1.1. General Introduction

Solid state materials have pivotal role in the progress of human kind since the ancient time. Usage of solid state materials starts from the Stone Age. In that period man used sharp stone as weapons. But in the next era, metals are the most profounded material. Properties of naturally available materials were known by trial and error method. Solid state chemistry deals with synthesis, structure characterization and applications of materials. The back bone of new technological development is the solid state chemistry. Solid state materials include metals, semiconductors, high Tc super conductors, polymers, magnetic materials, hydrogen storage materials, etc.

Evolution of nanomaterial became one of the revolutionary aspects in the modern science and technology. Because of the extremely complicated nature and exhibiting wide variety in their composition and structural characteristics, knowledge of solid state reactions have always been a most intriguing task. Studies regarding the factors which influencing the solid state reactions are of both fundamental and practical importance. Hence, the control of the reaction rate is an important objective. Certain solid state reactions need higher reactivity (in case of solid propellants and catalysts) whereas other required lower reaction rate as in the case of oxidation and corrosion of metals. Therefore it is essential to have knowledge of the basic mechanism of reaction of solids, so as to control the reaction rate in specified situation.
Solid state studies have three aspects; *the phenomenological, the thermodynamic* and *the kinetic*. The phenomenological study is associated with qualitative and semi qualitative observation of the phenomena occurring during the reaction. The thermodynamic aspects include initial, final and equilibrium states of the system and to the stimulating force behind the transformation. The rates of transformation of the reactant to product are reflected in the kinetic aspects. This can be done at controlled set of conditions while the mechanism describes the complete set of reaction stages leading to the products.

In solution state, kinetic aspects of the reaction are expressed in terms of concentration of the reactant and product. Reaction rate in solid state are diffusion controlled. Rules regulating the kinetics of solid state reactions are different from those of reaction between liquids. Factors such as morphology, geometry of the reaction interface, diffusion of the reaction species, possibleness of the nucleation and anisotropy of the crystallites affect the rate of the reaction. Solid state reaction most often proceeds through the following four elementary steps:

1. Sorption phenomena (adsorption and desorption)

2. Reaction on the atomic scale (homogeneous or interphase reactions)

3. Nucleation of a new phase (in the bulk or at the surface of the reacting solid)
4. Transport phenomena (diffusion and migration)

Solid state reactions can be classified as follows:

(a) Solid-solid reaction
(b) Solid-liquid reaction
(c) Solid-gas reaction
(d) Reactions of single solid (e.g., solid state decomposition)

Among these, we are concerned only with solid state decomposition reaction.

1.1.1. Solid state reaction kinetics

Chemical kinetics provides mathematical models for explaining and forecasting the transformation rate of a chemical system. The fundamental concept of chemical kinetics is based on the law of mass action established by Cato M. Guldberg (1836-1902) and Peter Waage (1833-1900) in the latter half of nineteenth century, where equilibrium constant were derived in terms of kinetic data and rate equations. Solid state kinetics or heterogeneous kinetics is the challenging areas of research since the past years. Many methods are available for studying solid state kinetics. The first work in the solid state kinetics was done by Kujirai and Akahira in 1925\(^{3}\) on the effect of temperature on the degradation of fibrous industrial materials. There have been established a number of methods for studying the solid state kinetics using data obtained from thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) in
addition to variety of other methods. Solid state kinetics can be studied via either isothermal or non-isothermal experimental condition. Among these, non-isothermal method is more preferred over isothermal because all interesting information can be obtained from a single experimental run\(^4\textsuperscript{-6}\). The mathematical method chosen for predicting kinetics may be model fitting, single heating rate or isoconversional methods. Among these methods, model fitting method is most popular\(^7\). Isoconversional methods are model free methods, which allow the prediction of kinetic parameters without evaluating the reaction model and pre-exponential factor. Besides, these methods allow the activation energy to be determined as a function of the extent of conversion\(^7\). In this method, the kinetic analysis is carried out over a set of kinetic runs at a fixed value of conversion function. The reaction rate is predicted as a function of temperature only.

1.1.1.1. Model fitting method

Using model fitting method, mechanism of the solid state reaction can be predicted. For this purpose usually Coats Redfern method\(^8\) is used.

\[
\int_0^\alpha \frac{d(\alpha)}{f(\alpha)} = g(\alpha) = \int_0^\beta \frac{A e^{-Ea/RT}}{\beta} \, dT
\]

where \(g(\alpha)\) represents the reaction model, which describe specific solid state reaction mechanism. The plots of \(\ln [g (\alpha)/T^2]\) vs \(1/T\) were drawn for each model by the linear regression method. The model giving the best fit i.e., maximum correlation coefficient (approximately to unity) is taken as the best model describing the mechanism of the reaction.
From the plot, $E_a$ and $A$ can be calculated from slope and intercept respectively.

The mechanism of solid state reaction are generally occurs with reorganization of chemical bonds and molecular changes which causes for the transformation of reactant to products. The rate of the formation of solid state reaction products at the reaction interface is largely dependent on the effective surface area and surface concentration of reactants and intermediates.

1.1.1.2. Isoconversional methods

These methods can be used to calculate kinetic parameters such as $E_a$ and $A$. This method doesn’t need the knowledge of particular reaction model describing the solid state reaction. In the model free method, rate of reaction at a constant conversion is supposed to be a function of temperature only. The commonly used isoconversional methods are KAS\(^9\), Kissinger\(^{10}\), FWO\(^{11,12}\), Friedman\(^{13,14}\) and iterative isoconversional method\(^{15,16}\).

1.1.1.2.1. Kissinger-Akahira-Sunose (KAS)

The equation corresponding to KAS method is:

$$\ln \left[ \frac{\beta}{T^2} \right] = \ln \left[ \frac{AR}{E_g(\alpha)} \right] - \frac{E}{RT}$$

(2)

Apparent activation energy $E_a$ can be calculated from the slope of the linear representation of $\ln \beta/T^2$ vs. $1/T$ with a given value of $\alpha$. 
The value of pre-exponential factor $A$ can be obtained from the intercept if the form of integral reaction model $g(\alpha)$ is known.

**1.1.1.2.2. Flynn-Wall-Ozawa (FWO)**

The equation based on FWO method is:

$$\ln \beta = \ln \left[ \frac{AE}{Rg(\alpha)} \right] - 5.331 - 1.052\frac{E}{RT}$$ (3)

Using linear representation of $\ln \beta$ vs. $1/T$, $Ea$ and $A$ can be obtained from the slope and intercept respectively.

**1.1.1.2.3. Kissinger method**

The Kissinger method, which was utilized to determine the apparent activation energy for the overall reaction from the DSC curves or DTG curves recorded at different $\beta$.

$$\ln \left( \frac{\beta}{T_p^2} \right) = \ln \left[ -\frac{f(\alpha_p)AR}{d\alpha/Ea} \right] - \frac{Ea}{RT_p}$$ (4)

Where, $T_p$ is the peak maximum temperature characteristics for the overall reaction. The Kissinger plots $ln (\beta/T_p^2)$ versus $T_p^{-1}$. From the values of slope and intercept, $Ea$ and $A$ respectively can be determined.
1.1.1.2.4. Friedman method

For the estimation of $E_a$ and $A$, Friedman plot was used.

$$
\ln \left( \frac{d\alpha}{dt} \right) = \ln \left[ \frac{A}{f(\alpha)} \right] - \frac{E_a}{RT}
$$

In this method, $\ln(d\alpha/dt)$ is plotted against $1/T$. From the values of slope and intercept, $E_a$ and $A$ can be calculated.

1.1.1.2.5. Iterative isoconversional method

To calculate the approximate value of activation energy $E_a$ approaching to the exact value can be determined by the iterative procedure\textsuperscript{15-17}. It is based on the following equation:

$$
\ln \frac{\beta}{h(x)T^2} = \ln \frac{AR}{g(\alpha)E_a} - \frac{E_a}{RT}
$$

(6)

where $h(x)$ can be expressed by the fourth Senum and Yang approximation formulae\textsuperscript{18}:

$$
\frac{4}{x^4 + 20x^3 + 120x^2 + 240x + 120} \frac{x^4 + 88x^3 + 96x}{x^4 + 18x^3 + 88x^2 + 96x}
$$

(7)

where $x = \frac{E_a}{RT}$

Zhipeng et al\textsuperscript{19} performed the following procedure for the calculation of $E_a$ by the iterative method: (i) assume $h(x) = 1$ to calculate the initial value of the activation energy $E_{a1}$. The conventional isoconversional method stops the calculation of $E_a$ at this
step. (ii) Using the value of $Ea_1$, a new value of $Ea_2$ can be calculated from the plot of $\ln \left[ \frac{\beta}{h(x)} \right] T^2$ vs. $1/T$ (iii) Replace $Ea_1$ with $Ea_2$ and repeat step (ii). When $Ea_i - Ea_{(i-1)} < 0.01 \text{ KJ mol}^{-1}$, the value of $Ea_i$ is considered to be the exact value of activation energy. The estimation of activation energy doesn’t require the knowledge of reaction model, $g(\alpha)$. Therefore this method is model independent.

1.1.2. Solid state kinetics of multistage reactions

The main cause of multistage reactions is physico-geometrical constraints which may occur due to the changes in reaction conditions as the reaction advances. Koga et al. stated that complex reaction proceeds in a combination of multistep behavior controlled by physico-geometrical features of solid state reactions and successive chemical reaction schemes. During the early stage of reaction, a smooth surface product layer is generated between the reactant and reaction interface. Upon thermal decomposition, this surface product layer come into action i.e., it will impede the diffusional removal of gaseous molecules. This causes to increase the internal pressure of the reactant leading to change in the reaction condition at the reaction interface. Presence of cracks and holes on the surface of the product played as diffusion channel for the removal of gaseous products. Due to the experimental inconvenience of separately tracking the component process, deconvolution of overall kinetic information into reaction component is the only possible method for interpreting the reaction scheme of successive processes. Hence kinetic analysis of the decomposition process was performed using the kinetic deconvolution method.
In this method, a formal kinetic analysis was performed by assuming a single step reaction for the overall reaction using the fundamental kinetic equation\(^\text{25}\).

\[
\frac{d\alpha}{dt} = Ae^{-\frac{E_a}{RT}} f(\alpha)
\]  

(8)

where \(t\) is time, \(T\) the temperature, \(R\) the ideal gas constant, \(A\) the apparent Arrhenius pre-exponential factor, \(Ea\) the apparent activation energy and \(f(\alpha)\) the apparent kinetic model function used to describe the physico-geometrical reaction mechanism as a function of the fractional reaction, \(\alpha\). Based on Eq. (14), plots of \(\ln (d\alpha/dt) vs T^{-1}\) at different \(\alpha\) for the series of kinetic data recorded under linear non-isothermal condition. After the kinetic characterization of independent reaction processes, the overall process is studied by the cumulative equation.

\[
\frac{d\alpha}{dt} = \sum_{i=1}^{n} c_i A_i \exp\left(-\frac{E_{a,i}}{RT}\right) f_i(\alpha_i)
\]  

(9)

\[
\sum_{i=1}^{n} c_i = 1 \quad \sum_{i=1}^{n} c_i \alpha_i = \alpha
\]

With \(i=1\) and \(i=1\)

where \(n\) and \(c\) are the number of component step and contribution ratio of each reaction step to the overall process while \(A, Ea\) and \(f(\alpha)\) are Arrhenius parameter, activation energy and kinetic model function in different forms respectively.
The present investigations covers the area of solid state reaction kinetics of coordination compounds of oxalate ligand formed with rare earth metal Ce, up to the formation of nano/micro ceria under the atmosphere of air as well as N₂. Reaction kinetics was performed through the detailed kinetic strategy of deconvolution procedure.

1.1.3. Oxalate as the ligand

Oxalate, C₂O₄²⁻ is the dianion, is an excellent bidentate ligand for metal ions forming 5-membered MO₂C₂ ring. X-ray crystallographic studies revealed that the anion adopted either a planar conformation with D₂h molecular symmetry or approximate D₂d symmetry where O-C-C-O dihedrals approach 90°. Most often, D₂h symmetry of the free oxalate dianion is selected for the allocation of IR absorption spectra of a number of metal-oxalate compounds²⁶,²⁷. The conformation adopted by the oxalate anion depends on the size of metal to which it is confined as well as the extent to which hydrogen atom bonded in the crystal.

![oxalate anion](image)

**Fig. 1** The structure of free oxalate dianion
1.1.4. Cerium oxalate decahydrate

Rare earth metal Ce forms insoluble precipitate with oxalic acid or oxalate salt. It has the general formula Ce$_2$(C$_2$O$_4$)$_3$·10H$_2$O. The crystal structure of cerium oxalate decahydrate like all other lanthanide oxalates was proposed to have monoclinic structure with space group of P$2_{1}$/C. The proposed structure consists of 2D network with edge sharing of 1:5:3 co-ordinations polyhedral identical to the (020) set of planes. Each Ce atom is surrounded by three chelating oxalate ligands and three aqua ligands. The remaining seven lattice water molecules are spreaded over the intervening space. Fig. 2 represents schematic representation of cerium oxalate decahydrate.

![Schematic representation of cerium oxalate decahydrate](image)

**Fig. 2** Schematic representation of cerium oxalate decahydrate

Cerium or cerous oxalate is a white crystalline solid. It is an *antiemetic drug* used for vomiting and nausea. Usually antiemetic are effective for treating motion sickness and side effects of opioid analgesics, general anesthetics, antipsychotic medication and chemotherapy against cancer. Cerium oxalate can be utilized safely for
the severe cases of gastroenteritis and morning sickness of pregnant women. Fig. 3 shows the schematic representation of anhydrous cerium oxalate.

In material synthesis field, cerium oxalate is an important material because it can generate most promising biomaterial ceria via thermal decomposition method. In order to modify the properties of ceria for suitable applications, control over the parameters of oxalate precursor is essential.

![Schematic representation of cerium oxalate](image)

**Fig. 3** Schematic representation of cerium oxalate

Nano ceria can be prepared through a variety of methods such as hydrothermal, solvothermal, sol-gel, micro emulsion, thermal decomposition, etc. CeO₂ nano particle were prepared by rapid thermal decomposition by microwave heating of cerium oxalate and concluded that shape of resultant specimen depends on the precursor material shape. Using thermal decomposition method, particle size and shape can be effectively controlled. It can produce highly homogeneous nano particle. It requires shorter preparation time and fewer impurities in the final product. Hydrothermal and
solvothermal synthesis have found the limitations of temperature. Even though combustion synthesis is a good method with regard to time, it is difficult to control size and shape of the particles formed. Fig. 4 represents schematic illustrations of cubic structure of ceria.

![Schematic representation of CeO\textsubscript{2} crystal](image)

**Fig. 4** Schematic representation of CeO\textsubscript{2} crystal

Because of the reduction property of oxalate dianion, thermal decomposition process of metal oxalates is relatively complicated. It involves the cleavage of C-C bond, since the products are CO and CO\textsubscript{2} which consists of one carbon atom each. In most of the time, the C-C bond breaking is the rate determining step\textsuperscript{37}. During this process, the transfer of an electron from C\textsubscript{2}O\textsubscript{4}\textsuperscript{2-} to the cation occurs, which is assumed to be the first stage of decomposition, leading to the breakage of C-C bond\textsuperscript{38}. Both external and internal factors affect the solid state reaction. Internal factors include lattice spacing, symmetry, surface area and lattice defects (interstitial, vacancies, impurities, electrons, holes and dislocations). External factors such as applied voltage, pressure, temperature, pretreatment and irradiation affect the solid state
thermal decomposition reaction. Pretreatments of the sample by mechanical grinding, doping, irradiation, etc., can affect the rate as well as temperature of decomposition of oxalates. The solid state material can be bombarded with neutrons, protons or other particles, or pre-treatment with X-ray, UV ray or γ irradiation. Most often this can generate electronic or atomic imperfections, cause to the shortening of the induction period and to an increase in the rate constant of thermal decomposition\textsuperscript{1}. Literature survey reported that most of the studies regarding pre-irradiation of the sample with γ-ray enhanced the decomposition reaction by decreasing the activation energy and the effect was increased with amount of irradiation\textsuperscript{39,40–42}. In certain cases, treatment itself bring both dehydration and decomposition of the materials\textsuperscript{38,43,44}. Nature of the dopants greatly affects the decomposition temperature as well as rate\textsuperscript{45,46}. The lattice structure of the solid has predominant role in the kinetics of solid state reaction than that from liquid or gaseous state chemical reaction.

In solid state science, the information regarding the kinetic parameters such as activation energy and decomposition temperature are important factor for determining the reaction mechanism. The basic fact underlying the distinct features of a material is the reaction mechanism associated with the preparation. Moreover, there are many practical applications based on the reaction rate and temperature dependence. The industry needs the measurement of kinetic parameters, which will become more helpful for proper installation and programming condition, otherwise the manufacture of materials would become uneconomic. Therefore, using thermo analytical experiments
and accurate mathematical treatment of the data hopes the establishment of kinetic characteristics essential for the industrial thermal processes.

1.1.5. Applications of ceria and ceria based nano materials

Potential performances of rare earth oxide ceria have great work of art. It constitutes as the most promising biomaterial. Ceria constitutes as the one of the major components of TWCs for the removal of toxic automobile exhaust gases, humidity sensors, oxygen sensors and oxygen permeation membrane systems. On reducing the size of CeO$_2$ to nanometers, it possesses highly interesting properties because it allows the modification of surface area to volume ratio. Ceria performs as excellent UV absorbents and filters. It can be utilized as the good absorbent for the removal of fluoride ion and arsenic based compounds. It have substantial role in the dispersed fields such as catalysis, sensors, solid electrolytes and polishing powders. Due to the presence of O-H group on the surface of ceria, it becomes more reactive as an adsorbent for the removal of pollutants from water even at higher temperatures. Manifestation of oxygen vacancies have predominant role for performing ceria as an eventual material. Because of its oxygen storage capacity, it is utilized as solid electrolyte in solid oxide fuel cell. It can inactivate some of the most toxic ROS such as super oxide radical, hydrogen peroxide and nitrosyl radical. Researchers proposed that nano ceria act as radical scavenger of H$_2$O$_2$ in normal tissues but as a producer of H$_2$O$_2$ in cancer environment. These properties of ceria largely depend on its particle shape, size, surface chemistry, surface additives and ligand that
involves in redox reaction\textsuperscript{57–59}. Anti–invasive behavior of nanoceria was observed in human melanoma cells, whereas antitumor and anti-antigenic effects were studied \textit{in vivo} tumor model\textsuperscript{60}.

Doping of ceria with rare earth elements (Gd, Nd, La and Th) enhanced the oxygen ion conductivity and the mechanical properties\textsuperscript{61}. Other important characteristics of ceria include oxygen ion conductivity and oxygen storage capacity. The oxygen storage capacity of ceria increases on doping with metallic cations (\textit{e.g.}, Ca\textsuperscript{2+}, Ba\textsuperscript{2+}, Pb\textsuperscript{2+}, etc.)\textsuperscript{62}. The role of Cu\textsuperscript{2+} in the ceria lattice on the oxidation of CO over CuO/CeO\textsubscript{2} catalyst was discussed\textsuperscript{63}. Both redox couple Ce\textsuperscript{4+}/Ce\textsuperscript{3+} and Cu\textsuperscript{2+}/Cu\textsuperscript{1+} is involved in the reaction. Hence ceria can provide lattice oxygen for copper, thus increasing the oxidative properties of the binary system. Besides, it was reported that insertion of Co/Mn oxides in to the copper- ceria crystal lattice made substantially distinguishable behavior to the surfaces, which are coated on fiber glass system\textsuperscript{64}. Due to the existence of synergetic effect in the three components Co-Cu-Ce-O/FG system, it attributed its higher catalytic activity but the same is absent in the Mn-Cu-Ce-O/FG system. Moreover, the membrane – deposited active layer of CuO-CeO\textsubscript{2}/SG exposed higher catalytic activity for CO conversion\textsuperscript{65}.

Additionally it is worth to note that properties of ceria are monitored by structural and morphological parameters\textsuperscript{66–69}. Different morphologies of ceria are synthesized and studied, which involves nano rods, nano cube, octahedron or polyhedron, etc\textsuperscript{70}. It was investigated that CeO\textsubscript{2} nanorods selectively exhibits higher activity for CO oxidation and NO reduction\textsuperscript{71,72}, whereas nanocubes show superior
properties in soot combustion\textsuperscript{73}, hydrogen oxidation\textsuperscript{74} and preferential oxidation of CO\textsuperscript{75}. For water gas shift reaction processes, gold supported ceria nano rod performed as best catalyst than ceria, while Cu-based ceria polyhedral Nps\textsuperscript{76} contributed best structural support\textsuperscript{77,78}. But due to the existence of large proportion of reactive planes on the surface of ceria nanowire, made it as potential redox catalyst for CO oxidation. \textit{3D} flower like ceria has owned enhanced catalytic activity towards the oxidation of CO for the removal of As (V) and Cr (VI). Presence of large surface area and channels in the 3D flower ceria can provide better interaction between gas molecules and catalytic support\textsuperscript{79}.

The revolutionary upright of ‘nanotechnology’ brought progressive research challenges in the medical field designed for improving therapeutic strategies against various diseases threatening to our life. It improved the pharmacodynamics and pharmacokinetic properties of conventional chemotherapeutic agent and enhanced their efficacy with less toxicity\textsuperscript{80}. Among nano metal oxides, rare earth oxide ceria possess excellent antioxidant and anti-inflammatory properties. This happens because of its triggering nature of Ce\textsuperscript{3+} and Ce\textsuperscript{4+} oxidation state depending on the environment\textsuperscript{81,82}. The nature of oxygen storage capacity of it increases the antioxidant behavior. It performs as anticancerous drug for various cancer cell lines in different manner because it can reduce the oxidative stress induced by the generation of reactive oxygen species. Ceria can directly accept hydrogenated radicals from the blood stream and thus preventing the cell damage caused by the oxidative stress. Doping of the parent matrix with elements which can emits radiation by itself upon excitation in the
UV-visible region of the spectrum\textsuperscript{50}. Nano medicine with modified structure can kill tumor cell by increasing ROS level in tumor cells or by directing the nucleus or organ cells\textsuperscript{83}. Among p- block elements, Si and first transition series metal oxides such as Cu, Fe aroused the induced oxidative stress and cytotoxicity in airway epithelial cells. It was aroused that besides the surface and core oxide composition, size of nanoparticle has key role on imparting its effect on certain diseases\textsuperscript{84}. The present work includes synthesis of different series of Cu-Ce-O solid solutions from the oxalate precursor and correlation of cytotoxic effects of mixed oxides towards Dalton’s Lymphoma ascites cells. The findings of this analysis were discussed in detail in Chapter 6. PEGlycated ceria nanoparticle expressed enhanced radioprotection on human liver cell under γ-irradiation\textsuperscript{85}. Up to now, any investigations related with the influence of different shapes of ceria nanoparticle upon its anticancerous properties still not exist. The detailed discussion regarding this kind of cytotoxic behavior is involved in Chapter 7. Fig. 5 represents the schematic representation of normal cell and cancer cells.

![Fig. 5 Schematic illustration of normal and cancer cells](image)
1.1.6. Computational study

Computational aspects of electronic structure of ceria and ceria based materials were studied by *ab initio* quantum mechanical Density functional theory (DFT) package of Venna *ab initio* simulation Package (VASP 5.4.1). Band structure, density of states (DOS) and charge density distribution of ceria and copper doped ceria were compared.

1.1.6.1. Band structure and density of states

The band structure of a solid means the range of energies that an electron associated within the solid and range of energies that are not associated with an electron. A solid consists of large number of atoms. The atomic orbitals overlap with each other to form molecular orbitals with different energies. Since the solid consists of large number of atoms ($N \sim 10^{22}$), there are very large number of orbitals and hence they are much closely spaced in energy (of the order of $10^{-22}$eV). The closely space energy levels are considered as continuum, an energy band. In the formation of bands, most often valence electrons are treated. The width of the band depends on the extent of overlapping. Bands at higher energy are associated wider energies due to more overlap, but bands of core electrons are narrow due to the reduced level of overlap from the adjacent atomic orbital. Therefore, the band gaps generated by core electrons are large. In solids, the isolated atomic and molecular energy levels are broadening into bands of allowed energy state, which are separated by a forbidden energy gap. The qualitative description of an electronic conduction can be
predicted for materials with band gaps. For metals the forbidden energy band gap is negligible, while for semiconductors, the band gap is small (<3eV) and for insulators have wide band gap (>3eV). The determination of band gap of semiconductor materials is helpful to control its application in various fields. Another important thing associated with the determination of band gap is what is the Fermi energy of the semiconducting materials? Fermi energy is the energy of the highest occupied electronic state. Depending upon the nature of impurities present in the lattices, the value of Fermi energy state varies. For a typical solid, for each centimeter cube, about 10^{23} valence electrons contribute towards bonding. Hence the calculation of electronic structure of a solid must be a complex many-body problem, i.e., exact wave function and energy of each electron would depend on those of each other. Plane wave DFT can be utilized to characterize electronic structure calculation of extended system. The estimation of band structure method could help to understand total energy of all possible structure of the crystal, Fermi energy, density of states, optical properties, electron transport, bulk modulus, wave function of the electron and elastic properties. On limiting the movement of electron into fewer dimensions, the density of the states is modified near the band gap. In order to understand this electronic density near the band edge, we need to calculate DOS of the structure. The method of DFT can find solution to this problem.

DFT calculation for electronic structure of a semiconducting material is performed using Blochl tetrahedron method for interpolation in k-space. This theorem states that the wave functions of
the one electron Hamiltonian can be chosen to have the form of a plane wave times a function with the periodicity of the lattice.

Solid state materials are crystalline with periodic lattice. The ground state electronic structure of a solid is periodic in nature because of the same charge distribution in each unit cell. Therefore the potential $V(r)$ is also periodic with $V(r+R) = V(r)$, where $R$ is a vector joining the same point in two different unit cell\textsuperscript{86}. The complete calculation of band structure of a solid indeed takes this periodic lattice, making use of symmetry operations forming space groups. The execution of Schrödinger equation for the crystal lattice results the wave function, known as Bloch waves.

$$\psi_{nk}(\vec{r}) = e^{i\vec{k}.\vec{r}}u_{nk}(\vec{r})$$

(10)

Where $n$ is the band index which simply numbers the energy bands, $\vec{k}$ is the wave vector which is related to the direction of motion of the electron in the crystal. The wave vector takes any value in the Brillouin zone corresponding to the crystal lattice of solid. The particular high symmetry points or direction in the Brillouin zone is labeled as $\Gamma$, $\Lambda$, $\Delta$, $\Sigma$, etc. The energy of the electron changes with change in $\vec{k}$.

### 1.1.6.2. Theory of band structure in crystal

Periodic lattice of a crystal structure can be identified by Bravais lattice, which in turn can be determined by reciprocal lattice. The reciprocal lattice encloses the periodicity in a set of three reciprocal
lattice vectors \((\vec{b}_1, \vec{b}_2, \vec{b}_3)\). The periodic potential \(V(r)\) which exhibits same periodicity as the direct lattice can be represented as a Fourier series, whose only abiding components are those correlated with reciprocal lattice. So it can be represented as:

\[
V(\vec{r}) = \sum_k V_k e^{i\vec{k} \cdot \vec{r}}
\] (11)

where \(\vec{k} = m_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3\) with \(m_1, m_2\) and \(m_3\) being integers.

Using this theory one can be able to predict the band structure of a solid material by executing several ab initio methods. Some of the theories to predict the band structures of crystalline materials are discussed in brief. This includes Kronig- Penney model\(^{86}\), nearly free electron model\(^{86}\), tight-binding methods\(^{87}\), Korringa-Kohn-Rostoker (KKR) method\(^{86}\) and DFT methods.

1.1.6.2.1. Nearly free electron model

The major assumptions of this approximation are similar to the free electron model. In this approximation, metal crystal consists of positively charged metal ion, whose valence electrons are free to move around the metal ions in such a way that they constitute an electron gas. Further, the electron-electron repulsion is ignored and the potential field inside the crystal is aroused due to the positive ions are completely homogeneous in nature. This theory assumes that the potential in the periodic lattice in many ways exhibits small perturbation to that seen from the electron in free space. Based on this, the band structure is calculated by considering crystal potential even
though slight difference is exists from the constant free space potential. This model works particularly for metallic materials, where the distance between the adjacent atoms are small. Therefore the overlap of atomic orbitals and potentials on the adjacent atoms are relatively large.

1.1.6.2.2. Kronig-Penney model

This model assumes that an electron in a 1D-periodic potential. Periodic potential is considered as a periodic square waves. Using Schrödinger equation, the number of possible states that can be occupied by electrons can be determined. The major advantage of this theory is that the energy eigen values and eigen functions can be analyzed. Possible values of dispersion relations ($E$ vs $k$) and electronic density of states can be determined.

1.1.6.2.3. Korringa-Kohn-Rostoker (KKR) method

Here atoms are considered as the non-overlapping spheres (Muffin tin). Inside the sphere, the potential experienced by the electron is spherically symmetric about the given nucleus. The remaining interstitial regions are associated with screening potential which is approximated as constant. The potential continuum of atom centered spheres and interstitial regions are implemented using this theory.

1.1.6.2.4. Tight binding methods

This method is opposite to the nearly free electron model. In this approximation, electrons in the periodic lattice behave in same fashion
as the assembly of constituent atoms. This model yields solution to the
time independent single electron Schrödinger equation. Based on this
method, excellent description of the energy spectrum for bound states
up to rather small interval separations can be performed. This model
work best for seeking of low lying energy levels, and less accurate for
the higher level excited state properties.

1.1.6.2.5. Density Functional Theory

Nowadays, for the prediction of electronic structure of
crystalline materials, the most useful tool is DFT. It is not a model
but a theory considering ground state electronic density of states. It is a
microscopic first-principle theory of condensed matter physics for the
solution of electron-electron many body problems. DFT calculations
for the extended systems are performed based on the introduction of
exchange correlation term in the functional of electronic density. The
detailed description of the theory is given in section 1.1.6.4.

1.1.6.3. Density of states

Density of states describes the available occupied energy levels
per unit energy range in each zone. It can be determined by dividing
the volume of sphere having definite radius by the volume of a single
state. Therefore, the number of available quantum state having energy
levels between \( E \) and \( E+dE \) can be determined as follows:

\[
\frac{dN}{dE} = 8\Pi m \frac{(2mE)^{1/2}}{h^3} V
\]  

(12)

Where the quantity \( dN/dE \) is called the density of states
Metals are materials with non-zero DOS at the Fermi level. DOS can be separated into two regions: valence band and conduction band. Valence band is the collection of all occupied energy state, while the conduction band consists of unoccupied energy state. The band gap is the region where no DOS can be found. The slope of the DOS changes discontinuously in a number of places. These are known as van Hove singularities.  

From the last fifteen years, the revolutionary aspects of computational simulations are based on the use of first principle approach for exploring the properties of condensed matters. Using this approach many of the properties of the material can be explored by solving the Schrodinger equation for the electrons of the atom, molecule, and assemblies of atoms in solids or liquids. The combination of molecular dynamics and electronic structure methods called \textit{ab initio} molecular dynamics which can predict approximate solutions for the problems of many electron systems.

\textbf{1.1.6.4. Density Functional Theory}

DFT is the most powerful \textit{ab initio} tool for the theoretical characterization of material properties in the condensed system than other methods. The principle behind it is based on the calculation of energy of the system from the electron density rather than wave functions. This method is computationally less expensive giving most accurate results. The ancestors to DFT was Thomas-Fermi model, elaborated by Thomas and Fermi. Hohenberg-Kohn (HK) introduced a DFT having firm theoretical foothold. This theory rests on two
fundamental physical laws without using free parameters. The first theorem states that “the ground state energy from a Schrödinger equation is a unique functional of the electron density”. This theorem demonstrates the existence of one-to-one mapping between the ground state wave function and electron density. Second theorem established that ground state electron density which minimizes the energy of the overall functional is the true electron density with respect to the full solution of Schrödinger equation. But the main drawback of this theory was it ignores the exchange correlation functional. So the accuracy of the solution of Schrödinger equation can be improved by applying parameters suited with experiment.

The main goal of DFT is to substitute many-body electronic wave functions with the electronic density as a principal part. The idea underlying approximate solution for a problem is based on the selection of suitable potential to the level of appropriate approximation chosen for solving Schrödinger equation. Hence Hohenberg-Kohn-Sham DFT using pseudo potential i.e., Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA) has been the most powerful electronic structure calculation for the condensed matters.

In the many-electron systems, there exist strong interaction between electron and nuclei. Hence the all electron calculation involving core electrons make large computational burden. Most of the physical and chemical properties of solid materials are described in terms of distribution of valence electrons. The core electrons are participated negligibly in chemical bonding. Besides, their overlapping
with core electrons of neighboring atoms is imperceptible. Hence the environments of core electrons are not changes with changing the chemical environments of atoms. This implies the advantages of “frozen-core approximation”. Core electrons are treated as “frozen”. This led to the consideration of calculation of less electrons and Eigen states of Kohn-Sham equation. So the total energy scale is largely reduced when the core electrons are neglected from the calculation, which in turn helps to make the calculation of difference in energy between atomic wave functions much more stable. The substitution of ionic core potential by pseudo potential leads to the nod less valence wave functions. So the pseudo potential approach with Kohn-Sham DFT is more economic method. In fact, pseudo potential is substituted with electron density which from a chosen set of core electrons with smoothed density is used to match various properties of the true iron core. As a result, the properties of the core electrons are fixed in this approximation model in all consequent calculations. The major pseudo potential approximations are LDA and GGA. LDA is the simplest approximation which uses only local density to describe the approximate exchange-correlation functional. It is based upon exact exchange energy for a uniform electron gas. The results obtained using LDA with DFT doesn’t give exact solution to the Schrödinger equation because of the incorporation of true-exchange correlation functional. GGA assumes a gradient in charge density. This approximation is more physically significant than LDA. Majority of the problems of the isolated molecules are defined by using GGA. But it doesn’t applicable for the delocalized electrons in the uniform electron gas. Presently there are large varieties of GGA functional to give information about
gradient of electron density. Majorly used functional for solid state calculations are Perdew-Wang (PW91) and Perdew-Bruke-Ernzerhof (PBE) functionals\textsuperscript{89}.

\textbf{1.1.6.4.1. Kohn-Sham Equations}

The most powerful electronic structure theories like Kohn-Sham DFT using pseudo potential \textit{i.e.,} LDA and GGA have been implemented for the intractable many body problems of interacting electrons in a static external potential for the purpose of reducing to a problem of non-interacting electrons system\textsuperscript{93}. Conceptually, pseudo potential includes the external potential and the effects of Coulomb interactions between the electrons, \textit{e.g.,} the exchange and correlation interactions. Kohn-Sham equations have the form of Eq.13. The solution of this equation is for single electron wave function. The most common approach for the purpose of extended system is the expansion of single –particle Eigen states of the Kohn-Sham equation into a set of basis functions. The Schrödinger equation is utilized for the generation of expansion co-efficient, which then solved by various well established numerical methods.

$$\left[ \frac{\hbar^2}{2m} \nabla^2 + V(r) + V_H(r) + V_{XC}(r) \right]\psi_i(r) = \varepsilon_i \psi_i(r) \quad (13)$$

We consider extended periodic system with atoms at positions \(R + \tau\), where \(R\) represents a Bravais lattice vector locating a unit cell of the crystal and \(\tau\) represents a basis vector giving the positions within the unit cell. The energy operator, Hamiltonian for the energy of the system is given by
\[
\hat{H} = -\sum_{i=1}^{N} \frac{1}{2m} \nabla_i^2 + \sum_{i=1}^{N} V_{\text{ion}}(r_i) + \frac{1}{2} \sum_{i \neq j} \psi(r_i - r_j) + V_{I-I}
\] (14)

\[
\psi(r) = \frac{e^2}{|r|}
\] (15)

where \(N\) is the number of electrons at positions \(r_i\) with Coulomb potential as in Eq. 15

Static potential of the ion is formulated as

\[
V_{\text{ion}}(r) = \sum_{m,s} V_{\text{ion}}^{(s)}(r - R_m - \tau_s)
\] (16)

and ion-ion repulsion is given by

\[
V_{I-I} = \frac{1}{2} \sum_{mm,ss} \frac{Z_m Z_s e^2}{|R_m + \tau_s - R_m - \tau_s|}
\] (17)

Here, \(\hbar = 1, 2m = 1, e^2 = 2\) are Rydberg units, distance and energies are measured in Bohr and Rydberg units respectively. First three terms of Eq. 13 is taken as the electron energy operator \(H_{el}\)

The ground state electronic energy \(E_{el}\) of the system can be represented as

\[
E_{el} = T_0[n] + \int V_{\text{ion}}(r)n(r)dr + E_h[n] + E_{xc}[n]
\] (18)

where \(T_0[n]\) represent kinetic energy, \(E_h[n]\) stands for Hartee-Fock energy or classical interaction energy and \(E_{xc}\) is the exchange correlation energy of function \(n\) having density \(n(r)\).
Hence, Hartee-Fock energy can be described as

\[ E_h [n] = \frac{1}{2} \iint n(r)v(r-r')n(r')drdr' \]  \hspace{1cm} (19)

Considering the number-conserving variations of the true ground state electron density \( n_0(r) \), ground state electronic energy \( E_{el} \) is minimized.

\[ \delta \left\{ E^{el} [n] - \mu \int n(r)dr = 0 \right\} \]  \hspace{1cm} (20)

where, \( \mu \) is the chemical potential of the electronic system.

Kohn-Sham potential of the many body problems is obtained by the self-consistent calculation of the following equations

\[ \hat{H} \psi_i (r) = \left\{ -\frac{1}{2m} \nabla^2 + V_{eff} (r; n) \right\} \psi_i (r) = E_i \psi_i (r) \]  \hspace{1cm} (21)

where electron density

\[ n(r) = \sum_{i=1}^{N} |\psi_i (r)|^2 \]  \hspace{1cm} (22)

and \( V_{eff} (r; n) = V_{ion}(r)+V_h(r; n)+V_{xc}(r; n) \)  \hspace{1cm} (23)

\( \psi_i \) is the ortho normal eigen functions and \( E_i \) is the Eigen value of the operator \( \hat{H} \)

Hartee and exchange correlation potential functions\(^94\) are given as:
\[ V_h(r; n) = \int v(r - r')n(r')dr' \]  \hspace{1cm} (24)

\[ V_{xc}(r; n) = \frac{\delta E_{xc}[n]}{\delta n(r)} \]  \hspace{1cm} (25)

The exchange correlation functional is given by the sum of a correlation functional and exchange functional\(^{93}\). The assumption of LDA includes that exchange correlation energy of an electron at every point in space is equal to the exchange correlation energy per electron of a uniform electron gas. For the weakly correlated materials (semiconductors and simple metals) LDA gives most accurate result, while for studying bulk properties (elastic properties, bulk modulus etc.), GGA functional is more suitable. GGA\(^{95}\) assumes a gradient in the charge density. The gradient correction to the exchange correlation functional results in the formation of spin densities and their gradients in the function. Hence GGA can modify the quality of the LDA results.

1.1.6.5. Pseudo potential plane wave approach

Nowadays, pseudo potential plane wave approach became the bench mark model of the DFT method for calculating the ground state electronic properties of the extended system. The advantage of plane wave approach is that it leads to very efficient numerical calculation of Kohn-Sham equation\(^\text{96}\). For the extended system, the employment of pseudo potentials are carried out by using relatively small set of plane waves. Plane waves are exact Eigen functions of the homogeneous electron gas. They are ortho normal and energy independent. Plane wave are not biased to any particular atom. In solving equation, plane wave basis set with certain cut off wave vector is used. The size of
basis set is fixed by the convergence calculation controlled by a single parameter. Besides, it can be verified by simply increasing the length of the cut off vector. In the plane wave based calculations, the coulomb potential of the electron-nucleus interaction in the core region are substituted with pseudo potentials. The introduction of pseudo potentials replaces the true valence wave functions, the so-called pseudo wave functions correctly match with exact true valence wave functions outside the ionic core region. It considers Hartee potentials and the total charge density of the system\textsuperscript{96}.

1.2. Review of the work

Thermal decomposition studies were started by the thinking of Wendlandt \textit{et al}\textsuperscript{97}(1958). The thermal decomposition behavior of scandium, yttrium, lanthanum, cerium (III), neodymium, samarium, europium, gadolinium, holmium and erbium were carried out on thermo balance. Based on the thermal decomposition data, authors classified rare earth metal oxalates as three groups. First group containing La, Pr and Nd oxalates, second group involves: oxalates of Sm, Eu and Gd and third groups: Y, Ho and Er. First group oxalates undergoes decomposition without the formation of hydrates. Formation of oxides occurs at higher temperature than other two groups. Second group passes through the hydrates as intermediate. Temperature corresponding to the formation of oxide is lower than the first group. Third group oxalates go through the stable hydrate intermediate. Oxalates of Ce decompose at lower temperature than other rare earth oxalates. Wendlandt \textit{et al}\textsuperscript{98}(1959) carried out the investigation regarding the thermal decomposition of heavier rare earth metal
oxalates of terbium, dysprosium, thulium, ytterbium and lutetium in a thermo balance. It was found that oxalates began to response to temperature from 45 to 60°C. Thermal reaction passed through several intermediate formation and decomposition, and finally forms the oxide in the temperature range of 715 to 745°C.

From the reports of Wendlandt et al\textsuperscript{98} and Srivastava et al\textsuperscript{99} (1960), it was found that thermal dehydration of cerous oxalate occurred at 50-220°C, and the decomposition was completed at 360°C. The small weight loss was observed at above 360°C could be due to the occurrence of decomposition of small amount of carbonates which aroused from the decomposition of oxalates. Padmanabhan et al\textsuperscript{100} (1960) reported the formation of a dihydrate. It was reported that the temperature range of loss of water from the lanthanum oxalate varies between 55°C and 370°C. The thermal decomposition reaction of Lanthanum oxalate (La-Ox) starts at 400°C, and then at 550-750 °C, a stage corresponding to the formation of oxy carbonate intermediate is reached. The final stage of decomposition was occurred from 740°C and the weight loss became constant at 840°C corresponding to the formation of La\textsubscript{2}O\textsubscript{3}. Subba Rao et al\textsuperscript{101}(1965) brought out the mechanism of thermal decomposition of oxalates of La, Ce, Nd and Pr via TG from the temperature 30-1100°C both in air and CO\textsubscript{2} atmosphere. It was disclosed that under CO\textsubscript{2} atmosphere, the delayed nucleation and slow growth rate was became the reason for the delayed nature of the reaction. It was suggested by the authors that cerous oxalate starts dehydration above 150°C and continue the reaction at about 275°C, where the decomposition of oxalates starts to occur. At
about 375°C, sharp weight loss (51.2%) was observed and then weight loss (52.5%) was remained constant at 550 °C. It was discussed by the authors that even though the mechanism of decomposition was similar in the CO₂ atmosphere, the reaction followed with slowest steps. In CO₂ atmosphere, the decomposition was started at 325 °C. Sharp break in the weight loss at 450°C was corresponds to the formation of intermediate Ce₂O₃.CO₂, but this formation of intermediate is relatively less stable to be resolvable in the atmosphere of air. In the CO₂ condition, after 650°C onwards, the weight loss remains constant. Along with cerous oxalate, Subba Rao et al₁₀¹ also carried out the establishment of thermal decomposition mechanism of oxalates of La, Pr and Nd both in the atmosphere of air and CO₂. It was concluded that lanthanum oxalate takes the removal of water in the range of 100-300°C without any indication of intermediate hydrate. Thermal decomposition of praseodymium oxalate undergoes with similar fashion to the La-Ox in air. It follows through the formation of oxy carbonate intermediate and finally the formation of Pr₆O₁₁ in the temperature range of 550-650°C. Moreover, these authors also discussed the thermal decomposition behavior of Neodymium oxalate. The dehydration was occurred rapidly in the temperature range of 100-350°C. The decomposition stage corresponding to the formation of Nd₂O₃ occurs in the temperature range 700-740°C. Hence the authors concluded that except cerous oxalate, oxalate of Pr, La and Neodymium undergoes thermal decomposition reaction through the formation of oxy carbonate intermediate (M₂O₃.CO₂). The decomposition of the concerned oxalates was found to be delayed and sluggish in CO₂ atmosphere.
Agarwala et al\textsuperscript{102}(1961) brought out the investigation regarding the kinetics of decomposition of yttrium, cerous and zirconium oxalates \textit{via} thermo gravimetrically and differential thermo gravimetry. Moosath \textit{et al} \textsuperscript{103}(1963) described thermal decomposition behavior of oxalates of La, Pr and Nd on a Stanton thermo balance, and shown that these form a group based on their concerned process. These oxalates, before giving the final oxide product, yield basic carbonates, which are stable. The decomposition starts after the completion of dehydration rapidly, indicating the unstable nature of anhydrous oxalate. These authors studied about thermal decomposition behavior of oxalates of Sm, Eu, Gd, Tb and Dy and disclosed that no weight level corresponding to the hydrated intermediate was observed in the thermo gravimetric analysis. They also discussed that basic carbonate intermediate did not formed before the formation of oxide at higher temperature 690-720\degree C\textsuperscript{104}. Thermal behavior of heavier rare earth oxalates of Ho, Er, Tm, Yb, Lu, and Y were studied on a Stanton thermo balance and posted that dehydration of oxalates at lower temperature occurs through the formation of stable dihydrate in the temperature range of 230-330\degree C. Also they confirmed that these oxalates decomposed to form the final product oxide (680-700\degree C) without any stable intermediate\textsuperscript{105}. Group IV oxalates (Ce, Th) upon thermal decomposition shows anomalous behavior with respect to each other, but exhibited major difference from the decomposition behavior of other oxalates\textsuperscript{106}. De Almeida \textit{et al}\textsuperscript{107}(2012) postulated new insights regarding the thermal decomposition behavior of cerium oxalate under inert and oxidizing atmosphere. It was viewed as a resemblance to the thoughts of Subba Rao \textit{et al}\textsuperscript{101}, regardless of the atmosphere,
dehydration occurs at about 170°C without any intermediate hydrate, but thermal decomposition behavior is entirely different in both air and argon atmosphere. Under air, the decomposition takes place in one step between the temperature 270 and 450°C, releasing CO₂, whereas in argon, the decomposition occurs in two step between the temperature 350 and 800°C with the release of CO and CO₂. Gabal et al.³² (2012) synthesized CeO₂ nano powder via thermal decomposition of cerium oxalate. Thermal decomposition behavior was studied through DTA-DTG-TG measurements in air. They observed majorly two weight loss steps in the temperature region of 60-160 and 270-350°C. The first weight loss step with a broad endothermic DTA peak is associated with loss of 10 water molecules of Ce₂(C₂O₄)₃.10H₂O, forming anhydrous oxalate. Literature in 1960’s reported that anhydrous oxalate is very unstable and hence it undergoes rapid decomposition. On contrary to this, Gabal et al.³² disclosed that anhydrous cerium oxalate is stable up to 270°C, which undergoes exothermic decomposition at 350°C to form ceria nanoparticle. They calculated kinetic parameters for each thermal decomposition stage of precursor oxalate.

Up to now, there are few reports regarding thermal decomposition of mixed rare earth metal oxalates. Thermal decomposition of cerium oxalate and mixed cerium–gadolinium oxalate was studied. The corresponding mixed oxide (CeO₂)₀.₉(Gd₂O₃)₀.₁ is prepared by calcination¹⁰⁸. Ubaldini et al.¹⁰⁹ investigated the thermal properties of mixed cerium–gadolinium oxalate and found that their dehydration stages are similar to that of
gadolinium oxalate. Effect of additives to the precursor salt significantly governs the rate of decomposition. Selection of additives which cause to decrease the $Ea$ and increase the rate of process and its separation from the product is most considered. Furuichi et al\textsuperscript{110} studied the effect of transition metal oxide $\alpha$-Fe$_2$O$_3$ additive on the thermal decomposition of salts of halogen oxoacids, oxalates, azide, permanganate and oxides by gas-flow type DTA and X-ray diffraction pattern. It was shown that $\alpha$-Fe$_2$O$_3$ exhibited remarkable catalytic effect on the decomposition of halogen oxoacids, but it didn’t show any effect on other salts. The effect of ferro spinel additive Cd$_{1-x}$Co$_x$Fe$_2$O$_4$ ($x = 0.0$, $0.5$ and $1.0$) on kinetics and mechanism of thermal decomposition of lithium oxalate was studied\textsuperscript{111}. It was found that with increasing the concentration of cobalt, the rate of thermal decomposition was enhanced with $x$ in the order $0.0 < 0.5 < 1.0$. John et al\textsuperscript{112} explored the effect of semi conducting metal oxides CuO and TiO$_2$ on the thermal decomposition of sodium oxalate. It was suggested that regardless of n-type or p-type oxide, both CuO and TiO$_2$ enhanced the rate of thermal decomposition at lower concentration (1 wt%), whereas suppressed the rate at higher concentration because of the adsorption of CO, one of the byproduct. The effect of additives CuO, MnO$_2$ and TiO$_2$ on thermal decomposition kinetics of KIO$_4$ to KIO$_3$ was investigated\textsuperscript{113}. These oxides showed remarkably little effect on the rate of decomposition except with concentration of oxides 10 wt%, when observed small decrease of rate.

The multistep mass loss behaviors of solids are controlled by physico-geometrical constraints which may occur due to the changes in
reaction conditions as the reaction advances. In thermally stimulated processes, surface product layer is formed in the early stages of the reaction. The occurrence of geometrical restrictions between the surface product layer and the inward advancement of the reaction interface generated at the boundary between surface product layer and internal reactant. There are numerous works regarding the establishment of kinetic parameters of partially overlapped thermal decomposition processes. Koga et al. investigated the kinetic parameters responsible for the thermal degradation of ploy (L-lactic acid) via multistep kinetic approach. Using the similar methodology, kinetics of formation of Ag from Ag$_2$CO$_3$ was carried out.

Even though large numbers of investigations regarding the multistep kinetic behavior of solid state materials are established, solid state decomposition kinetics of hydrated cerium oxalate through multistep kinetic approach were not evaluated. So the authors interested to find out the effect of cationic dopant, nano semiconducting metal oxides, ferrites and oxalates upon the thermal behavior as well as its kinetics for the formation of ceria nanoparticles.

Potential growth of the ceria nano particle due to the unique physical and chemical properties, they possessed wide variety of applications in material science fields including catalysis, sensors, control of pollutants, etc. The emergence of the nano particles became great hazards to human health. This became reason for the researchers to rethink about the unknown biological effects underlying the nanoparticles.
Chen et al\textsuperscript{116} (2008) made comparative study on the cytotoxicity of metal oxide nano particles of Fe\textsubscript{2}O\textsubscript{3}, CuO and ZnO and their metal ion counter parts (Fe\textsuperscript{3+}, Cu\textsuperscript{2+} and Zn\textsuperscript{2+}) towards human SH-SY5Y neuroblastoma and H4 neuroglioma cells. For the purpose, they taken the test samples of concentration range of range of 0.01–100 mM for 48h, under the cell culture conditions: 95% O\textsubscript{2}, 5% CO\textsubscript{2}, 85% humidity, 37\textdegree{}C. Based on the cell viability test of nanoparticles and their metal ion counter parts, the most striking results were obtained for CuO. Significant cell death was observed for both H4 and SH-SY5Y cell lines. While the toxic effects of Fe\textsubscript{2}O\textsubscript{3} and ZnO were found to be marginal. Based on the evidence of their data, they argued the complex nature of neurotoxic response and hence they justified further through \textit{in vivo} studies.

Wang et al\textsuperscript{117}(2011) investigated the mechanism of \textit{in vitro} cytotoxicity of metal oxide nano particles (ZnO, TiO\textsubscript{2}, CuO and Co\textsubscript{3}O\textsubscript{4}) using catfish primary hepatocytes and human HepG2 cells. It was proved that CuO and ZnO exhibited significant toxicity in both HepG2 cells and catfish primary hepatocytes. The evidences verified that HepG2 cells are more sensitive than catfish primary hepatocytes towards the toxicity imposed by metal oxide nanoparticle. The authors arranged the tested metal oxides in the increasing order of their toxicity as follows: TiO\textsubscript{2} < Co\textsubscript{3}O\textsubscript{4} < ZnO < CuO. They reached into the conclusion giving mechanism for the toxicity imposed by nano particle in such a way that both ROS mediated cell death and damages to cell and mitochondrial membranes accounts for it.

Wang et al\textsuperscript{83}(2013) explored the possibility of cuprous oxide
nano particle for curing of melanoma and metastatic lung tumor based on B16-F10 mouse melanoma cells through both in vitro and in vivo models. The analysis was interpreted as cuprous oxide nano particle significantly reduced the growth of melanoma cell, inhibited the metastasis of B16-F10 cells and enhanced the survival rate of tumor bearing mice. As the nanoparticles are cleared from the organs rapidly, it causes to little systemic toxicity. Activity of cuprous oxide nano particle begins through the mitochondrion- mediated apoptosis pathways, it results in the release of cytochrome C from the mitochondrion and activated caspase-3 and caspase-9 after the nano particle entered the cells.

Ivask et al\textsuperscript{118}(2015) searched the cytotoxicity of nano particles of oxides of Al, Mg, Si, Mn, Cu, Fe, Ti, Co, W, Sb and Zn) towards three cell lines such as human alveolar epithelial cells A549, human epithelial colorectal cells Caco2 and murine fibroblast cell line Balb/c 3T3. For three cell lines, both nano particle and metal ion counterpart contribute comparative toxicity. Based on the analysis, the authors discussed that six metal oxides (oxides of Fe, Al, Mg, Si, Ti and W) did not show any toxic effect below100 μg/mL\textsuperscript{1}. For five metal oxides, the averaged 24h IC\textsubscript{50} value was found for three cell lines were 16.4 (Cu), 22.4 (Zn), 57.3 (Sb), 132.3 (Mn) and 129 μg/mL\textsuperscript{-1} (Co). The authors argued that oxides of Cu, Zn and Sb exposed the toxicity by releasing metal ions; whereas ROS mediated cytotoxicity was performed by oxides of Mn and Co.

Titma et al\textsuperscript{119}(2016) studied the in vitro cytotoxicity exhibited by antimony, copper, cobalt, manganese, titanium and zinc oxide nano
particle towards the alveolar and intestinal epithelial barrier cells. Here they executed time dependent toxicity of Nps (24h & 9 days incubation). The short term monitoring of incubation of Caco2 & A549 cells with 100 μg mL$^{-1}$ of Nps, Sb$_2$O$_3$, Mn$_3$O$_4$ and TiO$_2$ Nps didn’t show any toxic effect, but Co$_3$O$_4$ and ZnO shown moderate effect, while, CuO Nps exhibited toxicity below 100 μg mL$^{-1}$. Upon long term monitoring, both Mn$_3$O$_4$ and Sb$_2$O$_3$ displayed remarkably enhanced toxicity. Authors rechecked the analysis with trans-epithelial electrical resistance (TEER) measurements and concluded that Caco2 cells were more sensitive towards the toxic effects of Nps. This assay resulted that more toxic effect was by Sb$_2$O$_3$ Nps.

Rajiv et al$^{120}$(2016) made comparative assay on the cytotoxicity and genotoxicity of Co (II)&(III) oxides, Fe(III) oxides, silicon dioxide and aluminum oxide Nps towards the human lymphocytes via in vitro model. Short term exposure of human lymphocytes cell lines with Nps shows that Co$_3$O$_4$ Nps exhibited decrease in cell viability and increase in cell membrane damage. The reason for toxicity was ascribed due to the oxidative stress induced by ROS, lipid peroxidation, depletion of catalase, reduced glutathione and super oxide dismutase. In the concerned work, Al$_2$O$_3$ exposed least DNA damage. The difference in the antioxidant properties showed DNA damage and chromosomal aberrance in human lymphocytes.

Asati et al$^{59}$(2010) investigated that cerium oxide nano particle has acquired great potential of antioxidant nature and radio protective agents in cancer therapy. They prepared various polymer coated ceria nanoparticle for the surface functionalization. They engineered
different surface charges (positive, negative and neutral) on the polymer coated ceria nano particle and their internalization and toxicity towards normal cells and cancer cell lines. Nano ceria carrying positive or neutral charge get into the most of the cell lines, but nano ceria with negative charge on the surface internalizes mostly in cancer cells. Depending upon the surface charge of nano ceria, it enters into different cell compartments. Depending upon the internalization and subcellular localization of ceria nano particle, it affects the nature of cytotoxicity of ceria nano particle. Significant toxicity is observed when nano ceria enters into lysosome of the cancer cells, but for the entrance to cytoplasm, no significant toxicity was observed.

Xue et al\textsuperscript{121}(2011) established radical scavenging properties of ceria by the \textit{in vitro} simple photometric system. In the concerned reaction, when methyl violet treated with hydroxyl radical, its absorbance change. But in the presence of ceria, it protects methyl violet from the attack of OH radical by scavenging the radical by ceria. Hence radical scavenging ability of ceria is directly evidenced through the absorbance change.

Marzi et al\textsuperscript{122}(2013) proposed that cytotoxicity and genotoxicity of ceria nano particle towards different cell lines. They reached into the conclusion by executing long term and short term exposure \textit{in vitro} assay towards A549, CaCo2 and HepG2 cell lines. Both cytotoxicity and genotoxicity assay was performed over a concentration range of 0.5 to 5000\(\mu\)g\(\text{mL}^{-1}\). But it was found that no toxicity was observed by short term exposure, while long term exposure exhibited significant toxicity towards all the cancer cells. The
result also confirmed that the capacity of ceria nanoparticle to withstand the attack of oxidant like H$_2$O$_2$.

Clark et al$^{123}$ (2013) explored H$_2$O$_2$ mediated apoptosis of Ti-doped CeO$_2$ in tumor bearing cells. This catalase like activity of Nps was dependent on the specific cellular environment. The authors described that the study would become the preliminary step for the clinical studies and for the generation of new nanoparticle therapy.

Gao et al$^{124}$ (2014) reviewed on the novel therapeutic agent ceria Nps in cancer treatment. Based on the research data, authors argued that ceria Nps are able to show toxicity towards cancer cells, to inhibit invasion, and make sensitive the cancer cells to radiation therapy and chemotherapy. It exposes minimal toxicity to normal cells and protects cells from the generation of reactive oxygen species like OH radical. Since its affinity for scavenging hydroxyl radical, it protects the cells from the oxidative stress induced by the generation of ROS. It was shown that nano medicinal level of ceria was increased due to its dual capability as oxidant in cancer cell and antioxidant in normal cell. Hence it would become a substitute for reducing the harmful effect of the radiation therapy.

Kargar et al$^{125}$ (2015) synthesized ceria Nps using bio based material such as egg white. In vitro cytotoxic studies of the synthesized nanoparticle towards the human periodontal fibroblasts cells exhibited concentration dependent toxicity with non-toxic effect up to the concentration range of 800μg/mL$^{-1}$.

Diaconeasa et al$^{126}$ (2015) put forwarded that as ceria attained
radical scavenging properties, it find applications in the drug delivery or chemo therapy agents. Cytotoxicity and cellular uptake of nanoceria were tested on cultured human lung cancer cells. MTT assay resulted the cell viability test, exposed the toxicity expressed by the ceria nanoparticle. The results are dose dependent and exposure time decreased cell viability.

Gagnon et al\(^{127}\)(2015) reviewed on protective effect and toxicity of ceria. In the concerned area, reviewers’ attention goes into that the protective effect of ceria aroused due to its inherent oxygen storage capacity. Hence it is able to uptake and release oxygen reversibly. This was the main cause of its entry to the biomedical applications. They suggested that toxicity of ceria Nps depends on synthesis condition, physical and chemical properties, surface properties, cell type, exposition method and various other features associated with it.

Nelson et al\(^{128}\)(2016) made another review regarding the antioxidant behavior of cerium oxide Nps in biology and medicine. This review entitled on mechanism for antioxidant behavior, radical scavenging process, designing and method of preparation of radical scavenging ceria Nps, illustration of antioxidant capacity of ceria from \textit{in vitro} and \textit{in vivo} models, regeneration and therapeutic applications and for the treatment of photoreceptor degeneration. Based on their review, they ensured that ceria nano particles have capabilities to become a substitute for the therapeutic agents for treating oxidative-stress and nitrosative-stress related diseases and disorders.
Joydeep et al\textsuperscript{129}(2017) performed nano ceria mediated drug delivery of doxorubicin. This was carried out via the apoptosis of ovarian cancer cell. \textit{In vitro} analysis of DOX/CeO\textsubscript{2} proved higher cell proliferation inhibition and apoptosis compared with free DOX. They brought out the mechanism as that negatively charged ceria nanoparticle can couple with positively charged doxorubicin through the electrostatic interaction under the physiological condition resulting in the formation of doxorubicin-loaded nano ceria (DOX/CeO\textsubscript{2}). This complex can behave as a superior drug for the cancer cell than free DOX taking the advantage of higher cellular uptake and fast release from the organ.

Khan et al\textsuperscript{130}(2017) made an evaluation regarding the \textit{in vitro} cytotoxicity, biocompatibility and change in the expression of apoptosis regulatory protein induced by ceria nano crystals. Based on the Western blot assay, it was confirmed that ceria nano crystals directed to HT29 cancer cell lines varied the expression level of anti-apoptotic proteins Bcl2 and BclxL, whereas increased the expression level of Bax, PARP, and cytochrome c proteins. Specific ratios of Bax/Bcl2 protein are caused for cell death, which decides the death or life of particular cells with respect to an apoptosis stimulus. But higher ratios of Bax/Bcl2 robustly expressed inhibition of cellular resistance to apoptotic stimuli.

Up to now, large number of research regarding the cytotoxicity of ceria nanoparticles is performed. The main cause of its mechanism not yet understood. But the major reason for exhibiting the toxicity was argued that radical scavenging ability and antioxidant behavior. It can
reduce oxidative stress induced by the generation of ROS. Because of the inherited ability of oxygen storage capacity, it can uptake and release oxygen reversibly. Ceria act as oxidant for cancer cells whereas antioxidant for normal cell. Cytotoxicity of ceria nanoparticle depends on the synthesis condition, size and shape, surface charge, cell type, etc. In the present condition, we enquired how the presence of Cu$^{2+}$ in the lattice of nano plates of ceria affected the cytotoxicity towards DLA (Dalton’s Lymphoma Ascites cell) *in vitro*. We have prepared a series of oxides of Ce:Cu in different molar ratios via thermal decomposition of its oxalate.

Nolan *et al*\(^{131}\) (2005) studied the DFT calculations of bulk ceria and low index surfaces (111), (110) and (100). They contributed that the stabilities of the surfaces follows the order (111) > (110) > (100), whereas the surface relaxation pursued the inverse order. They analyzed the electronic properties of bulk and surfaces by means of charge, charge density and electronic density of states. They reminded that some partial ionic character in pure ceria along with covalent character. This confirmed that the Ce 4f states are above the Fermi level. On analyzing bulk and surface charge distribution, there appeared only small difference in the surface atoms when compared to bulk. DOS calculation of both shows major difference in the O 2p and Ce 5d states. They also contributed that DFT approach can’t predict accurately the delocalization of electrons in Ce$^{3+}$, partially reduced ceria because of the strong correlational effect of Ce 4f states. But the accurate prediction of electronic structure can be made within the
DFT+U formalism. They also found that the contribution of localization of Ce 4f correctly predicted the defect surfaces.

Castleton et al.\textsuperscript{132}(2007) made an examination on real space and electronic structure of oxygen vacancies in ceria with DFT+U approach using exchange correlational GGA and LDA. They performed several quantification schemes and found that the localization of the charge starts to be occurring at $U \sim 3\text{eV}$. The degree of localization of charge was reached to maximum at $U \sim 6\text{eV}$ for LDA+U approach and $U\sim5.5\text{eV}$ for GGA+U approach. They found that for higher $U$ value the localization of charge is decreased since the transfer of charge to the nearest neighbors. Maximum localization of about 80-90\% of the Ce 4f charge was located on the two nearest neighboring Ce ions. They rechecked the properties of defect free ceria utilizing LDA+U with $U = 3 – 4\text{eV}$. But the agreement of theoretical prediction of band structure with experiments was observed at $U = 7 – 8\text{eV}$. The best description of electronic localization with GGA functional was found to be with correlation term $U = 5\text{eV}$.

Loschen et al.\textsuperscript{133}(2008) performed plane wave DFT to investigate electronic structure of a series of CeO$_2$ Nps. They found that the strong correlation effect of 4f electron of Ce occurs due to the reduction of Ce$^{4+}$ to Ce$^{3+}$. In order to account the correct structure of ceria nanoparticle, DFT method choosing exchange correlation functional GGA or LDA was not sufficient. Hence they introduced Coulomb repulsion term U (Hubbard effective term) was introduced with DFT. Thus, they described that DFT+U approach is more efficient method for studying electronic structure of molecules, clusters and
extended solids. The most stable cluster species is cuboctahedral Ce₁₃O₂₆. Based on the DFT+U method, it can be predictable that highly co-ordinated ceria have more number of Ce⁴⁺ state, while low co-ordinated ceria possessed largely the reduce state Ce³⁺.

Zhang et al.¹³⁴(2008) carried out a systematic study on the adsorption of Au atoms on the various ceria surfaces. They show the crucial importance of Ce 4f states in the adsorption of Au atoms on the stoichiometric and reduced ceria surfaces. In the stoichiometric case (Ce⁴⁺), Ce 4f states (non-bonding) occupy above the Fermi level, whereas in the reduced (Ce³⁺) case, the partially occupied 4f state due to the removal of oxygen atoms lye just below the Fermi level. While adsorption of Au on the stoichiometric ceria surfaces, 4f states act as electron acceptor causing to the stabilization of adsorbed Au atoms on the surfaces. Reduced ceria surface with partially occupied 4f states behave as electron donor so as to stabilize adsorbed Au atoms. In the stoichiometric surfaces, the most preferred adsorption site for Au is on the bridge like site where two where Au directly binds with two oxygen atoms via O 2p- d (Au) mixing. In the reduced surface with oxygen vacancies, the suitable site for adsorption is near vacancy position. They found that the binding energy for adsorption of Au is higher at stoichiometric surfaces than in the Ce vacancy site.

Branda et al.¹³⁵(2010) investigated the interaction of Cu, Ag and Au atoms on the regular ceria surface (111) within the frame work of DFT+U using the exchange correlational LDA and GGA and compared the results with periodic surface slab model. The interaction of Cu and Ag based on all methods gave same qualitative description
of the stable active site with same order of stability and oxidized character of Cu and Ag on the surface of ceria. In the case of Au, the interactions are method dependent and due to the presence of nearly degeneracy between the solutions between cationic and neutral Au.

Tang et al\textsuperscript{136}(2012) made comparative studies on the adsorption behavior of Cu, Ag and Au atoms on the technologically important catalytic surfaces of ceria within the frame work of DFT+U. They generated a set of model configurations by placing metal atoms on the three surface sites, \textit{viz}, on top of an O, an O bridge site and a Ce bridge site. Before doing optimization, small distortions in the selected Ce-O distance were imposed in order to explore the energies associated with reduction of Ce\textsuperscript{4+} to Ce\textsuperscript{3+} during the adsorption of metal. Further the charge redistribution of adsorbed ceria surface was confirmed by spin density isosurfaces and site projected DOS. They reached into the conclusion that while adsorption, Cu and Au atoms are oxidized to Cu\textsuperscript{2+} and Au\textsuperscript{2+}. They pointed out that adsorption energies for O bridge site was higher at where the 2 Ce\textsuperscript{3+} are nearest neighbors exist, while for Ce bridge site, adsorption energies was higher for 3 Ce\textsuperscript{3+} nearest neighbors. They also found that CeO\textsubscript{2} exposed with (110) crystal plane exhibits higher adsorption energies than (111) crystal plane of ceria.

Jalborg et al\textsuperscript{137}(2014) calculated the electronic structure of super cells of CeO\textsubscript{2-δ} within the frame work of DFT+GGA. The equilibrium properties such as lattice constants, bulk moduli and magnetic moments of super cells are well characterized with exchange correlational GGA. Electronic excitations are simulated by robust-total energy calculation for constrained states with atomic core holes or
valence holes. Non-magnetic insulator pristine ceria become magnetic when it is reduced by removing oxygen atoms. They put forwarded that in the ground state oxygen deficient ceria, the partially occupied 4$f$ states lye near the Fermi level. The presence of 4$f$ electrons have predominant role in realizing catalytic properties of ceria and related materials.

Kehoe et al\textsuperscript{138}(2011) examined the effect of divalent dopants on the reducibility and oxygen storage capacity of ceria using DFT. For this purpose, they utilized the range of divalent dopants and characterized their effects. Based on their investigations they proposed the blueprints for the choice of dopants to enhance the reducibility and oxygen storage capacity of an oxide catalyst. They generalized the selection of effective dopants by incorporating the following ideas that: (a) the ionic radius of the dopant ion should be small enough to adopt the alternative positions in the lattice, (b) the coordination of the dopant ion in the respective binary oxide should be lower than that of the host ion in order to create under coordinated or weakly bound oxygen ion, (c) in the case of transition metals, the effect of driving force of altered crystal field splitting, which can lead to alternate coordination.

Lu et al\textsuperscript{139}(2011) studied the effect of copper dopant into the ceria lattice and (111) surface of ceria utilizing \textit{ab initio} quantum mechanical spin polarized density functional theory. They investigated the formation of oxygen vacancies and found that first oxygen vacancy is formed spontaneously while second is created easily in the doped system. Regardless of the number of oxygen vacancies in the lattice,
Cu is in +2 oxidation state and four coordinated in a close to planar structure. The formation energies for the oxygen vacancies are depend on charge compensation, structural relaxations and available Cu-O states. Formation energies for both first and second vacancies are smaller than that required for pure ceria (3.28eV). For the creation of first vacancy in the bulk-doped ceria, much larger decrease in energy (2.98eV) was found. This energy was attributed with 53% due to electronic effects and 47% due to large structural relaxation of doped system. For the creation of second oxygen vacancy, the energy needed was 0.89eV. This was attributed with 100% electronic effects.

Szabova et al\textsuperscript{140}(2013) studied the effect of Cu on stoichiometric and partially reduced ceria. It was observed that Cu adsorption on stoichiometric surface caused to the reduction, but on partially reduced surface it can regenerate partially oxidizing character of the ceria.

Vanpoucke et al\textsuperscript{141}(2014) studied the modification of the properties of ceria via aliovalent dopants Mg, V, Co, Cu, Zn, Nb, Ba, La, Sm, Gd, Yb and Bi to form fluorite type Ce\textsubscript{1-x} M\textsubscript{x}O\textsubscript{2-y} (where 0.00 ≤ x ≤ 0.25) theoretically by means of DFT+U formalism. Lattice parameter, dopant radii, bulk moduli and thermal expansion coefficient were calculated. The relative stability and oxygen vacancies of the solid solution were investigated. It was shown that the presence of oxygen vacancies in the doped system increased the lattice parameter whereas decreased the bulk moduli. They proposed that the defect formation energies are correlated with crystal and covalent radii of the dopant atoms. The introduction of aliovalent dopant exhibited
inverse relationship between change in thermal expansion coefficient and in bulk modulus. Different dopants impose differently in the ceria lattice. But the presence of oxygen vacancies in the doped system has much influence in the thermal expansion coefficient and bulk modulus. They proposed that bulk doping unfavorable with elements Cu, Co and Zn whereas favorable with La, Gd and Sm.

Again Vanpoucke et al\textsuperscript{142} (2014) studied the effect of group IV (a & b) elements (C, Si, Ge, Sn, Pb, Ti, Zr and Hf) as dopants to the ceria lattice within the frame work of DFT+U. They calculated the concentration dependent formation energies for the Ce\textsubscript{1-x}Z\textsubscript{x}O\textsubscript{2} where 0 \leq x \leq 0.2. Based on their investigations, they proposed that a roughly decreasing formation energies with ionic radius. They compared the effect of IV a & b elements on the properties of ceria, and found that group IV elements are better suitable for surface modification, while group IV b elements for bulk properties. The influence of dopants on the mechanical properties such as thermal expansion co-efficient and bulk modulus were discussed. It was shown that group IV a elements causes to increase thermal expansion co-efficient, while IV b elements made a small decrease in thermal expansion co-efficient. The inverse relationship of bulk modulus and thermal expansion co-efficient are maintained. Their results of analysis revealed that not only valence shell electrons but also filled orbitals can bring the modifications to ceria.

Musa Alaydrus et al\textsuperscript{143} (2016) investigated the atomic and electronic properties of Ln-doped CeO\textsubscript{2} (Ln = La, Pr, Nd, Pm, Sm, Eu and Gd] and pointed out that the contribution of 4f electrons to the
cation-anion interaction. They contributed to the literature that effect of dopants on the stable configuration and energies of oxygen ion migration in the doped CeO₂. In order to compensate the localization effects of 4f electrons of all Ln dopants, strong correlation term Hubbard U correction were treated within the DFT+GGA framework. This study revealed that the variable occupancy of 4f states was found to be important for early Ln elements to produce covalent interactions since those contain number of empty 4f orbitals. The covalent character of 4f electrons are generated by the delocalization due the hybridization of O 2p states. The presence of covalent interactions in Ln doped ceria essentially affects its oxygen vacancy formation and migration.

Chagas et al\cite{144}(2016) performed both experimental and theoretical investigations on the effect of doping concentration of Ni and Cu to the ceria lattice. From the experimental point of view, it was noticed that Ni forms solid solution through isomorphic substitution of Ce sites, this was retained around concentration of 9-10\% and above this limit it reached into saturation and hence the extra Ni atoms doesn’t affect the crystal structure of ceria. This was due to the formation of NiO phases as surface domain. The introduction of small percentage of Cu to the solid solution of NiCeO₆ neither disturbed the bulk structure of solid solution. This confirms the formation segregated phases of CuO domains. Theoretically these were proven by calculating the formation energies of solid solution. It was analysed that small addition of Ni can easily generate the solid solution, while arising the concentration above 6.25–9.37 Ni\% increased the formation
energy. The same effect was also observed in the doping of larger percentage of Cu to the Ni-Ce solid solution. Moreover, the strong contraction of lattice parameter was observed with larger concentration above 6.25–9.37 %.

1.3. Aim and scope of the work

The present investigation aims at synthesis, characterization of ceria and ceria based nano materials via multistage thermal decomposition strategy and allows the evaluation of kinetic characteristics of the thermal events responsible for the process. The need and significance of various additives such as oxalate, oxide and dopant in various concentrations on thermal decomposition behavior and kinetics of hydrated cerium oxalate are forecasted. No work on alterations in thermal decomposition behaviors of cerium oxalate caused by the surface morphology of oxalate precursor has been reported so far. This study covers how the anticancerous properties of nano ceria are effectuated with surface morphology and copper dopant concentrations. The derivation of electronic structure of ceria and ceria based materials still exist with experimental limitations. So, the theoretical studies by the use of plane wave density functional theory with proper exchange correlation functional are an upcoming domain.
1.4. References


14. Gotor FJ, Criado JM, Malek J, Koga N. Kinetic analysis of solid-state reactions: the universality of master plots for analyzing isothermal and


25. Koga N. Ozawa ’s kinetic method for analyzing thermoanalytical


72. Tana WS, Zhang M, Juan L, Li H, Li Y, Shen W. Morphology-


Overs A, Riess I. Properties of solid electrolyte gadolinia-doped ceria prepared by thermal decomposition of mixed ceriumgadolinium...


111. Girgis MM, El-Awad AM. Kinetics and mechanism of thermal decomposition of lithium oxalate catalysed by Cd₁₋ₓCoₓFe₂O₄ (x = 0.0, 0.5 and 1.0) ferrospinel additives. *Thermochim Acta.* 1993;214:291-303.


141. Vanpoucke DEP, Bultinck P, Cottenier S, Van Speybroeck V, Van

