equation) from XRD studies.

In nanoparticles the highest degree of confinement (3D) is observed. Campbell and Fauchet model clearly relate these changes to reasons described above[89]. Crystallite size (*d*) was estimated using the formula Γ (*cm*⁻¹) = 10 + 124.7/*d*(nm) where, Γ is the FWHM of the F_{2g} phonon mode [90]. The results agreed with TEM and XRD results.

A broad peak at ~520-660 cm⁻¹ corresponds to oxygen related defects [72,73]. This feature increases with substitution. The valence state of Ni²⁺ or Ni³⁺ is always less positive than Ce⁴⁺. To maintain charge neutrality of the lattice, oxygen vacancies (Vo) will be created. An estimation of V₀ was calculated from the ratio of the peak areas (~A_{Vo}/A_{F2g}) of these broad features to that of the F_{2g} peaks. This ratio increased with substitution.

4.3 Optical Properties:

Bandgap of the materials were estimated using UV-vis spectroscopy [Figure 4.6 (a, b)]. CeO₂ has been reported to show both direct and indirect bandgap [90]. Extrapolation of $(\alpha hv)^2$ vs hv plots were used to estimate direct bandgap while $(\alpha hv)^{1/2}$ vs hv plots provided indirect bandgap, where, α is the absorption coefficient. Absorption edge arises from direct transitions from top of the valence band (i.e. O 2p states) to empty Ce⁴⁺ 4f-shells [91].



Figure 4.6 Tauc-plot of $Ce_{1-x}Ni_xO_2$ for (a) Indirect transition (-inset shows bandgap decreasing with x from 3.03 to 2.45 eV), (b) Direct transition (-inset shows bandgap variation with x from, 3.37 to 3.13 eV) (c) Urbach energy increases with x from 0.153 to 0.698 eV (-inset shows Urbach fitting).

Sharpness of the absorption edge in UV-vis spectra reduces with substitution. This is associated with an increase in amount of tailing (Urbach tail). Structural deformation and disorder are responsible for such tail formation. Urbach energy, E_U , is calculated using: $\alpha = \alpha_{0^*} exp(E/E_U)$, where α is absorption coefficient [56]. E_U is calculated from the inverse slope of a straight line fit to a natural logarithm of the exponential decay of α , (i.e. the tail part near the absorption edge) [-inset Figure 4.6 (c)]. Urbach energy increases with Ni substitution from 0.153 eV for x=0 to 0.698 eV for x=0.1 [Figure 4.6 (c)]. This indicates increasing defects and disorder with Ni substitution. Defect states not only reduces bandgap but also results in phonon assisted electronic transitions. Hence chances of an indirect transition increases.

Due to smaller crystal radius and lesser charge of Ni compared to Ce^{4+} , Ni substitution in CeO_2 leads to lattice distortion and reduction of Ce^{4+} to Ce^{3+} . This leads to increased V_0 concentration which highly modifies the band structure of CeO_2 . These changes lead to formation of localized states and spatial distribution of band structure which gives rise to the possibility of both type of electronic transitions viz, direct and indirect.

4.4 Photoluminescence study:

In an ideal situation arises when all Ce ions are in Ce^{4+} state. The CeO_2 bandgap is ~6eV formed due to O2p (valence band, VB) and Ce 5d, 6s (conduction band, CB) [92]. A narrow sub-band ~1eV is formed due to the presence of empty $Ce^{4+}4f^{0}$ states [93]. This effectively reduces the bandgap to ~4.58eV (above VB) [92]. However, if Ce³⁺ ions exist, a $Ce^{3+}4f^{4}$ sub-band is formed ~1.2-1.5eV above the VB and 3.3eV below the CB [93]. This band behaves as a hole trap in the bandgap. This creates an energy gap of ~3.1-3.3eV between electrons in $Ce^{3+}4f^{-1}$ and the empty $Ce^{4+}4f^{0}$ sub-band. On the other hand, presence of oxygen vacancies (V₀) may create states inside the bandgap. Generally, a Vo can trap two electrons. The trapped state is generally represented in the literature as F or F^0 state. The F^0 state may lose one electron and become F^+ state. It can also lose two electrons to become F⁺⁺ state [94]. Theoretical calculations show that F^+ states are closer to VB compared to F^0 states [29,30]. However, F⁺⁺centers are located at about ~0.15-0.2eV below the CB [95]. F^{++} states act as electron traps [95]. There is a fundamental difference between the F^{++} state and the F^{+} or F^{0} state. F^{++} have no localized electrons whereas, F^+ and F^0 states have electrons with partially or fully occupied states [94].



Figure 4.7 (*a*) Photoluminescence spectra of $Ce_{1-x}Ni_xO_2$ samples reveal multiple peaks between 395–529 nm. The major bands are obtained at ~424 nm (2.92 eV, violet), ~457 nm (2.71 eV, blue), ~485 nm (2.56 eV, green-blue) and ~528 nm (2.34 eV, green). Multiple peaks have been fitted to analyze the contribution of each type of color contributions (*b*) Energy band diagram of CeO_2 shows presence of various trap centers between VB and CB which leads to various emission and delocalization of electrons (*c*) shows area variation of each color with composition PL mechanism in Ni substituted CeO_2 ; shows various emission quenches with substitution.

The F^+ and F^0 states are at ~1.7eV and ~2.1eV above the VB and ~3eV and ~2.74eV below CB [31,95]. However, excited states of F^+ and F^0 (F^{+*} and F^{0*}) states are empty states and are located near the CB. F^{+*} and F^{0*} excited states are ~0.4eV below CB [95]. The difference between F^0 and F^{0*} is ~2.1eV while F^{+*} and F^+ is 2.4-2.5eV [95]. Various complex defects like Ce³⁺–Vo–Ce³⁺may also exist [96]. Such complex defect states are explained as accidental recombination sites of a hole due to Ce³⁺ and an electron at V₀ site [97]. Such defects show Stokes-shifted broad luminescence [98]. Hence, these defects are located everywhere in the bandgap. Hence, it is found logical to fit a wide band PL data with multiple peaks to observe not only the major contributions involving well known defects states but also to analyze the complex defects are distributed in the lattice. It is also noted that $\text{Ce}^{3+}4f^{-1}$ electrons are not actually located at a single location. These can travel from one Ce atom to another. Thereby, depending on the availability of V₀ sites in the near vicinity and the distortions in the lattice, the respective energy levels are supposed to behave as multiple defect possibility in the lattice which forms simple and complex defect states all along the bandgap.

Photoluminescence (PL) spectra of the samples reveal broad spectra between 395-529 nm [Figure 4.7 (a)]. Multiple peaks were fitted to analyze the contribution of each type of color contributions in the PL spectra. The major bands are obtained at ~424 nm (2.92 eV, violet), ~457 nm (2.71 eV, blue), ~485 nm (2.56 eV, green-blue) and ~528 nm (2.34 eV, green). Apart from the above major contributions, very feeble contributions of yellow (2.1-2.17eV; ~579nm), orange (2-2.1eV; ~590nm) and red (1.65-2eV; ~620nm) emissions also take place. However, these emissions are negligible compared with the major bands.

The major violet band may be ascribed to $F^{++} \rightarrow Ce^{3+}4f^1$ transitions [99–107] .The blue-green and blue emissions are mostly the resultant of $F^{+*} \rightarrow F^+$ transitions while the green light comes from $F^{0*} \rightarrow F^0$ transitions [Figure 3.8 (c)]. PL intensity of the samples decreases with substitution. Individual color contribution also decreases in a similar way [Figure 4.7 (b)]. This shows that the recombination rate of charge carriers decreases with Ni substitution. This is a hint of increased photocatalytic behavior of CeO₂ due to charge delocalization [4]. Multiple non-radiative decay processes may happen due to multi-phonon processes in the system. These non-radiative processes seem to increase with substitution. The multiphonon processes increase mostly due to distortion in the lattice. As Ni²⁺ substitute Ce⁴⁺ to maintain charge neutrality, Vo increase in the lattice to maintain charge neutrality. The increasing V₀ concentration has two electrons which leads in the reduction of Ce⁴⁺ \rightarrow Ce³⁺ [Figure 4.8 (a, b and c)]. Hence, Ce³⁺ concentration increases at the surface and grain boundaries. These act as a trap centers and behave as non-radiative recombination center, thereby repressing the emission intensity [94,108,109]. Lattice strain increases. This reflects in the electronic structure and thereby reduces bandgap.

Catalytic activities are most active at the location of surface oxygen vacancies [110]. Bulk oxygen defects generally do not contribute to catalytic activities. The V₀ formation happens easier at the surface than in bulk. The surface Vo also are expected to segregate. Energy of surface Ce^{3+} formation is lesser compared to its bulk counterpart. Hence in general, V₀ is more likely to form at the surface. The appearance of Ce^{3+} is a sign of adaptability of the material to frequently accept and transfer an oxygen atom by changing the valence state of Ce. Disordered surfaces are a result of considerable number of defects. These disordered surfaces generally give rise to mid-bandgap states. These states may hybridize with Ce4f states and can form continuous states which can even merge with the conduction band [111]. Such states therefore form band tails which result in non-radiative decay. This is an adverse result for photoluminescence. Such samples where surface states are dominant are therefore PL-quenched samples. This generally is the scenario for mixed valent cerium oxide samples, where Ce^{3+} forms at the surface along with the V₀. Bulk defects on the other hand serve more as radiative recombination centers and hence are sources of strong photoluminescence [112,113].

On the other hand, the presence of Ce^{3+} in the bulk is also a possible scenario. These Ce^{3+} ions can be present in the grains as well as in the grain boundaries. The presence of Ce^{3+} in the grain boundaries is mostly due to the irregular atomic structure of the boundaries which is a signature of absence of V₀ and a larger Ce^{3+} [114]. The migration of Ce^{3+} and hence the V₀ to the grain boundaries therefore contribute to two extra electrons which contribute to the conduction. A rise of conductivity is often observed in Ce^{3+} rich mixed phase sample [115]. However, in these samples the conductivity is extremely low hinting at Ce^{3+} states being available only as surface defects.



Figure 4.8 (a) Shows Ce^{3+} vs Vo relationship, with increase in Ce^{3+} %, Vo increasing exponentially (b) with increase in Vo strain increases in lattice following exponential relationship (c) Shows strain and Eu increasing linearly.

A complex impedance measurement was done for pellets of the same samples sintered at high temperature. The results reveal very high impedance and increasing grain and grain boundary contributions of the samples. The conductivity reduces with substitution. Thus, Ni^{3+} substitution enhances V₀, which in turn generates Ce^{3+} . The Ce^{3+} and V₀, instead of being in the bulk, in the grains and grain boundaries, migrate to the surface to dampen the photoluminescence.



Figure 4.9 shows (a) Micro-hardness variation with load (b) indentation size variation with load (c) Microhardness variation with substitution (d) All models applied; HK model is suitable for our samples

4.5 Micro-hardness study

Hardness of the samples decreases with Ni substitution [Figure 4.9 (c)] in good agreement with the increasing. We applied all existing models in literature to explain the hardness as discussed in previous chapter.

We found that only Hays–Kendall (HK) model is in good agreement in explaining the elastic/plastic behavior of our samples. This model is applicable for materials in which elastic deformation appears below a certain limit of the applied load above which the plastic deformation starts suddenly. Only upon application of a critical load, the indenter can penetrate into the material, resulting in an actual effective load of $F_{eff} = F$ -Fc falling on the sample expressed by Hays–Kendall relationship [F_{eff} = F–Fc = $A_{HK}d^2$; where, A_{HK} is a proportionality constant]. The hardness, $H_{HK} =$ 1854.4 A_{HK} , decreases with increasing substitution. It is to be noted that hardness values from this model is nearly of the same values as the Vickers hardness and follows the same decreasing trend [Fig. 4.9 (b)]. Hence material follow first elastic then plastic deformation.

4.6 Conclusions

Single phase, homogeneous, nanocrystalline, sol-gel synthesized Ni substituted CeO₂ has the same cubic fluorite structure as that of pure CeO₂. XRD and HRTEM analysis confirms the same crystal structure and crystallite size. Strain seems to increase while crystallite size decreases with the substitution. On the other hand, Ni substitution reduces the bandgap considerably. As lower valent Ni²⁺ substitute Ce⁴⁺, Vo increases in the lattice to maintain charge neutrality. The increasing Vo concentration has two electrons which lead to reduction of Ce⁴⁺ \rightarrow Ce³⁺ and subsequent increase the lattice strain is observed. XANES analysis supports the observations that Ce⁴⁺ is reduced to Ce³⁺. The Ce³⁺ concentration increases with substitution. Electronic properties get modified and thereby reduce the bandgap. Reduction in bandgap is due to increased disorder mainly due to formation of defect states between

valance band and conduction band. Raman study reveals that the F_{2g} peaks become asymmetric and FWHM increases with substitution. This implies increased inhomogeneous strain in the lattice and phonon confinement. With increased substitution, PL intensity of the samples decreases. The non-radiative processes increase with substitution. The multi-phonon processes increase with substitution due to increased defect states and lattice distortion which leads to non-radiative emissions. Since recombination rate of charge carriers decreases with Ni substitution, the photocatalytic behavior of CeO₂ will be enhanced.

Chapter 5

Effect of Co-Ni co-substitution on structural, optoelectronic, magnetic and mechanical properties of CeO₂

This chapter aims a detailed comparative study of Co/Ni substitution and co-substitution on structural, optical and photoluminescence properties of CeO₂. This chapter covers sample preparation followed by characterizations of see properties of materials. We prepared samples using a modifiedsol-gel combustion process followed by solid-state sintering forcrystallization of these samples. After synthesis samples werecharacterized by XRD and HRTEM to ensure phase purity, crystallinity and crystal structure of these samples.Rietveld refinement wascarried out estimate structural variations with to compositions. Vibrational studies were verified by observing variations in phononmodes in Raman spectra of these materials. Local structural properties and oxidation states of samples were investigated using EXAFS and XANES study respectively. Optoelectronic properties were studied by UV-visible and photoluminescence (PL). Latticedisorder and Vo quantities were estimated using X-ray absorption (XAS), UV-vis and Ramanspectroscopy. Single phase Co/Ni substituted CeO₂ nanoparticles reveal the importance of oxygen vacancies on the electronic properties of the materials.

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5.1 Synthesis

Co and Ni substituted CeO₂ samples i.e. CeO₂ (CO), Ce_{0.9}Co_{0.1}O₂ (CCO), Ce_{0.9}Ni_{0.1}O₂ (CNO) and Ce_{0.9}Co_{0.05}Ni_{0.05}O₂ (CCNO) were prepared using sol-gel method. Precursors solutions were prepared by dissolving [Ce(NO₃)₃], [Co(NO₃)₂] and [Ni(NO₃)₂] in separate beakers in double distilled de-ionized water (DIW). Experimental details can be found in chapter 2. The resultant powders were calcined at 450°C for 6 h to get rid of carbon and nitrogen compounds.

5.2 Structural properties

(I) **XRD**:

X-ray diffraction patterns of all samples reveal (111), (200), (220), (311), (222), (400), (331) and (420) reflection planes of a CeO₂ cubic fluorite structure (Figure 5.1(a)). Diffraction patterns of Co and Ni related compounds were not found, which indicates proper substitution. With substitution, peaks shift nominally to higher angles with respect to pure CeO₂ (CO). Eight coordinated Ce ions may exist in two valance states Ce³⁺ (crystal radius ~1.11 Å) and Ce⁴⁺ (1.28 Å). Whatever may be the valence state of Co or Ni, (~0.65-1.04 Å) Ce ions are larger than the substituent ions. Since XRD reveals that the samples are predominantly in CeO₂ phase, therefore Ce is mostly in Ce⁴⁺(VIII) state. It is expected that substitution with Co/Ni having lower crystal radii than Ce ions lead to decrease in lattice parameters. Rietveld refinement was performed using FullProf software (Figure 5.1(c)).

It is observed that lattice parameters decrease with substitution (Figure 5.1(b)) according to expectation. While CCO is the most contracted, lattice parameters decrease lesser for CCNO, than CCO and CNO. On the other hand, the inter-axial angles of the unit cell remain constant (=90°). Unit cell volume contracts accordingly.



Figure 5.1 (a) XRD data of Co/Ni substituted CeO_2 samples confirms a cubic fluorite structure having space group Fm3m (b) Variation of lattice parameter, strain and bond length with x (c) proper Rietveld fitting of CCO sample (d) Crystallite size variation with x.

Bond lengths were evaluated from refined crystallography index files (CIF). Bond lengths were found to decrease for the CCO and CNO samples. However, for the CCNO sample, bond length was comparable to CO. However, the changes in bond length seems nominal.

Crystallite size was evaluated from Debye-Scherer's equation: D= $K\lambda/\beta\cos\theta$ (where, K=0.9). Crystallite size was observed to decrease in the order CCO, CNO, being least for CCNO (Figure 1c). Strain was evaluated using Williamson-Hall equation [116]: $[\beta\cos\theta/\lambda = 1/D + \in\sin\theta/\lambda]$, where β is full width at half maxima (FWHM), D is crystallite size, \in is lattice strain, θ is angle of incidence and λ is wavelength

(1.5406 Å) of Cu-k α radiation. Strain increases with substitution (Figure 5.1(b)). Highest strain is observed in CNO followed by CCO but is relatively lower in CCNO. The smaller crystallite size in Co and Ni substitution may be due to increased strain and defects. This reduces long range ordering.

(II) EXAFS and XANES study:

Valence states of all constituent elements were examined using XANES analysis at the Ce-L_{III} and K-edges of Co and Ni. For all the edges, the samples have similar shapes. The shapes were fitted by a combination of an arctangent and Gaussian functions for the Ce-L_{III} edge, with linear combination technique using the same Athena software (Figure 5.2 (b). Ce-L_{III} edges consist of four peaks, A (5730.9 eV), B (5724.1 eV), C (5719.3 eV) and D (5714.1 eV) (Figure 5.2 (a)) A and B are stronger than C while D is the pre-edge (Figure 5 (a)-inset). A and B represents mixture of multi-electron transitions with final state of $2p4f^{0}5d^*$ and $2p4f^{d}5d^*L$. For above notations, $2p \rightarrow$ Ce 2p holes, $5d^* \rightarrow$ excited electrons in 5d states and L \rightarrow holes in anion ligand orbital (O 2p). Peak C corresponds to Ce in Ce³⁺ valence state. Peak D can be attributed to final states of O2*p*-Ce5*d* hybridizations due to crystal field splitting of Ce 5d states causing delocalization of d character at the bottom of conduction band [59].

The quantification of Ce valance in all samples has been done by using area ratio of Ce^{3+} (C) and Ce^{4+} (A+B) as [59–61]:

$$Ce^{3+} = \frac{C}{A+B+C} \times 100$$
$$Ce^{4+} = \frac{A+B}{A+B+C} \times 100$$

The above analysis reveals a major Ce^{4+} state (~84-75%) and a considerable Ce^{3+} contribution (~16-25%). Concentration of Ce^{3+}

increases from ~16% in CO to ~22% in CCO, ~20% in CNO and ~25% in CCNO. Note that in CeO₂, Ce is expected to be primarily in Ce⁴⁺ state. Hence, presence of Ce³⁺ hints at O-vacancies, V₀, in lattice.



Figure 5.2(*a*) XANES spectra at Ce-L_{III} edge of all samples reveal mixed valence state of Ce⁴⁺ and Ce³⁺; (b) XANES fitting of CCO using Athena software shows 22% Ce³⁺ present with inset showing Ce³⁺ concentration increasing with substitution; (c) Ni K-edge XANES spectra revealing dominant Ni²⁺ state with inset showing proper fitting with 2+ charge state; (d) Co K-edge XANES spectra revealing dominant Co²⁺ state with inset showing proper fitting with 2+ charge state.

The XANES spectra of both Co and Ni K edge consist of one main edge and a pre-edge feature. The more intense main-edge region located at higher energy results from a dipolar $1s \rightarrow 4p$ transition [117,118]. The pre-edge features result from a $1s \rightarrow 3d$ excitation[119]. Since this is a
quadrupolar transition, it is much less intense than the higher energy dipolar transition. From the position of the XANES spectra it may be inferred that Co/Ni are predominantly in 2+ oxidation state [Figure 5.2 (c, d)]. From XANES fitting it was found that ~ 89% is in Co^{2+} state in CCO, which increased up to ~92% in CCNO. On the other hand, Ni^{2+} is ~ 86% in CNO which slightly decreased to 85%. From these values of presence of different valence states of Ce, Co and Ni in these samples, the calculated estimate of Vo in CO is 7.2% while in CNO and CCO is 18.3% and 19.4% respectively. However, in CCNO the estimated amount of Vo is ~ 20.7%. This difference in Vo% may be induced by increase in Ce^{3+} concentration due to Co, Ni and Co/Ni incorporation. One should take note of the fact although the CCNO sample is expected to be somewhere in between CCO and CNO samples, it shows much higher Vo than both CCO and CNO. Theoretical studies have revealed that the interaction of Ni^{3+} with Co^{2+} in the absence of Vo has a special interaction in the Ce^{4+} lattice[120]. Such electronic interactions are most probably going to affect electronic states and hence modify the Vo population.

 $O^{2-}(IV)$ has a crystal radius of 1.24 Å, comparable to $Ce^{3+}(VIII)$ (crystal radius ~1.28 Å). Both are larger than $Ce^{4+}(VIII)$ (1.11 Å). Similarly, $Co^{2+}(VIII)$ (~1.04 Å) and $Ni^{2+}(VIII)$ (~0.98Å) is much smaller than all the three above. Note that $Co^{3+/4+}$ (VIII) and $Ni^{3+/4+}$ (VIII) should be yet smaller than all the above. Hence Co/Ni incorporation will positively lead to lattice distortion. Lack of oxygen in the pure CeO_2 is a common feature and is observed using various types of synthesis [62]. Hence, in the absence of oxygen and the space being filled up by smaller radii ions, it is logical for a lesser charge but higher ionic radii ion to fill in the space. Ce^{3+} meets the criteria and hence an increased proportion of Ce^{3+} is observed with substitution (Table 5.1).

	Ce4+%	Ce ³⁺ %	Co ²⁺ %	Co ³⁺ %	Ni ²⁺ %	Ni ⁴⁺ %	Vo%
CO	75.6	14.4	0	0	0	0	7.2
CNO	72	18	0	0	86.1	13.9	18.305
CCO	70.2	19.8	89.7	10.3	0	0	19.385
CCNO	67.5	22.5	46.35	3.65	42.55	7.45	20.695

Table 5.1: Variation in oxidation states of Ce, Co, Ni and Vo obtain by XANES fitting for Ce L_{III}-edge and Co/Ni K-edge.

The local structure of the absorbing atom is obtained from quantitative analysis of Ce-L_{III} edge and Co/Ni K edge EXAFS spectra [Figure 5.3 (a, c)]. The absorption function χ (E) is defined in terms of the absorption spectra μ (*E*) as follows [121]:

$$\chi(E) = \frac{\mu(E) - \mu_0(E_0)}{\Delta \mu_0(E_0)}$$
(2)

where, E_0 is absorption edge energy, μ_0 (E_0) is the bare atom background and $\Delta \mu_0$ (E_0) is the step size of $\mu(E)$ at the absorption edge. The wave number dependent absorption coefficient χ (k) was obtained from energy dependent absorption coefficient $\chi(E)$ as follows,

$$k^{2} = \frac{2m(E - E_{0})}{\hbar^{2}}$$
(3)

where, m is the mass of electron, for amplification of oscillation at high k, χ (k) is weighted by k² and the χ (R) versus R spectra are generated by Fourier transform of $\chi(k)k^2$ functions in R-space, in terms of the real distances from the center of the absorbing atom.

The EXAFS data at Ce-L_{III} edge looks similar for all samples [Fig. 5.3]. Also, the Ni and Co edges appears like the Ce edge of the samples. This indicates proper substitution of Ce by Co/Ni. The positions of the R

space peaks are slightly different which hints at different bond lengths. Hence, an EXAFS fitting seemed essential.



Figure 5.3 *EXAFS spectra and fitting at Ce-L_{III}-edge and Co/Ni K-edges* for all samples reveal similar local environment with moderate modifications: (a) Ce edge of pure CO, (b) Ce and Co edges for CCO, (c) Ce and Ni edges for CNO, and (Ce, Co and Ni edges for CCNO samples.

EXAFS data analysis program available within Demeter software package was used to analyze the EXAFS data [121]. ATHENA was used to subtract the background of the absorption spectra. It was thereafter used to Fourier-transform the resultant data to χ (R) versus R data. This data was used for theoretical model fitting using ARTEMIS software, starting from a standard pure CeO₂ crystallographic structure and thereafter simulating a modified structure matching the experimental data. Theoretical fits are obtained by refining bond length, coordination number and disorder factor. The theoretical and experimental data of Ce-L_{III} edge for all the samples shows good fits [Fig. 5.3 (a, b)]. The obtained fitting results are shown in Table 5.2 and 5.3.

The first peak corresponds to contributions from eight oxygen atoms surrounding Ce at ~2.29 Å (observed at a smaller bond length without phase correction), a bit smaller than the bulk Ce-O bond length (2.33 Å). Second peak corresponds to the second coordination shell of 12 Ce atoms at ~ 3.5 Å and the third peak of the third coordination shell containing 24 oxygen atoms at ~ 4 Å. Oxygen coordination decreases with substitution, hinting at increase in oxygen vacancies with substitution. With substitution Ce-O bond length decreases. Reduction in Ce-O bond length is expected owing to higher ionic radii of Ce⁴⁺ than the Co²⁺ and Ni²⁺. One also observes a shorter Ce–O and Ce–Ce bond lengths for the Co/Ni doped samples in comparison to the pure CeO₂. The shorter bond lengths lead to disorder and strain in lattice. Disorder factors are observed to increase with substitution but for CCNO sample reduces and becomes comparable to pure CO. A similar fitting process was adopted for Ni and Co data. It is observed that Ni-O and Co-O bond lengths are smaller than the Ce-O bond lengths. This agrees with the XANES results. The first peak in Co and Ni substituted CeO₂ has contribution of first oxygen shell at distance of 1.86 Å and 2.02 Å representing Co-O and Ni-O bond lengths. Both Co-O and Ni-O bond lengths are lesser than Ce-O which is due to smaller size of Co and Ni compared to Ce.

Path	Parameters	CO	CCO	CNO	CCNO
Ce-0 (1)	R (Å)	2.27(1)	2.24(3)	2.25(3)	2.27(2)
	N	8.0(1)	7.24(3)	7.20(2)	6.96(2)
	σ² (Ų)	0.0087(2)	0.0098(2)	0.0095(4)	0.0088(3)
Ce-Ce	R (Å)	3.78(2)	3.77(3)	3.77(3)	3.76(2)
	N	12.0(3)	10.86(4)	10.80(2)	10.44(4)
	σ² (Ų)	0.0083(2)	0.0117(2)	0.0109(3)	0.0091(2)
Ce-0 (2)	R (Å)	4.40(2)	4.39(2)	4.38(3)	4.39(2)
	N	24.0(1)	21.65(4)	21.60(3)	20.88(3)
	σ² (Ų)	0.0076(2)	0.0107(2)	0.0117(4)	0.0088(3)

Table 5.2: Bond length, coordination number and disorder factor obtain by EXAFS fitting for Ce- L_{III} edge.

Table 5.3: Bond length, coordination number and disorder factor obtain by EXAFS fitting for Co K-edge and Ni K-edge.

Path	Parameter s	ссо	CNO	CCNO
Co-O	R (Å)	1.86(3)		1.90(2)
	N	5.4(2)	-	5.7(3)
	σ² (Ų)	0.0012(3)	-	0.0031(2)
Ni-O	R (Å)	-	2.02(3)	2.03(2)
	N	-	6.0(2)	5.40(1)
	σ² (Ų)		0.0025(2)	0.0049(3)

(III) HRTEM:

HRTEM studies reveal aggregation of crystallites. This is common in nanoparticles synthesized by sol-gel method. Stable energy state in nanoparticles is achieved by agglomeration [122]. Also the presence of hydroxyl ions facilitates agglomeration [88]. HRTEM images of CO, CCO, CNO and CCNO nanocrystals are shown in [Figure 5.4 (a, b, c and d)].



Figure 5.4 *HRTEM images reveal proper crystalline nature and average crystallite size of (a) CO ~7.4nm and (b, c and d) CCO, CNO and CCNO ~5nm with (111) and (200) plane termination for all samples. (Insets) FTT of HRTEM images revealing d-spacings in agreement with XRD results (f) SAED ring patterns of polycrystalline samples show (200), (111), (220) and (311) reflections with d-spacing corresponding to CeO₂ structure.*

For CO, average size crystallite is ~7.4 (\pm 0.5) nm. With Co and Ni substitution, size reduces to ~5 (\pm 0.5) nm for Co/Ni substituted samples. These results follow the same trend as XRD results. Nanoparticles appears to have thermodynamically stable (111) and (200) termination faces [57]. Well-defined ring-like lattice fringes in SAED patterns confirm the

polycrystalline nature of synthesized samples [Figure 5.4 (f)]. In case of CO the rings are not continuous indicating the larger particles than the substituted samples. Fourier transforms of selected HRTEM images provide lattice parameters and d-spacings, equivalent to XRD studies.

(IV) Raman Analysis:

A strong triply degenerate F_{2g} Raman phonon mode at ~461cm⁻¹ of CeO₂, belonging to a fluorite structure, is observed in all the samples (Figure 5.5 (a)). This represents a CeO₈ symmetric stretching vibration. The CO sample reveals a better symmetry than the substituted ones. In a defectfree crystalline semiconductor (bulk) material one expects perfect symmetry. Factors like defects, strain, phonon confinement, size distribution, etc. can be responsible for asymmetric changes in the phonon mode profile[65]. Size plays an important role in Raman peak shifts [62]. Most probably reduction of size is responsible for red shift. However, literature also mentions that phonon confinement and inhomogeneous strain affect the Raman phonon modes in materials [62]. Hence, the reduced symmetry in the substituted samples compared to CO strongly indicates reduced crystallinity and increased inhomogeneous strain in these materials.

A broad feature in the range $520 \sim 660 \text{ cm}^{-1}$ is also observed in all samples. This feature also arises from a CeO₈ stretching vibration but is highly sensitive to oxygen related disorder²². Oxygen related defects have been held responsible for this feature [72,73]. In the CO sample this feature is present but is extremely weak and negligibly small as compared to the substituted samples. This feature broadens and becomes more

asymmetric (lower half widths are larger than higher half width) with substitution [Fig. 5.5 (a, b)]. This feature is expected to increase with substitution as both Co and Ni are valance state lesser than 4+. Hence, the presence of these ions is substituted sites in the lattice with invoke loss of lattice oxygen to maintain charge stability and neutrality of the lattice. Hence, substitution will cause generation of oxygen vacancies, (Vo). A quantitative analysis of V₀ fraction has been estimated from A_{Vo}/A_{F2g} ratio.



Figure 5.5 (a) Systematic broadening and nominal red shift of F_{2g} phonon mode at ~461 cm⁻¹ in modified Co/Ni substituted CeO₂; a broad feature in the range 520-660 cm⁻¹ associated with oxygen defects becomes stronger with substitution (-inset shows Raman peak fitting) (b) shows Variation peak position, FWHM, asymmetry and in Vo fraction with Co/Ni substitution in CeO₂.

This ratio was found to increase with substitution indicating increasing oxygen vacancies with substitution. Oxygen vacancies are nominally more in CCO than CNO but increases further in CCNO sample [Figure 5.5 (b)]. Oxygen defects on the other hand are known to generate F centers which will be discussed later in photoluminescence section. Hence these have spectroscopic implications related to bandgap and PL emissions.

5.3 Optical Properties:

The UV-visible absorption spectra of CO, CCO, CNO and CCNO samples are shown in [Figure 5.6 (a, b)]. CeO₂ is reported to have both direct and indirect bandgap [90]. The illumination of UV light excites electrons from the valence band to the conduction band with and without the help of phonons. However, a very low energy ($<10^{-2}$ eV) phonon is involved in the indirect transition [123]. Hence, in CeO₂, the indirect transition is less prominent than the direct transition. Both direct and indirect band-gap estimation has been done by extrapolation of $(\alpha hv)^2$ vs hv and $(\alpha hv)^{1/2}$ vs hvplots, where, α is the absorption coefficient. Absorption edge arises from direct transitions from top of the valence band (O 2p states) to empty 4f-shells of Ce⁴⁺[91]. Oxygen vacancies play an important role in occupying states closer to the band edge and thereby modifying the bandgap. A trend consistent with the Vo calculations from XANES studies matches with that of bandgap. As Vo increases bandgap decreases and is lowest for CCNO. The F⁰, F⁺ and F⁺⁺ states get affected with the increase in Vo concentration. As a result, the direct bandgap reduces from 3.35 eV in CO to 2.84 eV in CCNO. On the other hand, the indirect bandgap reduces considerably from 3.0eV in CO to 1.8 eV in CCNO. The bandgap reduction trend is in the order CO, CNO, CCO and CCNO which is like the trend of increasing Vo%.



Figure 5.6 Tauc-plot of Co/Ni substituted CeO₂ samples for (a) Indirect transition (-inset bandgap variation with composition) (b) Direct transition (-inset bandgap variation with composition) (c) Schematic presentation of direct and indirect transitions (d) Urbach energy increases with Co/Ni substitution (-inset shows Urbach tail fitting).

Sharpness of the absorption edge in UV-vis spectra reduces while edge tailing (Urbach tail) increases with substitution. Structural deformations and disorder are responsible for such tail formation. Urbach energy, E_U , was calculated using: $\alpha = \alpha_{0*} exp(E/E_U)$, where α is absorption coefficient [56]. Calculation of α was done by taking natural logarithm of exponential decay (only tail part) near the absorption edge. Inverse of the slope of a straight-line fit represents E_U . Urbach energy increases with Co/Ni substitution from 0.153 eV (CO) to 0.913 eV (CCNO) [Figure 5.6 (d)]. Hence, defects and disorder increase with Co/Ni substitution and is highest for CCNO. These defect states not only cause reduction of bandgap but also results in phonon assisted electronic transitions. Lattice distortion and reduction of Ce⁴⁺ to Ce³⁺ because of substitution by smaller sized and lesser charged Co/Ni in place of Ce highly modifies the band structure of substituted CeO₂. Such changes may lead to formation of localized states and modification of band structure. Such modifications raise the possibility of both direct and indirect (phonon assisted) electronic transitions. Note that the increasing trend in Eu, is at par with the decreasing trend in bandgap and is in the order CO, CNO, CCO and CCNO which is like the trend of increasing Vo%.

5.4 Photoluminescence study:

Ce has an electronic configuration of $[Xe]4f^{4}5d^{1}6s^{2}$. Hence, Ce⁴⁺ can be represented as $[Xe]4f^0$ while Ce^{3+} can be represented as $[Xe]4f^1$. Hence, in Ce⁴⁺ ion one has electronic contributions from 6s, 5d as well as 4f electrons. However, in Ce^{3+} contributions are only from 6s and 5d electrons. This will modify the nature of hybridization and as a result the bond properties. In an ideal situation where all Ce ions are in Ce⁴⁺ state, the CeO₂ bandgap, E_g , is ~6 eV. E_g is formed due to the separation of the valence band, VB (formed due to O2p orbitals) and conduction band, CB (Ce 5d, 6s) [92]. A narrow sub-band ~1 eV is also formed due to the presence of empty $Ce^{4+}4f^{0}$ states [93]. This effectively reduces the bandgap to ~4.58 eV (above VB) [92]. However, if Ce3+ ions exist, a $Ce^{3+}4f$ sub-band is formed ~1.2-1.5 eV above the VB and 3.3 eV below the CB [93]. This band behaves as a hole trap in the bandgap. This creates an energy gap of ~3.1-3.3 eV between available electrons in $Ce^{3+}4f^{4}$ and the empty $Ce^{4+}4t^{0}$ sub-band. On the other hand, presence of oxygen vacancies, V₀, may create states inside the bandgap. Generally, a V₀, can trap two electrons. The trapped state is generally represented in literature as F or F^0 state. The F^0 state may lose one electron and becomes F^+ state and further loses two electrons to become F^{++} state [94]. Theoretical calculations show that F^+ states are closer to VB compared to F^0 states [29,30]. However, F^{++} centers are located at about ~0.15-0.2eV below the CB [95]. F^{++} states act as electron traps [95]. There is a fundamental difference between the F^{++} state and the F^{+} or F^{0} states. While F^{++} have no localized electrons F^+ and F^0 states have electrons and are partially and fully occupied states [94]. The F^+ and F^0 states are ~1.7 eV and ~2.1 eV above the VB and ~3 eV and ~2.74 eV below CB [31,95]. However, excited states of F^+ and F^0 states are also empty states and are located near the CB and are denoted as F^{+*} and F^{0*} . F^{+*} and F^{0*} excited states are ~0.4 eV below CB [95]. Difference between F^0 and F^{0*} is ~2.1 eV, while, that of F^{+*} and F⁺ is 2.4-2.5eV [95]. Various complex defects like Ce³⁺–Vo– Ce^{3+} may also exist [96]. Such complex defect states has been explained as accidental recombination sites of a hole due to Ce^{3+} and an electron at the V₀ site [97]. Such defects show a Stokes-shifted broad luminescence [98]. Hence, such defects are located everywhere in the bandgap. Hence, it was found logical to fit a wide band PL data with multiple peaks to observe not only the major contributions involving well known defects states but also gather knowledge about how complex defects are distributed in the lattice. It is also to be noted that a $Ce^{3+}4f^{4}$ electron is not actually located at a single location but in fact can travel from one Ce atom to another. Thereby, depending on the availability of V_O sites in the near vicinity and the distortions in the lattice the respective energy levels are supposed to behave as multiple defect possibility in the lattice, forming simple and complex defect states all along the bandgap.

Photoluminescence (PL) spectra of the samples reveal multiple peaks between 395-529 nm [Figure 5.7 (a)]. The luminescence is not very strong but is helpful to understand the defect states present in the materials. Multiple peaks have been fitted to analyze the contribution of each type of color contributions in the PL spectra. The major bands are obtained at ~424 nm (2.92 eV, violet), ~457 nm (2.71 eV, blue), ~485 nm (2.56 eV, green-blue) and ~528 nm (2.34 eV, green). Apart from the above major contributions, very feeble contributions of yellow (2.1–2.17 eV; ~579nm), orange (2-2.1 eV; ~590 nm) and red (1.65–2 eV; ~620 nm)

emissions also take place. But these emissions are negligible compared with the major bands.

The major violet band may be ascribed to $F^{++} \rightarrow \text{Ce}^{3+}4f^4$ transitions [99–107]. The blue-green and blue emissions are mostly a resultant of $F^{+*} \rightarrow F^+$ transitions while the green light comes from $F^{0*} \rightarrow F^0$ transitions [Figure 5.7 (c)].



Figure 5.7 (a) Photoluminescence spectra of CCNO series samples reveal multiple peaks between 395–529 nm. The major bands are obtained at ~424 nm (2.92 eV, violet), ~457 nm (2.71 eV, blue), ~485 nm (2.56 eV, green-blue) and ~528 nm (2.34 eV, green). Multiple peaks have been fitted to analyze the contribution of each type of color contributions (b) Energy band diagram of CeO₂ shows presence of various trap centers between VB and CB which leads to various emission and delocalization of electrons (c) shows area variation of each color with composition PL mechanism; shows various emission quenches with substitution.

PL intensity of the samples decreases with substitution. Individual color contribution decreases in a similar way [Figure 5.7 (b)]. Multiple non-radiative decay processes may happen due to multi-phonon processes in the system. These non-radiative processes seem to enhance with substitution. The multi-phonon processes increase most probably due to distortion in the lattice. $\text{Co}^{2+}/\text{Ni}^{2+}$ incorporation increases V₀ (reduction of blue emission) and thereby converts $\text{Ce}^{4+}\rightarrow\text{Ce}^{3+}$ concentration at the surface and grain boundaries.

These act as trap centers and behave as non-radiative recombination center, thereby repressing the emission intensity [94,108,109]. Decrease in PL intensity of CeO_2 with Co/Ni substitution insures that recombination rate of charge carriers decreases which makes it better material for photocatalytic applications.

EXAFS study shows that Ce–O co-ordination number is decreasing. This indicates increase of Vo [Figure 5.8 (a)]. This also confirms with the necessity of maintaining charge neutrality in lattice. Increase of Vo is also supported by Raman analysis. As Vo increases in CeO₂ lattice it leaves two extra electrons in system which leads reduction of Ce⁴⁺ \rightarrow Ce³⁺. Defects due to Co/Ni originate from structural disorders. All these defects lead to changes in the band. Electronic states are created between VB and CB which appears as tail in bandgap [Figure 5.8 (b)].



Fig. 5.8. (a) shows Ce^{3+} vs Vo relationship with increase in Ce^{3+} % Vo increasing exponentially (b) with increase in Vo strain increases in lattice following exponential relationship (c) Shows strain and Eu increasing linearly.

5.5 Conclusions

Single phase, homogeneous, nanocrystalline, sol-gel synthesized Co/Ni substituted CeO₂ have similar cubic fluorite structure as that of pure CeO₂. Structural studies from XRD data is confirmed by HRTEM yielding same crystal structure and crystallite size. Strain seems to increase while crystallite size decreases with substitution. On the other hand, the bandgap reduces considerably due to Co and Ni co-substitution. The reduction in bandgap and increase in Urbach energy can be related to the increases in As Ce⁴⁺ is substituted by mainly Co²⁺/Ni²⁺, Vo increases to Vo%. maintain charge neutrality of the lattice. Each Vo is equivalent to two electrons which further leads to reduction of Ce^{4+} to Ce^{3+} . Ce^{3+} is larger than Ce⁴⁺ and thereby increases lattice strain. This is reflected in electronic structure and bandgap is reduced. Reduction in bandgap is due to increased disorder mainly due to formation of defect states between valance band and conduction band. Raman studies reveal increase of asymmetry and FWHM of the F_{2g} peak with substitution. This again

implies increased lattice strain. Also, Vo related peaks increase with substitution. This is pointing out the increase in defect concentration with substitution. EXAFS studies reveal reduction of oxygen coordination which implies increase in Vo concentration with substitution. XANES analysis also supports a similar scenario as Ce³⁺ concentration increases with substitution. From PL studies increased lattice distortion leads to increased non-radiative processes, which decrease the luminescence intensity. Multi-phonon processes increase with substitution due to increasing defect states and lattice distortion which leads to non-radiative emissions. Thus, Co/Ni substitution of Ce causes lattice distortion due to structural defects, but maintains CeO₂ structure, thereby reducing the bandgap and decreasing radiative emissions of the materials. Co/Ni (CCNO) co-substituted samples appears to be more promising for photocatalytic and solar applications than pure (CO) and single substituted (CCO/CNO) samples owing to huge shift of bandgap from UV to visible region along with less lattice distortion.

Chapter 6

Effect of Mn, Co-Mn and Mn-Ni co-substitution on structural, optical, magnetic and mechanical properties of CeO₂

This chapter aims at a detailed study of Mn, Co-Mn and Mn-Ni substitution and co-substitution on structural, optical, magnetic and mechanical properties of CeO_2 . It covers sample preparation followed by properties characterization of the materials. Samples were prepared using modified sol-gel process followed by solid-state sintering. After synthesis samples were characterized by XRD, SAED and HRTEM to ensure phase purity, crystallinity and crystal structure of these samples. Rietveld refinement was carried out to estimate structural variations with composition. Vibrational studies were verified by observing variations in phonon modes in Raman spectra of these materials. Local structure and oxidation states of samples were investigated using EXAFS and XANES studies respectively. Optical, magnetic and mechanical properties were studied using UV-visible PPMS and Vickers's microhardness tester. Lattice disorder and Vo quantities were estimated using X-ray absorption (XAS), UV-vis and Raman spectroscopy. Single phase Mn/Co/Ni substituted CeO₂ nanoparticles reveal the importance of oxygen vacancies on the electronic and magnetic properties of the materials.

5.1 Synthesis

Ce_{1-*x*}Mn_{*x*}O₂samples with x = 0 (CMO0), 0.025 (CMO2), 0.05 (CMO5), 0.1 (CMO10) were prepared along with Ce_{0.9}(Co_{1-*x*}Mn_{*x*})_{0.1}O₂samples with x = 0 (CCO) 0.5 (CCMO) and 1 (CMO) and Ce_{0.9}(Mn_{1-*x*}Ni_{*x*})_{0.1}O₂samples with x = 0 (CMO) 0.5 (CMNO) and 1 (CNO) using sol-gel method. Precursors solutions were prepared by dissolving [Ce(NO₃)₃], [Mn(NO₃)₂], [Co(NO₃)₂] and [Ni(NO₃)₂] in separate beakers in double distilled de-ionized water (DIW). Experimental details can be found in chapter 2. The resultant powders were calcined at 450°C for 6 h to get rid of carbon and nitrogen compounds.

5.2 Structural properties

(I) **XRD**:

X-ray diffraction patterns of all samples reveal (111), (200), (220), (311), (222), (400), (331) and (420) reflection planes of a CeO₂ cubic fluorite structure (Figure 6.1 and 6.2). Diffraction patterns of compounds of Mn, Co and Ni were not found, which indicates proper substitution. With substitution, peaks shift nominally to higher angles with respect to pure CeO₂ (CO). Eight coordinated Ce ions may exist in two valance states Ce³⁺ (crystal radius ~1.11 Å) and Ce⁴⁺ (1.28 Å). Whatever may be the valence state of Mn, Co or Ni, (~0.65-1.1 Å), Ce ions are larger than the substituent ions. Since XRD reveals that the samples are predominantly in CeO₂ phase, therefore Ce should bepredominantly in the Ce⁴⁺(VIII) state. However, lower valence state of the substituent ions may lead to oxygen vacancies, which may subsequently give rise to lower valent Ce³⁺ states. It is expected that substitution with Mn/Co/Ni having lower crystal radii than Ce ions lead to decrease in lattice parameters. Rietveld refinement was performed using FullProf software.



Figure 6.1 XRD data of Mn substituted CeO_2 samples confirms a cubic fluorite structure having space group Fm3m (-inset shows variation of lattice parameter with x



Figure 6.2 XRD data of Co-Mn and Mn-Ni co-substituted CeO₂ samples confirms a cubic fluorite structure having space group Fm3m

It is observed that lattice parameters decrease with substitution (Figure 6.1(inset) and 6.3) according to expectation owing to lesser ionic radii of Mn, Co and Ni. This leads to lattice distortion and strain.

While CMO is the most contracted, lattice parameters decrease lesser for co-doped CCMO and CMNO than CMO, CCO and CNO. Unit cell volume contracts accordingly.



Figure 6.3 (a) Williamson-Hall plot of CMO samples (b) Variation of lattice strain and crystallite size with x. Increment in strain leads to reduction in crystallite size.



Figure 6.4 shows variation in (a) lattice parameter (b) crystallite size and (c) strain of CCMO and CMNO samples



Figure 6.5 (a) XANES spectra at Ce-L_{III} edge of all samples show mixed valence state of Ce^{4+} and Ce^{3+} ; (b) XANES fitting of CMO using Athena software shows with substitution; (c) Mn K-edge XANES spectra revealing dominant $Mn^{3+/4+}$ state; (d) Mn K-edge XANES spectra fitting

Crystallite size was evaluated from Debye-Scherer's equation: D= $K\lambda/\beta\cos\theta$ (where, K=0.9) which decreased with Mn, Co-Mn and Mn-Ni substitution (Figure 6.3 and 6.4). Strain was evaluated using Williamson-Hall equation[116]: $[\beta \cos\theta/\lambda = 1/D + \varepsilon \sin\theta/\lambda]$, where β is full width at half maxima (FWHM), D is crystallite size, ε is lattice strain, θ is angle of incidence and λ is wavelength (1.5406 Å) of Cu- k_{α} radiation (Figure 6.3(a)). Strain is increases with substitution (Figure 6.3(b) and 6.4 (c)). Highest strain is observed in CMO but lesser in Co-Mn and Mn-Ni substituted samples. This may to generation of oxygen vacancies related defects which balances the shrinkage of lattice.

(II) EXAFS and XANES study:

Valence states of all constituent elements were examined using XANES analysis at the Ce-L_{III} and K-edges of Mn, Co and Ni. For all the edges, the samples have similar shapes (Figure 6.5 (a)). The shapes were fitted as discussed in previous chapters. All other details can be found in previous chapter related to transitions. The quantification of Ce^{3+} was performed using previously explained procedure. This analysis reveals a major Ce^{4+} state (~84-73%) and a considerable Ce^{3+} contribution (~16-27%).

Table 6.1: Variation in oxidation states of Ce, Mn and Vo obtain by XANES fitting for Ce L_{III} -edge and Mn K-edge.

	Ce4+ (%)	Ce³+ (%)	Mn²+(%)	Mn ³⁺ (%)	Mn**(%)	Vo(%)
co	83.35	16.65 (3)	-	-	-	7.49 (3)
CM02	82.48	17.52 (1)	0	42.8 (3)	57.21 (2)	15.97 (2)
СМО5	80.71	23.97 (2)	0	41.31 (2)	59.35 (3)	16.67 (4)
CMO10	80.42	26.77 (2)	10.06 (3)	78.72 (4)	11.27 (1)	16.91 (2)

Concentration of Ce^{3+} increases from ~16% in CO to ~26.8% in CMO. Note that in CeO₂, Ce is expected to be primarily in Ce⁴⁺ state. Hence, presence of Ce³⁺ hints at O-vacancies, V₀, in lattice.

The XANES spectra at Mn, Co and Ni K edge consist of one main edge and a pre-edge feature. The more intense main-edge region located at higher energy results from a dipolar $1s \rightarrow 4p$ transition [117,118]. The preedge features result from a $1s \rightarrow 3d$ excitation[119]. Since this is a quadrupolar transition, it is much less intense than the higher energy dipolar transition. From the position of the XANES spectra it may be inferred that Mnis predominantly in 3+/4+ oxidation state [Figure 6.3 (c, d)]. The Vo% may be induced by increase in Ce³⁺ concentration due to Mn, Co-Mn and Mn-Ni incorporation.

The local structure of the absorbing atom is obtained from quantitative analysis of Ce-L_{III} edge and Mn/Co/Ni K edge EXAFS spectra [Figure 6.7(a, b)]. The EXAFS data at Ce-L_{III} edge looks similar for all samples [Fig. 6.7 and 6.8]. Also, the Mn, Ni and Co edges appears like the Ce edge of the samples. This indicates proper substitution of Ce by Mn/Co/Ni.The positions of the R space peaks are slightly different which hints at different bond lengths. Hence, an EXAFS fitting seemed essential.



Figure 6.6 (a) XANES spectra at Ce-L_{III} edge of all samples reveal mixed valence state of Ce^{4+} and Ce^{3+} ; (b) Ce^{3+} concentration increasing with substitution



Figure 6.7 EXAFS spectra and fitting at Ce-L_{III}-edge and Mn K-edges for all samples reveal similar local environment with moderate modifications:

Path	Parameters	СМОО	CM02	смо5	СМО10
Ce-0 (1)	R (Å)	2.27 (1)	2.26 (2)	2.26 (2)	2.25 (3)
	N	8 (1)	7.94 (2)	7.87 (1)	7.39 (2)
	σ² (Ų)	0.0087 (4)	0.0089 (2)	0.0095 (3)	0.0102 (2)
Ce-Ce	R (Å)	3.78 (2)	3.77 (3)	3.76 (2)	3.75 (1)
	N	12 (3)	11.88 (2)	11.88 (2)	10.80 (3)
	σ² (Ų)	0.0083(2)	0.0089 (3)	0.0093 (3)	0.011 (3)
Ce-0 (2)	R (Å)	4.40(2)	4.39 (3)	4.39 (2)	4.38 (2)
	N	24 (1)	23.76 (3)	23.76 (2)	21.60 (2)
	σ² (Ų)	0.0076(2)	0.0086 (3)	0.0091 (2)	0.0117 (1)
Mn-O	R (Å)		1.88 (1)	1.88 (2)	1.87 (1)
	N	-	5.13 (1)	5. 77 (2)	6.0 (2)
	σ² (Ų)	ž	0.005 (2)	0.0054 (1)	0.0063 (3)

Table 6.2: Bond length, coordination number and disorder factor obtain by EXAFS fitting for Ce L_{III}-edge and Mn K-edge.

EXAFS data analysis program available within Demeter software package was used to analyze the EXAFS data [121]. ATHENA was used to subtract the background of the absorption spectra. It was thereafter used to Fourier-transform the resultant data to χ (R) versus R data. This data was used for theoretical model fitting using ARTEMIS software, starting from a standard pure CeO₂ crystallographic structure and thereafter simulating a modified structure matching the experimental data. Theoretical fits are obtained by refining bond length, coordination number and disorder factor. The theoretical and experimental data of Ce-L_{III} edge for all the samples shows good fits [Fig. 6.7 (a, b)]. The obtained fitting results are shown in Table 6.2 and 6.3. The first peak corresponds to contributions from eight oxygen atoms surrounding Ce at ~2.29 Å (observed at a smaller bond length without phase correction), a bit smaller than the bulk Ce–O bond length (2.33 Å). Second peak corresponds to the second coordination shell of 12 Ce atoms at ~ 3.5 Å and the third peak of the third coordination shell containing 24 oxygen atoms at ~ 4 Å. Oxygen coordination decreases with substitution, hinting at increase in oxygen vacancies with substitution. With substitution Ce–O bond length decreases. Reduction in Ce–O bond length is expected owing to higher ionic radii of Ce⁴⁺ than the Mn³⁺/Mn⁴⁺, Co²⁺and Ni²⁺. One also observes a shorter Ce–O and Ce–Ce bond lengths for the Mn/Co/Ni doped samples in comparison to the pure CeO₂. The shorter bond lengths lead to disorder and strain in lattice. Disorder factors are observed to increase with substitution but for CCMO and CMNO sample reduces and becomes comparable to pure CO.

A similar fitting process was adopted for Mn, Ni and Co data. It is observed that Mn-O, Ni-O and Co-O bond lengths are smaller than the Ce-O bond lengths. This agrees with the XANES results. The first peak in Mn, Co and Ni substituted CeO₂ has contribution of first oxygen shell at distance of 1.86 Å and 2.02 Å representing Mn-o, Co-O and Ni-O bond lengths. Mn-O, Co-O and Ni-O bond lengths are lesser than Ce–O which is due to smaller size of Mn, Co and Ni compared to Ce.

(III) HRTEM:

HRTEM studies reveal aggregation of crystallites. This is common in nanoparticles synthesized by sol-gel method. Stable energy state in nanoparticles is achieved by agglomeration [122]. Also the presence of hydroxyl ions facilitates agglomeration [88]. Representative HRTEM images of CMO5 is shown in [Figure 6.9].For CMO5, average size crystallite is ~5.5 (\pm 0.5) nm. These results follow the similar trend as XRD results. Nanoparticles appears to have thermodynamically stable

(111) and (200) termination faces [57]. Well-defined ring-like lattice fringes in SAED patterns confirm the polycrystalline nature of synthesized samples [Figure 6.9 (b)].



Figure 6.8 EXAFS spectra fitting of all the CCMO and CMNO samples

In case of CO the rings are not continuous indicating the larger particles than the substituted samples. Fourier transforms of selected HRTEM images provide lattice parameters and d-spacings, equivalent to XRD studies.

Table 6.3: Bond length, coordination number and disorder factor obtain byEXAFS fitting for Ce- L_{III} -edge and Co, Mn and Ni K-edge.

Path	Parameters	СО	ссмо	СМИО
Ce-0 (1)	R (Å)	2.27 (1)	2.26 (2)	2.26 (3)
	N	8 (1)	7.17 (1)	7.03 (2)
	σ² (Ų)	0.0087 (4)	0.0092 (3)	0.0089 (2)
Ce-Ce	R (Å)	3.78 (2)	3.76 (2)	3.77 (1)
	N	12 (3)	10.63 (2)	10.56 (3)
	σ² (Ų)	0.0083(2)	0.0093 (3)	0.0089 (3)
Ce-0 (2)	R (Å)	4.40(2)	4.39 (2)	4.38 (2)
	N	24 (1)	21.17 (2)	21.03 (2)
	σ² (Ų)	0.0076(2)	0.0091 (2)	0.0086(1)
Mn-0	R (Å)	-	1.84 (1)	1.88 (1)
	N	-	5. 13 (1)	5.35 (2)
	σ² (Ų)	-	0.0065 (1)	0.0063 (1)



Figure 6.9 *HRTEM images reveal proper crystalline nature and average crystallite size of CMO5 (a)* ~5.5nm and (b) SAED ring patterns of polycrystalline samples show (200), (111), (220) and (311) reflections with d-spacing corresponding to CeO₂ structure (c) EDX shows incorporation of Mn in CeO₂(d) Elemental mapping shows homogeneous distribution of Mn in ceria lattice.

(IV) Raman Analysis:

A strong triply degenerate F_{2g} Raman phonon mode at ~461cm⁻¹ of CeO₂, belonging to a fluorite structure, is observed in all the samples (Figure 6.10 (a)). This represents a CeO₈ symmetric stretching vibration. The CO sample reveals a better symmetry than the substituted ones. In a defect-free crystalline semiconductor (bulk) material one expects perfect symmetry. Factors like defects, strain, phonon confinement, size distribution, etc. can be responsible for asymmetric changes in the phonon mode profile [65]. Size plays an important role in Raman peak shifts [62]. Most probably reduction of size is responsible for red shift. However, literature also mentions that phonon confinement and inhomogeneous strain affect the Raman phonon modes in materials [62]. Hence, the reduced symmetry in the substituted samples compared to CO strongly

indicates reduced crystallinity and increased inhomogeneous strain in these materials.



Figure 6.10 (a) Systematic broadening and nominal red shift of F_{2g} phonon mode at ~461 cm⁻¹ in modified Mn substituted CeO₂; a broad feature in the range 520-660 cm⁻¹ associated with oxygen defects becomes stronger with substitution (b) shows Variation peak position and FWHM, with strain.

A broad feature in the range $520 \sim 660 \text{ cm}^{-1}$ is also observed in all samples. This feature also arises from a CeO₈ stretching vibration but is highly sensitive to oxygen related disorder²². Oxygen related defects have been held responsible for this feature [72,73]. In the CO sample this feature is present but is extremely weak and negligibly small as compared to the substituted samples. This feature broadens and becomes more asymmetric (lower half widths are larger than higher half width) with substitution [Figure 6.10 (a, b)]. This feature is expected to increase with substitution as both Co and Ni are valance state lesser than 4+. Hence, the presence of these ions is substituted sites in the lattice with invoke loss of lattice oxygen to maintain charge stability and neutrality of the lattice. Hence, substitution will cause generation of oxygen vacancies, (Vo).

6.3 Optical Properties:

The UV-visible absorption spectra of CO, CMO, CCMO and CMNO samples are shown in [Figure 6.11 (a, b)]. CeO₂ is reported to have both direct and indirect bandgap [90]. The illumination of UV light excites electrons from the valence band to the conduction band with and without the help of phonons. However, a very low energy ($<10^{-2}$ eV) phonon is involved in the indirect transition [123]. Hence, in CeO₂, the indirect transition is less prominent than the direct transition. Both direct and indirect band-gap estimation has been done by extrapolation of $(\alpha hv)^2$ vs hv and $(\alpha hv)^{1/2}$ vs hv plots, where, α is the absorption coefficient. Absorption edge arises from direct transitions from top of the valence band (O 2p states) to empty 4f-shells of Ce^{4+} [91]. Oxygen vacancies play an important role in occupying states closer to the band edge and thereby modifying the bandgap. A trend consistent with the Vo calculations from XANES studies matches with that of bandgap. As Vo increases bandgap decreases and is lowest for CMNO. As a result, the direct bandgap of CO reduces from 3.35 eV to 3.12, 3.16 and 2.98 eV for CMO, CCMO and CMNO respectively. On the other hand, the indirect bandgap of CO reduces considerably from 3.0eV to 2.16 eV, 2.23 and 1.92 eV CMO, CCMO and CMNO respectively.



Figure 6.11 Tauc-plot of Mn substituted CeO_2 samples for (a) Indirect transition (b) indirect bandgap variation with x (c) Direct transition (d) Direct bandgap variation with x.



Figure 6.12 Urbach energy increases with Mn substitution (-inset shows Urbach tail fitting) owing to formation of new bands between VB and CB.



Figure 6.13 Tauc-plot of Co/Mn and Mn/Ni substituted CeO₂ samples for (a) CCMO samples; bandgap reduces with Co and Mn substitution (b) CNMO samples; bandgap reduces with Co and Mn substitution and highest reduction occur with Mn-Ni co-substituted samples (c) Urbach energy increases with Co/Mn and Mn/Ni co-substitution and highest for Mn-Ni co-substituted samples.

Sharpness of the absorption edge in UV-vis spectra reduces while edge tailing (Urbach tail) increases with substitution. Structural deformations and disorder are responsible for such tail formation. Urbach energy, E_U , was calculated using: $\alpha = \alpha_{0^*} exp(E/E_U)$, where α is absorption coefficient [56]. Calculation of α was done by taking natural logarithm of exponential decay (only tail part) near the absorption edge. Inverse of the slope of a straight-line fit represents E_U . Urbach energy increases with Mn/Co/Ni substitution from 0.153 eV (CO) to 1.06 eV (CCNO) [Figure 6.13 (c)]. Hence, defects and disorder increase with Mn/Co/Ni substitution and is highest for CMNO. These defect states not only cause reduction of bandgap but also results in phonon assisted electronic transitions. Lattice distortion and reduction of Ce⁴⁺ to Ce³⁺ because of substitution by smaller sized and lesser charged Mn/Co/Ni in place of Ce highly modifies the band structure of substituted CeO₂. Such variations may lead to creation of local states and alteration of band structure. Such changesincrease the possibility of both direct and indirect (phonon assisted) electronic transitions.

6.3 Magnetic Properties:

The hysteresis loops of the CCMO and CMNO series measured at10 K indicates that the magnetization is not saturated even at 50 kOe. However, the low field regions of the loops show coercivity (Hc) and remanence magnetization (Mr) points out the presence of weak ferromagnetic interactions in the compounds.CeO₂ show very weak saturation magnetization, Ms ~ 0.0355 emu/g and remnant magnetization, Mr ~ 0.0009 emu/g at 10K and 5 T field which (Ms, Mr) increases to (2.913; 0.0026 emu/g), (1.6031; 0.0112 emu/g) and (1.9078; 0.0015 emu/g) for CMO, CCMO and CMNO samples respectively [Figure 6.14-6.17].



Figure 6.14 Hysteresis loops (M–H) of CCMO measured at (a) 300 K and (b)10 K between –50 kOe and 50 kOe.



Figure 6.15 Variation in M_s, M_R and H_c with composition at 300 K and 10 K in CCMO samples.



Figure 6.16 Hysteresis loops (M–H) of CCMO measured at (a) 300 K and (b)10 K between –50 kOe and 50 kOe.

Presence of oxygen vacancies in all the samples is confirmed from the EXAFS and XANES studies. The Mn, Co and Ni ions are mostly in the 2p state and certain amount of Ce ions is in the 3p state which may induce weak RT-FM. The complex interactions between oxygen vacancies related defects and Ce or Mn/Co/Ni are under investigation.



Figure 6.17 Figure 6.13 Variation in M_S , M_R and H_C with composition at 300 K and 10 K in CMNO samples.
6.4 Micro-hardness study:

Hardness of the samples decreases with Ni substitution [Figure 6.18 (c)] in good agreement with the increasing. We applied all existing models in literature to explain the hardness as discussed in previous chapter.



Figure 6.18 shows (a) Microhardness variation with load (b) indentation size variation with load (c) Microhardness variation with substitution; All models applied, HK model is suitable for CMO samples.

We found that only Hays–Kendall (HK) model is in good agreement in explaining the elastic/plastic behavior of our samples. This model is applicable for materials in which elastic deformation appears below a certain limit of the applied load above which the plastic deformation starts suddenly. Only upon application of a critical load, the indenter can penetrate into the material, resulting in an actual effective load of F_{eff} = F-Fc falling on the sample expressed by Hays–Kendall relationship [F_{eff} = F – Fc = $A_{HK} d^2$; where, A_{HK} is a proportionality constant]. The hardness, H_{HK} = 1854.4 A_{HK} , decreases with increasing substitution. It is to be noted that hardness values from this model is nearly of the same values as the Vickers hardness and follows the same decreasing trend [Figure 6.18 (b)]. Hence material follow first elastic then plastic deformation.

6.5 Conclusions

Single phase, homogeneous, nanocrystalline, sol-gel synthesized Mn/Co/Ni substituted and co-substituted= CeO₂ have similar cubic fluorite structure as that of pure CeO₂. Structural studies from XRD data is confirmed by HRTEM, yielding same crystal structure and crystallite size. Strain seems to increase while crystallite size decreases with substitution. On the other hand, the bandgap reduces considerably due to Mn, Co and Ni co-substitution. The reduction in bandgap and increase in Urbach energy can be related to the increases in Vo%. As Ce⁴⁺ is substituted by mainly Mn³⁺/Mn⁴⁺/Co²⁺/Ni²⁺, Vo increases to maintain charge neutrality of the lattice. Each Vo is equivalent to two electrons which further leads to reduction of Ce^{4+} to Ce^{3+} . This is reflected in electronic structure and bandgap is reduced. Reduction in bandgap is due to increased disorder mainly due to formation of defect states between valance band and conduction band. Raman studies reveal increase of asymmetry and FWHM of the F_{2g} peak with substitution. This again implies increased lattice strain. Also, Vo related peaks increase with substitution. This is pointing out the increase in defect concentration with substitution. EXAFS studies reveal reduction of oxygen coordination which implies increase in V_o concentration with substitution. XANES analysis also supports a similar scenario as Ce³⁺ concentration increases with substitution. Samples

shows very weak ferromagnetic properties which is highest for CMO samples. Hence these materials show good properties for photocatalysis and biomedical applications.

Chapter 7

Conclusions and Future Research Scope

7.1 Conclusions

Structure, optical, photoluminescence and mechanical properties of modified sol-gel prepared cerium oxide ceramics have been investigated. Samples are in single phase. Cerium oxide was modified by single (Mn, Co and Ni) and co-substitution(Co-Ni, Co-Mn and Mn-Ni) of transition elements. A concise results-based summary and future scope is provided here.

7.1 Mn/Co/Ni modified CeO₂:

The influence of Mn/Co/Ni substitution on structural, optical, photoluminescence and mechanical properties were investigated. Samples are prepared by sol-gel combustion method and followed by solid-state sintering. Powder X-ray diffraction was carried out to examine the lattice dynamics with compositions at ambient temperature. There were no secondary phases observed in any of the samples. Rietveld refinement was performed for all the XRD data, to evaluate structural variation with substitutions. With Mn/Co/Ni substitution, a reduction in lattice parameter is observed for all the series. Lattice strain is calculated from Williamson-Hall method, increases for all the substitutions.

This increase may be due to substitution of larger size $Ce^{4+}(VIII)$ (1.11 Å) ions by smaller $Mn^{2+}/Mn^{3+}/Mn^{4+}(0.96-1.11\text{\AA})/Co^{2+}/Co^{3+}(0.9-1.04)$ Å)/Ni²⁺/Ni³⁺(0.85-0.96 Å) ions. Crystallite size decreases with substitution as estimated from Scherrer's method from 6.70 ± 0.03 nm to 4.40 ± 0.01 for Mn, 4.43 ± 0.02 for Co and 4.31 ± 0.02 for Ni series respectively. This decrease may be due to increased strain which restricts crystallite growth.

Particle size and lattice properties were further studied byHRTEM. It is observed crystallites agglomerate and form aggregates, toachieve more stable energy state in all the series. This phenomenon is common factor in nanoparticles, synthesized using wet chemicalsynthesis method. The presence of hydroxyl ions facilitates agglomeration which allows the nanoparticles to achieve more stable energy states. Well-defined lattice fringes in HRTEM micrographs indicate crystallinenature of the samples in all series. It also reveals termination planes of the nanocrystals. A lattice spacing of 0.31 nmis common in most nanoparticles which can be attributed toa (111) reflection plane. Mn/Co/Ni substituted CeO₂ nanoparticles appear to have thermodynamically stable termination faces of (111) and (200). HRTEM studies further confirm the crystallite size of the samples. Using ImageJ software, theaverage size of crystallites of pure CeO₂ is estimated to be ~7.4 (\pm 0.5) nm, which reduces with substitution to ~5.0 (\pm 0.4) for Mn series, ~4.7 (\pm 0.3) for Co series and ~4.5 (\pm 0.5) nm for Ni series respectively. These results agree with the XRD results. Also, the crystallite sizes are smaller or comparable to the Bohr excitation radius for CeO₂. Hence, quantum confinement effect can beexpected in these materials. SAED patterns of a collection of nanoparticles as wellas

Fourier transforms of HRTEM images reveal concentricbright rings corresponding to (111), (200), (220) and (311)planes representing for all the series.EDX studies of Mn/Co/Ni series samples confirm Mn/Co/Ni incorporation in ceria samples.

Mn, Co and Ni series samples show strong phonon modes at ~462.5 cm⁻¹ and broadfeatures in the energy range 520~660 cm⁻¹. The strong peak ~462.5 cm⁻¹ is a triply degenerate F_{2g} mode belonging to CeO₂ fluorite structure. This represents a CeO₈ symmetric stretchingvibration. This mode is very sensitive to the vibrations of oxygen around the Ce ion. The F_{2g} peak redshifts, broadens and becomes more asymmetric (lower half widths are larger than higher halfwidth) with substitution for all the three series. Asymmetry is a consequence of phonon confinement whilered shifting is a consequence of increasing homogeneous strain. The red shifted asymmetricallybroadened F_{2g} phonon mode with increasing incorporation, strongly hints at phononconfinement accompanied with an inhomogeneous strain present in samples. The increasing asymmetry and broadening nature of the F2g phonon modes matcheswell with the increasing strain and decreasing size. A broad peak at ~520-660 cm⁻¹ corresponds to oxygen related defects which increases with substitution as we discussed in XRD.

Majority of Ce ions were found to be in Ce⁴⁺ state (~84-80%) for all the pure and modified CeO₂samples. However, a considerable amount of Ce³⁺ states (~16-25%) is also observed.Concentration of Ce³⁺ increases

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from ~16% to ~26% forMn series, ~22% for Ni series and ~25% forCo series samples. Co and Ni are mostly observed in 2+/3+ valence state whereas, Mn has significant 4+ valence state also. Notably, in CeO₂, Ce is expected to be rimarily in Ce⁴⁺ state. However, the presence of Ce³⁺ along with the incorporated lesser valence ions leads to high Vo content in the samplesto maintain charge neutrality in the lattice. For the pure CeO₂, Vo% is recorded to be ~8.32%. Hence, as Mn/Co/Ni concentration increases, oxygenvacancy concentration correspondingly increases. EXAFS analysis shows, oxygen coordination decreases with substitution which hints increase in oxygen vacancies with substitution, is in unison with Raman, XANESexperiments. EXAFS studies also show that Ce-O bond length decreases with Co/Ni substitution, agrees with XRD results. The Mn/Co/Ni K-edge EXAFS data are likeCe L_{III}-edge data of CeO₂. This analogousbehavior indicates a similar environment of the Ni and Ce ions, thereby suggesting a propersubstitution of Ce by Mn/Co/Ni. However, the first shell i.e., Ni–O/Co–O/Mn–O bond lengths are smaller than the Ce-O shell. This may beinferred that the smaller size of Mn, Ni and Co ions results in smallerbond lengths, which in turn tries tolessen the bond length of Ce-O. Shorter Ce-O and Ce-Ce bond lengths for the Mn, Co and Ni substituted samples re observed in comparison to the pure CeO₂.

CeO₂ has been reported to show both direct and indirect bandgap. Absorption edge arises from direct transitionsfrom top of the valence band (i.e. O 2p states) to empty Ce⁴⁺ 4f-shells. Sharpness of the absorption edge in UV-vis spectra reduces with Mn, Co and Ni substitution. This is associated with an increase n amount of tailing (Urbach tail). Structural deformation and disorder are responsible for suchtail formation. Urbach energy increases with Mn/Co/Ni substitution from 0.153 eV for to0.709 eV for Mn series, 0.665 eV for Co series 0.575 eV for Ni series. This indicates increasing defects and disorder with Mn/Co/Ni substitution. Defect states not only reduces bandgap but also results in phonon assisted electronic transitions. Hence chances of an indirecttransition increases. Due to smaller crystal radius and lesser charge of Mn/Co/Ni compared to Ce^{4+} , substitution in CeO₂ leads to lattice distortion and reduction of Ce^{4+} to Ce^{3+} . This also leads to increased Vo concentration which highly modifies the band structure of CeO₂. These changeslead to formation of localized states and spatial distribution of band structure which gives rise tothe possibility of both type of electronic transitions viz, direct and indirect.

Photoluminescence (PL) spectra of the samples reveal broad spectra between 395-529 nm. The major bands are obtained at ~424 nm (2.92 eV, violet), ~457 nm (2.71 eV, blue),~485 nm (2.56 eV, green-blue) and ~528 nm (2.34 eV, green). Apart from the above majorcontributions, very feeble contributions of yellow (2.1-2.17eV; ~579nm), orange (2-2.1eV; ~590nm) and red (1.65-2eV; ~620nm) emissions also take place. However, these emissions arenegligible compared with the major bands. The major violet band may be ascribed to $F^{++} \rightarrow Ce^{3+}4f^{d}$ transitions. The blue-greenand blue emissions are mostly the resultant of $F^{+*} \rightarrow F^{+}$ transitions while the green lightcomes from $F^{0*} \rightarrow F^{0}$ transitions. PL intensity of the samples decreases withsubstitution for all Mn/Co/Ni substituted samples. Individual color contribution also decreases in a similar way. Thisshows that the recombination rate of charge carriers decreases with substitutions, which enhances its efficacy for catalytic applications.

The hardness of the materials is related to the bond strength which is correlated with strain and defects of the lattice. Sintering temperature is optimized to avoid ambiguity of the effect of pores in the pellets which is 1100°C for Mn series and 1400°C for Co and Ni series. FESEM images shows a continuous topography with grains in tight contact witheach other without pores or gaps left on the surface. Vickers micro-hardness of the pellets decreases with increasing applied load which infer to indentation size effect (ISE) as n is lesser than 2.Hardness decreases with increasing substitution in theall the three series samples. The effective bond strength between modified combinations of Ce/Mn, Ce/Co or Ce/Ni ions, instead of only Ce ion with O ion, may be weaker due to the size and valence state of the effective ions. Microhardness is supposed to decrease due to such weaker bond strengths. With substitution, strain is observed to increase. It isalso observed that oxygen vacancies increased with substitution. Hence with increased substitution lattice is supposed to be weaker, resulting in

lesser hardness of the material. Several models, including Proportional Specimen Resistance (PSR) model, Elastic/PlasticDeformation (EPD) model and Hays-Kendall (H–K) model are used to study the hardness with ISE behavior. Hays-Kendall (H–K) model appears to most suited for predicting the behavior of present series samples.In this, after a preliminary critical load Fc, a plastic deformation is observed. The hardness H_{HK} =1854.4A1_{HK}, from the Hays-Kendall model decreases with substitution for all the three series and is in close agreement with the experimental Vickers hardness. Fc is positive and increases showing decrease of hardness in these materials certifying the presence of both elastic and plastic deformation.

7.2 Major Findings:

(i) Lattice parameters:

Lattice parameters are calculated by Rietveld refinement, using Fullprof software [Figure7.2].

(a) CCO: a, b, c reduces in CCO with increasing substitution [Figure 7.2(a)]due to lesser ionic radius of Co^{2+}/Co^{3+} compared to Ce^{4+} .

(b) CNO: a, b, c reduces in CNO with increasing substitution [Figure 7.2
(b)] due to lesser ionic radius of Ni²⁺/Ni³⁺compared to Ce⁴⁺.

(c) CMO: a, b, c reduces in CMO with increasing substitution but lesser in comparison to CCO and CNO [Figure 7.2 (c)] due to lesser ionic radius of $Mn^{2+}/Mn^{3+}/Mn^{4+}$ compared to Ce⁴⁺.

d) CCNO: a, b, c nominally decreases in CCNO with substitution[Figure 7.2(d)] due to incorporation of two lesser ionic radius of Co^{2+}/Co^{3+} and Ni^{2+}/Ni^{3+} compared to Ce^{4+} . This decrease in lattice parameters is lesser in comparison to singly substituted ones i.e. CCO and CNO. This may be due to presence of higher Vo concentration which causes reduction of Ce^{4+} to larger size Ce^{3+} . This change in Ce valence, counteract reduction of lattice parameter by smaller size Co and Ni. This reflect in very less change in lattice parameter.

e) CCMO: LikeCCNO,a, b, c nominally decreases in CCMO with substitution[Figure 7.2(e)] due to incorporation of to lesser ionic radius of Co^{2+}/Co^{3+} and $Mn^{2+}/Mn^{3+}/Mn^{4+}$ compared to Ce^{4+} . This decrease in lattice parameters is lesser in comparison to singly substituted ones i.e. CCO and CMO. This is due to presence of higher Vo concentration in comparison to singly substituted (CCO/CMO) which causes reduction of Ce^{4+} to larger sizeCe^{3+.} This counteract reduction of lattice parameter by smaller size Co and Mn and reflect in lattice parameter.

(f) CMNO: Like CCNO and CCMO, a, b, c nominally decreases in CMNO with substitution[Figure 7.2(f)] due to incorporation of to lesser ionic radius of $Mn^{2+}/Mn^{3+}/Mn^{4+}$ and Ni^{2+}/Ni^{3+} compared to Ce⁴⁺. Since Vo concentration leads to higher concentration of larger Ce³⁺ which compensate decrease in lattice parameter by smaller Mn and Ni.



Figure 7.2: Variation in lattice parameter in (a) CNO (b) CCO (c) CMO (d) CCNO (e) CCMO and (f) CMNO samples. Lattice parameters decrease maximum with Mn substitution among singly substituted CeO₂, whereas, decreases least with Co-Ni co-substitution.

(ii) Lattice Strain:

Lattice strain is calculated using Williamson–Hall method for all the series.

(a) CCO: For all compositions strain is higher compared to pure CeO_2 , due to reduction in lattice parameter with smaller size Co substitution [Figure 7.3(a)].

(b) CNO: Like CCO, lattice strain in ceria increases with Ni substitution owing to replacement of larger Ce ions with smaller Ni ions [Figure7.3(b)]. Strain in CNO series is higher than CCO owing to more decrease in lattice parameter of CNO than CCO which depends on the sizes of Ni and Co respectively. (c) CMO:In CMO also, strain increases with Mn substitution owing to replacement of larger Ce ions with smaller Mn ions [Figure7.3 (c)]. However, strain in CMO is lesser than CCO and CNO owing to comparable size of Mn ions with Ce ions.

(d) CCNO:With incorporation of both Co and Ni simultaneously in CeO₂, it shows less strain in the lattice than singly substituted (Co/Ni) ceria with same concentration [Figure7.3 (d)]. This drastic change in lattice strain occur due to the presence of higher Vo concentration in CCNO than CCO/CNO which leads to higher Ce³⁺ concentration. These Vo compensate lattice shrinkage due to substitution of larger Ce ions with smaller Co/Ni ions.



Figure 7.3: Variation in strainin (a) CNO (b) CCO (c) CMO (d) CCNO (e) CCMOand (f) CMNO samples. Least change in strain is observed for CCNO and CNMO samples owing highest increment in defect states concentration.

(e) CCMO: Like CCNO, strain in ceria lattice relatively decrease with cosubstitution of Co and Mn than substitution of Ce by Co/Mn separately [Figure7.3 (e)]. This is due to Vo concentration as discussed above. However, strain in CCMO is lesser than CCNO owing to relatively larger size of Mn ions than Co ions. Hence, lattice contracts lesser in CCMO than CCNO.

(f) CMNO:In CMNO also, strain is observed to be lesser than their singly substituted counterparts [Figure7.3 (f)]. The cause of this is similar as in CCNO and CCMO. Strain in CMNO is lesser than CCNO and higher than CCMO. Since Co has larger size than Ni, hence with Mn it helps in reducing strain.

(iii) Crystallite size and Particle size:

Crystallite size was calculated from XRD using Schererequation while particle size was calculated from FESEM and HRTEM using imageJ software. Particle and crystallite size follow the same trend as that of lattice strain.



Figure 7.4: *Variation in crystallite size in (a) CNO (b) CCO (c) CMO (d)* CCNO (e) CCMOand (f) CMNO samples.

It is discussed that strain is related to the surfacetermination and therefore controls the crystallite size and thereby theparticle size as well. This trend and strain correlated crystallite orparticle size dependence is observed in all the doped and co-substituted samples and is represented in [Figure 7.4].

7.2.3 Opto-electronic properties:

(i) Bandgap and Urbach energy:

Strain and lattice distortion lead to the formation of electronic states in the bandgap closeto the band edges. These states are generally known as band tails. Thesestates are instrumental in effectively reducing the bandgap. The Urbachenergy related to these states is calculated revealing directcorrelation with strain [Figure 7.5]. Bandgap decrease with

increasing Urbach energy and vice versa [Figure 7.6]. This correlation isapplicable for all samples discussed in this thesis.



Figure 7.5: Variation in Bandgapin (a) CNO (b) CCO (c) CMO (d) CCNO (e) CCMO and (f) CMNO samples. Among singly substituted samples Mn substituted samples shows highest reduction in bandgap however with co-substitution Co-Ni and Mn-Ni samples shows highest reduction in bandgap.

(ii) **Photoluminescence:** PL spectra of the samples reveal broad spectra between 395-529 nm. The major violet band ascribed to $F^{++} \rightarrow Ce^{3+}4f^{-1}$ transitions, blue greenand blue emissions to $F^{+*} \rightarrow F^{+}$ transitions while the green lightcomes from $F^{0*} \rightarrow F^{0}$ transitions. PL intensity of the samples decrease with substitution in all the series. However, in co-substituted samples like CCNO, CCMO and CMNO emission quenching is higher than singly substituted samples (CCO, CNO and CMO).



Figure 7.6: Variation in Urbach energy in (a) CNO (b) CCO (c) CMO (d) CCNO (e) CCMO and (f) CMNO samples. Urbach energy increases maximum with Mn substitution among singly substituted CeO₂, whereas, increases maximum with Mn-Ni co-substitution. This reflects in bandgap reduction as well owing to formation of band tails in VB and CB.

In singly substituted samples CMO has the highest quenching of emission owing to highest concentration of oxygen vacancies. Vo leads to nonradiative emission by forming different F-centers between bands, hence responsible for PL intensity suppression. Among co-substitution series CCMO has highest suppression owing to highest presence of Vo.

Individual color contribution also decreases in a similar way which shows that the recombination rate of charge carriers decreases with substitutions.A Vo is associated with two available electrons at the vacant site. Ceria when doped withTM ions may generate two scenarios of these electrons' localization. In the first type, theelectrons may be shared one each to a dopant cation and the other to the host (viaCe⁴⁺ to Ce³⁺). In the second type, both electrons join either a dopant or a host ion. Such defectsmay be the source of multiple states creation inside the bandgap, responsible for multiple non-radiativedecay processes. These non-radiative processes seem to increase with substitutionimplying the strong role of divalent/trivalent ions to the substituted lattice. The creation ofmore Vo due to these lesser charged ions, not only increases the Vo population but alsoinduces $Ce^{4+} \rightarrow Ce^{3+}$ conversion. On top of that structural distortion andstrain in the lattice leads to generation of multiphonon processes. This reflects in the electronic structure and thereby reduces bandgap. Thus, to maintain charge neutrality, lesser valence ionsubstitutions place of Ce⁴⁺ leads to changes in the electronic and structural properties leading to decrease of the PL emission.

7.2.4 XANES and EXAFS studies

Valence states of all constituent elements were examined using XANES analysis at the Ce-L_{III} and K-edges of Ni, Co and Mn. For all the edges, the samples have similar spectra. Ce-L_{III} edges consist of four peaks. The spectra were fitted by a combination of an arctangent and Gaussian functions for the Ce-L_{III} edge, with linear combination technique using the same Athena software. This reveals a major Ce⁴⁺ state (~84-75%) and a considerable Ce³⁺ contribution (~16–25%). Concentration of Ce³⁺ increases with substitution. Note that in CeO₂, Ce is expected to be primarily in Ce⁴⁺ state. Hence, presence of Ce³⁺ hints at O-vacancies in the

lattice. From the position of the XANES spectra it may be inferred that Co/Ni are predominantly in 2+ oxidation state, while Mn is in 4+ and 3+oxidation state.

The local structure of the absorbing atom is obtained from quantitative analysis of Ce-L_{III} edge and Ni/Co/Mn K edge EXAFS spectra. The EXAFS data at Ce-L_{III} edge looks similar for all samples. Also, the Ni, Co and Mn edges appear like the Ce edge of the samples. This indicates proper substitution of Ce by Ni, Co and Mn. The positions of the R-space peaks are slightly different which hints at different bond lengths. EXAFS data analysis program available within Demeter software package was used to analyze the EXAFS data. ATHENA was used to subtract the background of the absorption spectra. Oxygen coordination decreases with substitution, hinting at increase in oxygen vacancies with substitution. With substitution Ce-O bond length decreases. Reduction in Ce–O bond length is expected, owing to higher ionic radii of Ce⁴⁺ than the Ni²⁺, Co²⁺ and Mn³⁺, One also observes a shorter Ce–O and Ce–Ce bond lengths for the Ni/Co/Mn doped samples in comparison to the pure CeO₂. The shorter bond lengths lead to disorder and strain in lattice. Disorder factors are observed to increase with substitution, but for CCNO sample it becomes comparable to pure CeO₂. A similar fitting process was adopted for Ni and Co data. It is observed that Ni-O and Co-O bond lengths are smaller than the Ce-O bond lengths. This agrees with the XANES results.

Both Co–O and Ni–O bond lengths are lesser than Ce–O which is due to smaller size of Co and Ni compared to Ce.

7.2.5. Mechanical behavior of modified CeO₂:

Vickers indentation method is used for assessing mechanical behavior of modified CeO₂. We applied all existing models in literature to explain the hardness. We found that onlyHays-Kendall (HK) model is in good agreement in explaining theelastic/plastic behavior of our samples. This model is applicable for the materialsin which elastic deformation appears below a certain limit of theapplied load, above which the plastic deformation starts suddenly. Onlyupon application of a critical load, Fc the indenter can penetratethematerial, resulting in an actual effective load of $F_{eff}=F-Fc$ falling on the sample expressed by Hays-Kendall relationship $[F_{eff} = F - F_C = A_{HK}d^2]$. The hardness decreases with increasing substitution. It is to be noted thathardness values from this model is nearly of the same values as the Vickers hardness and follows the same decreasing trend. The F_C parameter also decreases with increasing substitution indicating that the elastic component also decreases, which is a direct reflection f irregularity in the lattice. Note that the values of Fc are positivewhich once more confirms an ISE (Indentation Size Effect) behavior which means hardness decreases with load. It may be pointed out that this positive Fc is a signature of the presence of both elastic (reversible) and plastic (irreversible) deformations in the sample and negative Fc plastic (irreversible) deformations.

7.3 Future Scope:

Based on above findings, aliovalent substituted ceria-based material can be explored for various applications like photocatalysis, biomedical, SOFC etc. Theoretical study using density functional theory or other techniques will be useful to understand abrupt change in bandgap owing to co-substitution. Study of the effect of co-substitution on electrical properties and its correlation with structure. Investigation on its sensing behavior towards gases and light.

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