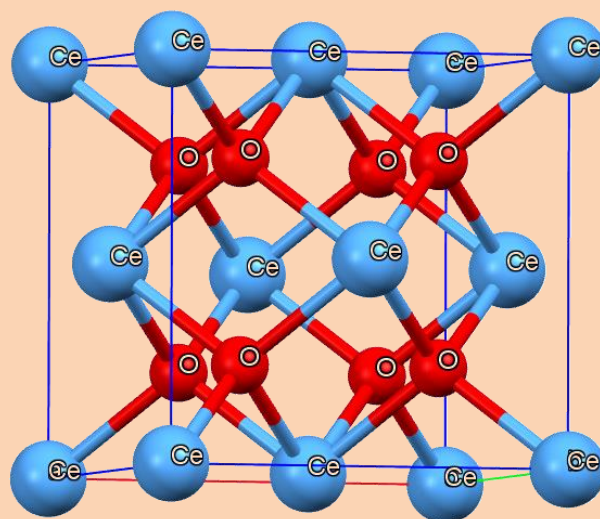


CeO₂, Ce_{1-x}A_xO₂ and CeAO₃ (Co, Ni, Mn, Fe) related structure

Effect of aliovalent substitution on structural, optoelectronic, electrical, magnetic and mechanical properties of CeO₂, Ce_{1-x}A_xO₂ and CeAO₃ (Co, Ni, Mn, Fe) related structure

Part I

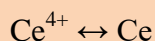
Cerium dioxide is a significant rare earth oxide which has been explored for their structural and chemical properties, reduction behaviour and non-stoichiometry, oxygen storage capacity and metal-ceria interactions. CeO₂ is a promising candidate for its application in environmental catalysis, redox catalysis and wet catalytic oxidation of organic pollutants. Ceria is pale yellow in colour probably due to O²⁻ Ce⁴⁺ charge transfer. Ceria is known to crystallize in a fluorite (CaF₂) type of structure. It has a face-centred cubic unit cell (fcc) with space group Fm3m over the whole temperature range from room temperature to the melting point. In CeO₂ structure, each cerium cation is coordinated to eight equivalent oxygen anions at the corner of a cube and each anion is tetrahedrally coordinated by four cations. The structure can be viewed as a ccp array of cerium ions with oxygen occupying all the tetrahedral holes where as the octahedral sites remain vacant.



Defects in a crystal structure are the deviations from the perfect periodic lattice. Defects in ceria can be classified into intrinsic and extrinsic. Intrinsic defects may be present because of thermal disorder or can be created by reaction between the solid and the surrounding atmosphere. (redox processes) The two most common types of crystalline intrinsic defects in ionic materials are Frenkel and Schottky defects.

CeO₂, readily exhibit Frenkel disorder in which an atom is displaced from its regular site to an interstitial site, thus forming a defect pair. Extrinsic defects are formed by impurities or by the introduction of aliovalent dopants.

Cerium oxide has been widely used as an oxygen storage component for three-way catalyst formulation. Oxygen storage capacity (OSC) is defined as the capability to store and release oxygen. A very simplified picture of the redox behavior of CeO₂:



The most important application of ceria lays in this unique property namely its ability to shift easily between reduced and oxidized states. Anyway, the fluorite structure of ceria can withstand high levels of oxygen nonstoichiometry without changing its structural type. CeO₂ containing materials have been receiving a great deal of attention in recent years due to their extensive use for Oxygen Storage Capacity (OSC) in three-way automotive catalysts and have more recently found application for hydrocarbon oxidation in diesel emissions. The technological applicability of CeO₂-containing materials is expanding very rapidly.

Ceria nanoparticles are extremely interesting materials with a wide range of applications. These materials may be applicable as diluted magnetic oxides (DMO) (for nanoelectrical devices), as fluorescence material, in three-way catalysis (TWC), in fuel cells as electrolyte, polishing agent in the microelectronic industry and anti-cancer activities. Ce is an abundant (66.5 ppm) material although being a rare earth element. In fact it is more abundant than Cu (60 ppm). Because of its amplexness, and uncommon properties such as retention of oxygen, transport of oxygen ions, good mechanical properties, stableness in a wide range of temperature ~30 to 2700°C, high reactivity in catalysis, makes ceria highly applicable as a functional material. Semiconductor oxides (TiO₂, ZnO, SnO₂) doped with Fe, Ni, Co, Mn, have generated enormous interest in introducing new functionalities in the past few decades. This has created a growing interest to investigate other stable oxides like CeO₂. Reports of modified properties in doped CeO₂ with increased functionalities are available.

Today search for new sources of energy is critically important. Solid Oxide Fuel Cells (SOFC) is a solution. Stabilized zirconia is a standard material used in SOFC. But such SOFC operate at high temperatures ~1000°C. This increases cost and decreases life span of SOFC. Recently, ceria is being used to reduce the operating temperature of SOFC. Oxygen vacancies (V_O) play an important role in SOFC.

O-transport is facilitated through V_O . V_O can be increased by substituting Ce^{4+} by lower valent ions. Smaller particle size increases V_O as well as the surface area of the nanoparticles facilitating O-transport.

In spintronic semiconductors, both the spin and charge of ferromagnetically polarized carriers can be used to control device by coupling with an external magnetic field. CeO_2 is paramagnetic. Introduction of magnetic TM ions may introduce DMO properties. A structure correlated magnetic properties studies of TM modified CeO_2 is extremely interesting from physics and device aspects. Ni doping enhances ferromagnetic behavior of CeO_2 making the material suitable for next generation spintronic devices. Ni-Co co-doping suppresses the recombination rate of photo-generated charge carriers, which enhances photo-catalytic activity and structural stability. Extensive work on TM-doped $ZnO/TiO_2/SnO_2$ has been performed reporting room-temperature ferromagnetism (RTFM) without full understanding of the origin of ferromagnetism. This was followed by theoretical prediction of RTFM due to charge carriers and local spins having some exchange coupling. Contradictory AFM as well as FM interactions were reported. However, the real mechanism behind FM still remains obscured. A clear role of electronic structure related to FM is not explored so far. Co-doping with two metal ions enhances FM at low temperatures in most metal oxides. Hence, CeO_2 too deserves a similar detailed investigation. Ni doping also enhances anticancer activity. Hence, magnetic properties play a key role in spintronic devices, targeted cancer therapy and memory devices.

Several preparation methods have been used for the synthesis of ceria-based materials. This includes sol-gel, precipitation and coprecipitation, hydrothermal method, spray pyrolysis, chemical vapour deposition etc.²⁴ The properties of the final material are found to be dependent on the preparation method adopted. The sol-gel method is a homogeneous process which results in a continuous transformation of a solution into a hydrated solid precursor (hydrogel). A sol is a stable colloidal dispersion of small particles suspended in a liquid. These particles interact to form a continuous network of connected particles called a gel. In the sol preparation, the precursors undergo two chemical reactions: hydrolysis and condensation or polymerization, typically with acid or base as catalysts, to form small solid particles or clusters in a liquid (either organic or aqueous solvent). The advantages of the sol-gel process in general are high purity, homogeneity, and low temperature.

Substitution can manipulate the structural, magnetic and optoelectronic properties of nanostructures. Hence, co-doped CeO_2 nanomaterials should significantly affect the properties. I have already synthesized impurity-less, single phase, TM (Mn, Co, Ni) substituted cubic fluorite CeO_2 crystallite nanoparticles synthesized by Pechini sol-gel process. The process ensures structural and compositional homogeneity and is effective, economic and simple. The valence states have been confirmed as Ce^{4+} , Co^{2+}/Co^{3+} , $Mn^{2+}/Mn^{3+}/Mn^{4+}$ and Ni^{2+}/Ni^{3+} with proper substitution of Ce in CeO_2 structure from XPS,

XANES AND EXAFS analysis. Reitveld analysis of XRD data reveals decrease in lattice parameters, bondlengths, etc. which bears the scope of changes in the electronic properties of materials. Strain enhancement and crystallite size reduction is also observed. Enhancement of V_O was observed from XPS, EXAFS and Raman analysis. The weakening and red shifting of F_{2g} breathing phonon mode at 462 cm^{-1} reveals symmetrical breathing mode of Ce-O vibrational unit. This confirmed that structural defects such as oxygen vacancies cause reduction in the number of Ce-O vibrational unit.

Part II

For spintronic applications half-metallic ferromagnets (HMF) is one of the best candidate, which is due to uncommon electronic structure. Due to one spin direction of electron they act like metals and owing to other spin direction of electron they act like semiconductors. In recent times, HMF has been observed in various simple oxides, complex, heusler alloys and in pervovskite materials.

Cubic perovskite structured CeMnO_3 is a probable HMF candidate having magnetic moments owing to Mn-3d (metallic) and Ce-4f (semiconducting) electrons. GGA approximation confirms the metallic behavior while GGA+U approximation shows metallic majority-spin but semiconducting minority-spin bands. Hence, CeMnO_3 is a potential option for future spintronic applications. Moderate substitutions in these materials may further enhance the properties due to electronic changes related to structural and valence state changes.

