Synthesis and Characterization of Metal Doped Calcium Hydroxide for Thermo-Chemical Energy Storage

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Dedicated to

My Parents

Their love, encouragement, hard work, prayers and faith in me made me what I am today

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Abstract:

In the era of energy wastes, energy storage techniques are playing a promising role in the development of the resources to store energy. Our beloved Earth is losing the energy resources day by day and the main focus of scientists now a day is to discover renewable energy resources. A lot of systems are designed to store electrical and mechanical energy. But for the upcoming time, the heat storage is facing a lot of challenges as non renewable energy resources are going drastically down. In order to utilize and store heat we have to devise ways in which one can store heat in summers and utilize it in winters. Sensible and latent heat storage methods are now applicable and have tendency to store heat for a short duration like they can store heat in the morning when there is sunlight and can use that heat during the night when there is no thermal energy of sun. But storing thermal energy for long duration is really challenging in which one can store heat for months and a year. Theoretical calculations tell us that thermo-chemical energy storage has that tendency to store a large amount of heat even for a long time.

Thermo-chemical energy storage is helping us to store energy with many benefits as it is a cheap source of energy storage with high storage energy density. There are a lot of systems in thermo-chemical energy storage techniques by which we can store energy but $CaO/Ca(OH)_2$ reaction to store energy is of great interest as it is cheap, has high energy storage density and is easily available on market scale. But using this type of energy storage is not yet been applicable and is on its initial stages of research due to some restrictions and limitations especially because of the low thermal conductivity of $Ca(OH)_2$ which noticeably effects the rate of reaction and huge amount of heat is lost due to this. So improving thermal conductivity of $Ca(OH)_2$ will surely lead us one step ahead towards storing energy.

We all know that introducing an impurity always works and it remarkably changes the properties of the whole system. That's why idea of doping some elements in the parent compound plays a vital role. So, in this research, we have tried to synthesis and characterize doped $Ca(OH)_2$ with Nickel (Ni), Zinc (Zn) and Strontium (Sr) to improve thermal conductivity of $Ca(OH)_2$. X-Ray Diffraction and X-Ray Fluorescence has confirmed the doping and thermal properties are studies with the help of Thermal Gravimetric Analysis (TGA) and hot disk method to find thermal conductivity.

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List of Abbreviations

	Terms	**Abbreviation**
1.	Electrical Energy Storage	(EES)
2.	Mechanical Energy Storage	(MES)
3.	Compressed Air Energy Storage Systems	(CAES)
4.	Flywheel Energy Storage Systems	(FESS)
5.	Thermal Energy Storage	(TES)
6.	Sensible Energy Storage	(SES)
7.	Latent Energy Storage	(LES)
8.	Thermo-Chemical Energy Storage	(TCES)
9.	Heat Transfer Fluid	(HTF)
10.	X-Ray Diffraction	(XRD)
11.	X-Ray Florescence	(XRF)
12.	Fourier Transform Infrared Spectroscopy	(FTIR)
13.	Thermal Gravimetric Analysis	(TGA)

Chapter 1

Introduction

1.1) Recent Energy Foundation:

The evolution and growth of a country is highly based on the consumption of its “Energy Resources”. By having a responsible approach to avail those energy resources, we can escort to a shining future. There are nine significant zones of energy resources. They are classified into two classes: nonrenewable and renewable, out of which our main concern is on renewable energy resources. But the question is “Why do we need to stick our head in renewable energy resources?” The answer is simple and can be easily given by nonrenewable energy resources.

1.1.1) Non-Renewable Energy Resources:

These are also recognized as limited energy resources as they take an extended time to be refilled for example coal, oil, natural gas and nuclear energy mutually known as Fossil Fuels. Around 150 years ago, man designed the mechanism to obtain energy from the fossil fuels. Fossil fuels fulfill the maximum section of today’s energy market. As stated in a report published by International Energy Agency (IEA) in 2015, it was concluded in a survey that fuels full of carbon contribute towards a large area of today’s energy requirement i.e. coal (29.20%), oil (32.91%) , nuclear (4.44%), gas (23.85%) and only 9.6% is extracted from renewable energy resources.

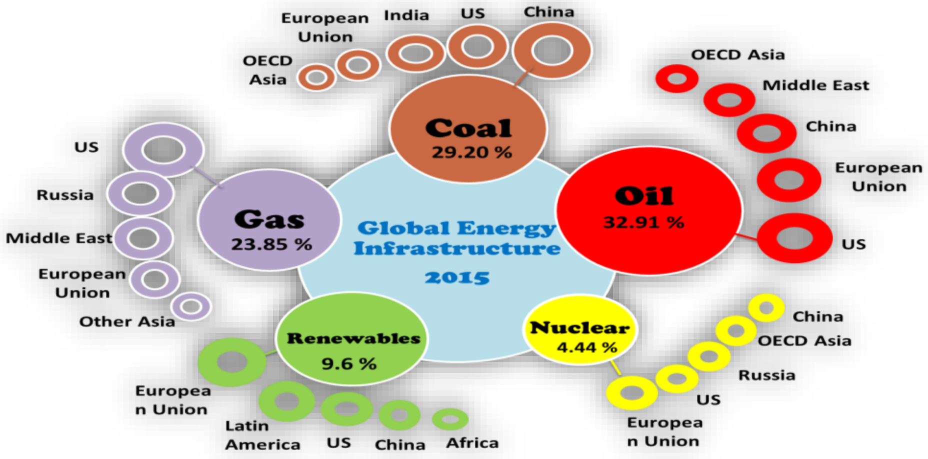

Fig. 1.1: Global energy production (IEA Report 2015).

As it can be seen in Fig.1.1**,** most of the advance countries are connected in the utilization of fossil fuels and if it keeps on proceeding past the year 2080, the world would be secluded from these energy rich resources. Moreover, per year, the price of oil barrel is also 7 times higher than that of 30 years before. The difference between the old and new upcoming consumption of energy resources can easily be estimated by the figure below in which utilization of annual oil resources is shown.

Fig 1.2) In this picture of 1970's, an average American family consumes this amount of barrels annually which is now increased 40% [1]

That's why our main concern, now a day, is to find out as many methods to store energy as we possibly can. So the scientists are now focusing to achieve new goals towards energy storage and are working on the different types ranging from electrical to thermo-chemical energy storage.

1.1.2) Renewable Energy Resources:

After knowing all the upcoming complications, the main concern of scientists goes towards the renewable energy resources. They devised many ways to store energy in the form of electric energy, mechanical energy and even thermal energy. So they divided types of energy storages and started working on each type. Main types of energy storage include electrical energy storage (EES), mechanical energy storage (MES) and thermal energy storage (TES) out of which thermal energy storage is of our concern. It’s further divided into three types known as sensible energy storage, latent energy storage and thermo-chemical energy storage. The diagram given below improves our understanding of types of energy storages.

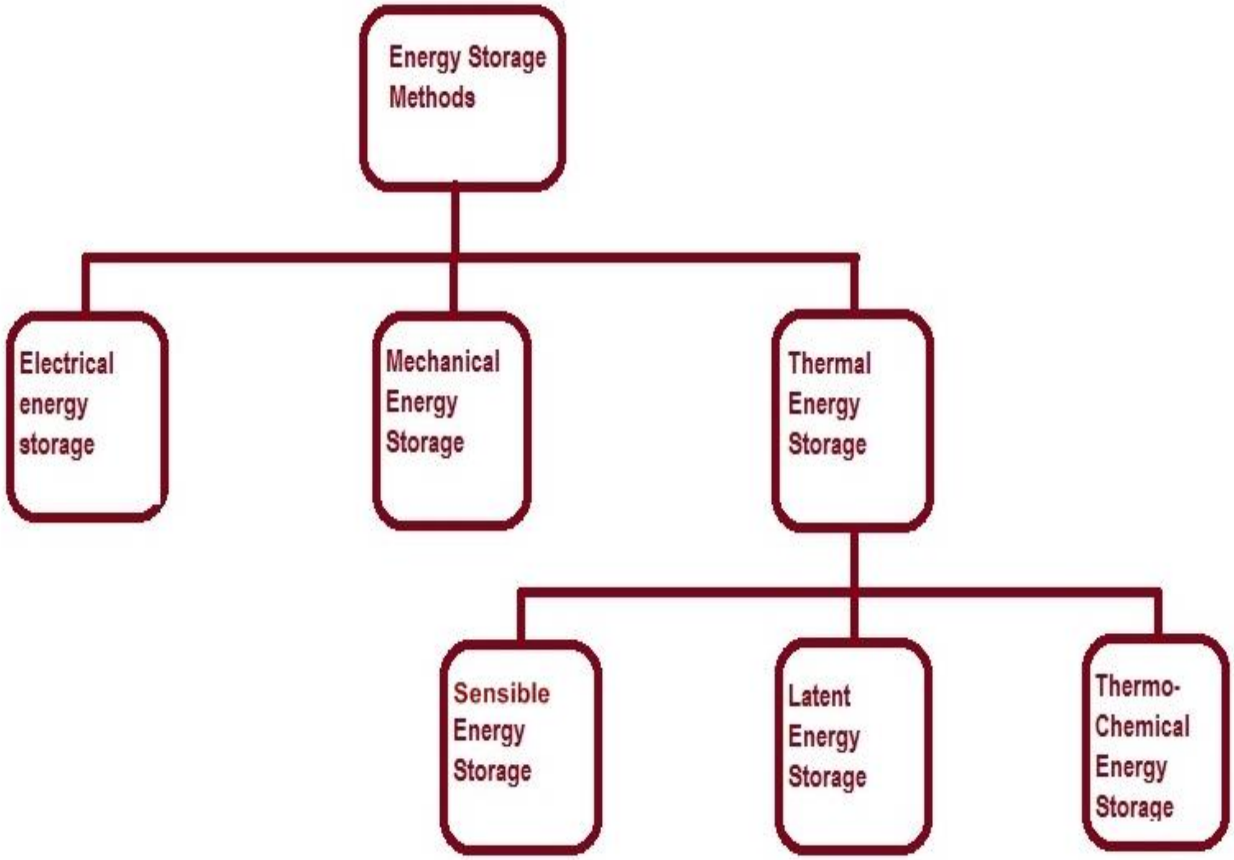

Fig 1.3) Types of energy storage

1.2) Types Of Energy Storage:

1.2.1) Electrical energy storage (EES):

As we know that electricity is a commodity which cannot be preserved or consumed. The electricity generated from non-renewable energy resources is not sufficient to maintain the balance between demand and supply [2]. So, in order to cater stability problems, the storage systems are needed. Electrical energy storage system is another way of energy storage, with an advantage to release additional amount of power to the grid when required. EES is the most common type of energy storage which can easily be seen at domestic and commercial level. It is most applied type of energy storage. Batteries are the main devices to store electrical energy. Most commonly used battery is lead acid and Ni-Cd. [3]

Basic Principle when direct current is given to the battery, the chemical potentials are formed by the movement of positive and negative ions, hence an ionic reaction takes pace. And as soon as the direct current is cut off the chemical energy is converted into electric energy. Some examples of the types of batteries are: [4]

- Pb(lead) -Acid and Advanced Lead-Acid batteries
- Ni-Cadmium batteries
- Ni-Metal Hydride batteries
- Li-Ion batteries
- Na-Sulfur batteries
- Na-Ni Chloride batteries
- Li-ion capacitors

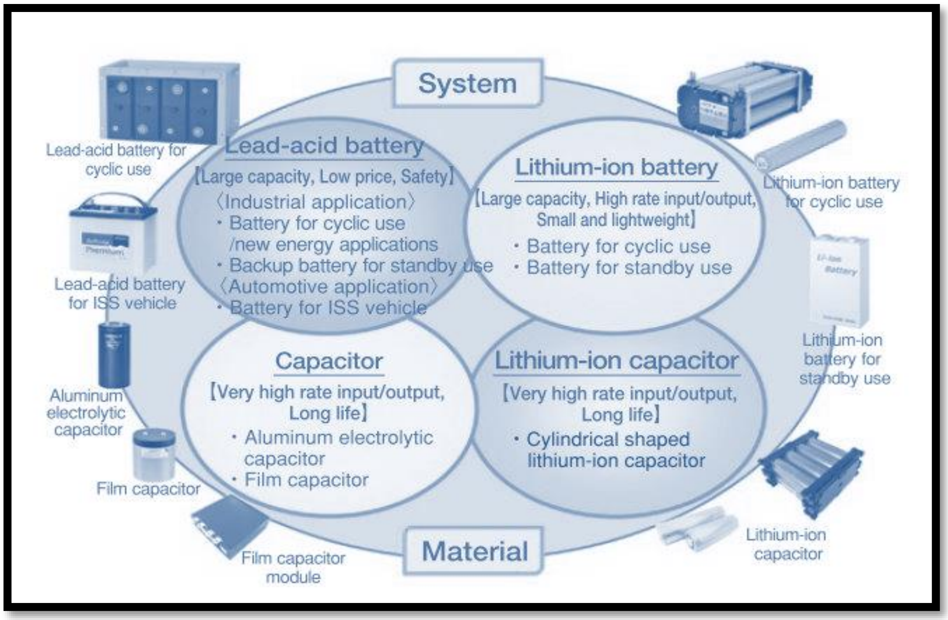

Fig 1.4) Different types of batteries used in EES[4]

Super capacitor: Another application of electrical energy storage is super capacitor (gold cap, super cap, ultra capacitor) which works on the similar principle of the conversion of chemical into electrical energy. This device can be used to store potential of an electric field. It has a gigantic capacitance limit in contrast to the other capacitors. Such type of device is still under research and when it will go to completion, it will have aptness to store much more times the energy per unit volume as in comparison to the batteries [5]. Moreover, it has ability to deliver and accept charge more rapidly than that of batteries.

1.2.2) Mechanical Energy Storage: (MES) Due to the imbalance between energy consumption and production, mechanical and electrical energy have become prime concern of the modern world. Mechanical energy storage systems include the following three types:

- Using gravitational force
- Pressure difference energy storage
- Fly wheel storage

Hydropower plants use the principles of gravitational energy storage; basically there are two reservoirs an upper reservoir and a lower one. In pumped hydroelectric storage, energy is stored in the form of water in an upper reservoir and it is pumped into the lower reservoir i.e. from higher elevation to lower elevation as shown in Fig 1.5. When there is a high demand of energy, electricity is generated in the same way as in conventional hydro stations by using this stored water. This stored water is used to run the turbines that carry out hydro power generation. When the energy is required in low amount i.e. during the nights and weekends the upper reservoir is again filled by pumping water to the upper reservoir. Now a day's reversible pump-turbine /motor-generator are more common and more beneficial as they are more reliable in balancing loads in power systems.

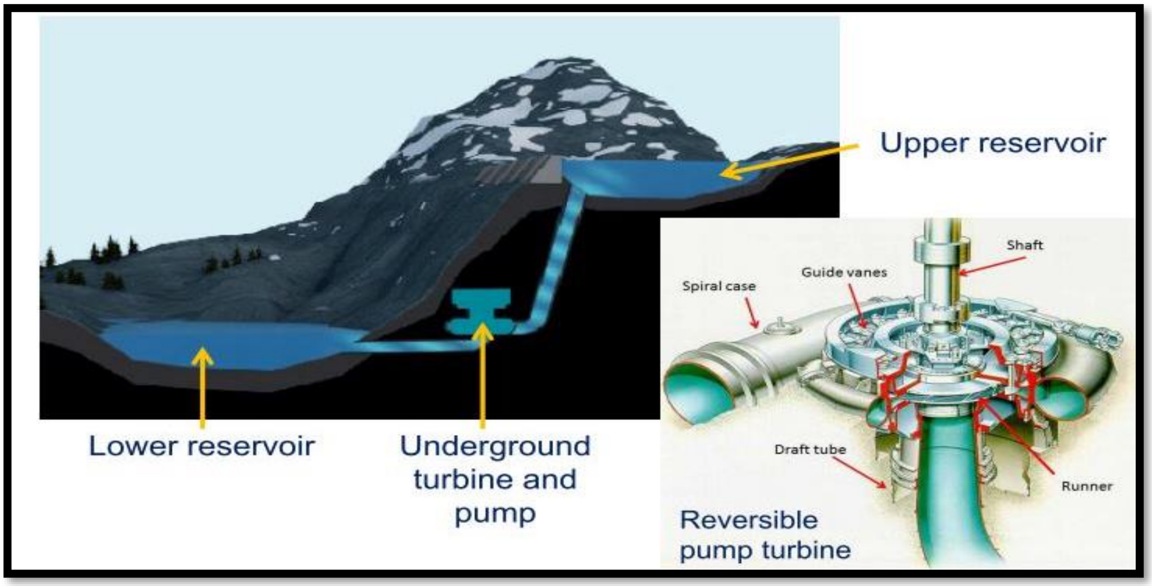

Fig 1.5) Principle of Pumped Hydro Energy Storage System [13]

The second type of mechanical energy storage which uses **Compressed air energy storage systems** (CAES). It is essentially the same as gas turbine systems with an addition of cavern for the storage of compressed air. During the night the air is compressed into the carven in a pressure range of 40 to 80 bars, which in turn is used to run the gas turbine in the day time as shown in figure 1.6. The major drawback associated with compressed air energy storage is its dependence on gas fossil fuels, moreover certain geological conditions are required to form a carven which are not found at all places.

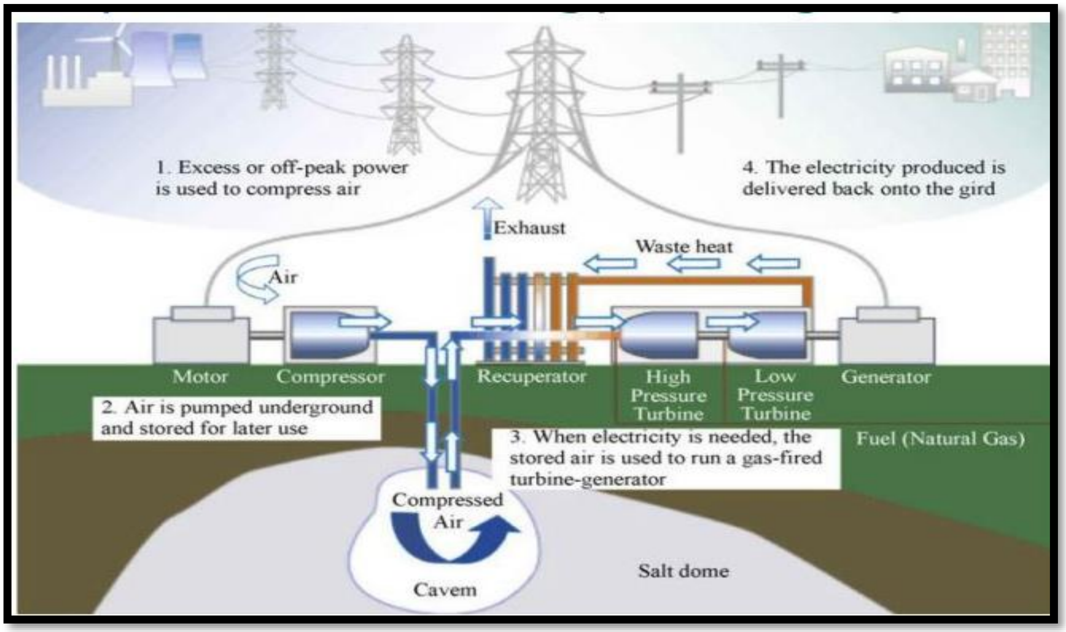

Fig 1.6) Compressed air energy storage systems (CAES) [14]

The third type of mechanical energy storage is **Flywheel energy storage systems** (FESS)**,** in which electrical energy is stored in form of kinetic energy. As we know the energy due to motion is known as kinetic energy. In FESS this motion is associated with a spinning mass, called rotor, which spins around a smooth enclosure. In modern high-speed flywheel energy storage system, a massive rotating cylinder supported on a stator by magnetically soared bearings is used, which rotates around enclosure when power generation is required as shown in figure 1.7.

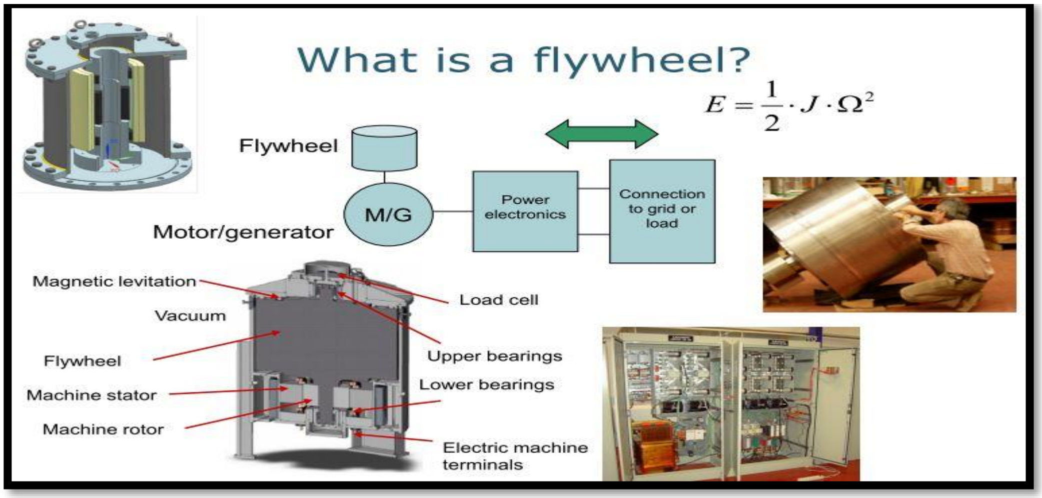

Fig1.7) Flywheel energy storage systems (FESS)

To convert kinetic energy into electrical energy the flywheel is connected to a motor-generator which interacts with the grid through modern power electronics. It is a highly advantageous storage system because of long life, low maintenance requirement and environmental friendly.

1.2.3) Thermal Energy Storage: The word “Thermal” is enough for us to understand the type of storage. As “Thermal” means something related to heat, it shows us that thermal energy storage (TES) is method of storing heat energy. As shown above, this heat storage is further divided into three types which are explained below.

a) **Sensible Energy Storage** (SES) is the most commonly applied type of thermal energy that has been applied since years, at both commercial and domestic level. In the mediums, such as water, rocks, sand etc, heat is stored by changing the temperature of the medium. The medium with high value of specific heat are preferred for such type of storage. There are two types of SES based on mediums, solid and liquid

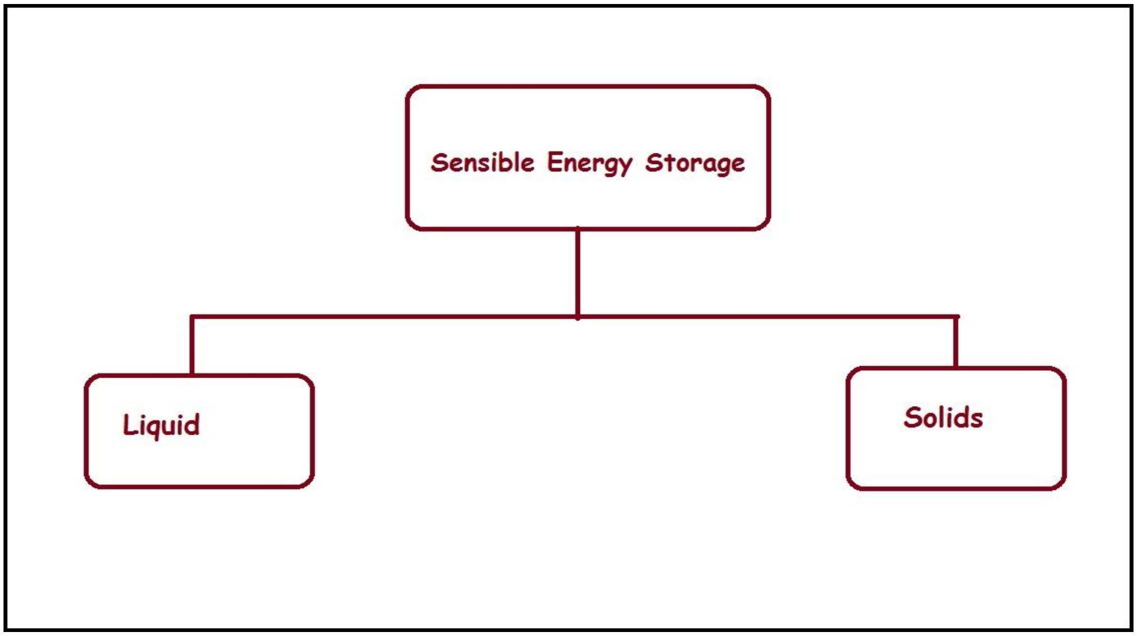

Fig 1.8) Types of sensible energy storage.

Coming towards liquids, we see that water has high value of specific heat capacity (4.186 joule/gram °C), moreover, it is the only medium that is available on the largest scale and is one of the cheapest medium. So it is used in hot water tanks for domestic purpose.

Hot water tank consists of a tank which stores water. This tank is highly insulated so that it may not lose heat. It is further connected to the heater, fossil fuel burner, furnace or solar heating instruments to heat that water at the desired temperature. This water is then used at domestic level or commercial level for laundry, bathing or washing.

Fig 1.9) Hot water tank connected with furnace [15]

The application of the other type of storage is **underground storage**. It is mainly for seasonal storage. It contains soil, sand or rocks as the medium of storage for both cooling and heating process. Water is an ideal energy carrier, so water is used as heat transfer fluid (HTF). It is taken into the ground and is carried out by U-shaped pipes which are merged into the ground by boreholes [6]. In the countries of too much cold weather, buildings and homes are heated by this application. Cold water is driven into the ground which absorbs heat from the medium and brings it back to heat exchanger. This heat exchanger absorbs heat from hot water, return it back to the ground again and along with this, it also takes the heat to heat pump and auxiliary boiler. In this way heat is then transferred to the buildings. The below diagram easily illustrates the phenomenon with the labeling.

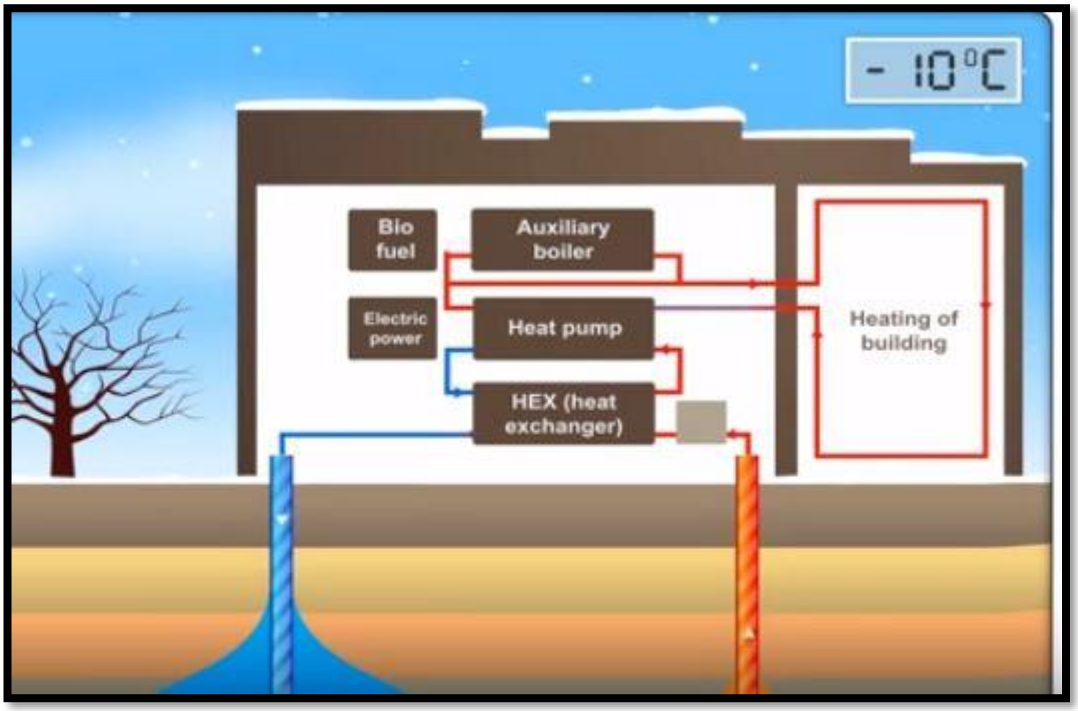

Fig 1.10) Mechanism of heating buildings is shown as an application of sensible energy storage.

While when the temperature outside is high (near 30°C), the auxiliary boiler and heat pump is closed. Cycle starts to run in opposite direction and now instead of heating, it starts to cool down the building.

Hence in this way we see there are a lot of advantages of SES as it is cheap, easily available and least complicated. Along with the advantages, it also has many disadvantages as it demands a large quantity of material and volume. Moreover, it cannot store energy at constant temperature [7]. So it leads us to think about latent energy storage.

b) **<u>Latent Energy Storage</u>** (LES) is based on the principle that some materials have ability to release or absorb energy when they change their physical state, e.g. solid to liquid, solid to gas, liquid to gas. This absorption of energy can help us to charge the material while the release of energy gives us the idea of discharging of the energy storage material. Hence, LES is the phase change storage of the material (PCM). It is also much applied type of storage and has many benefits. Although, it is not that simple like SES yet it does not demand large quantity or volume of storage material and has greater energy storage density at similar temperature as compared to SES which can easily be shown.

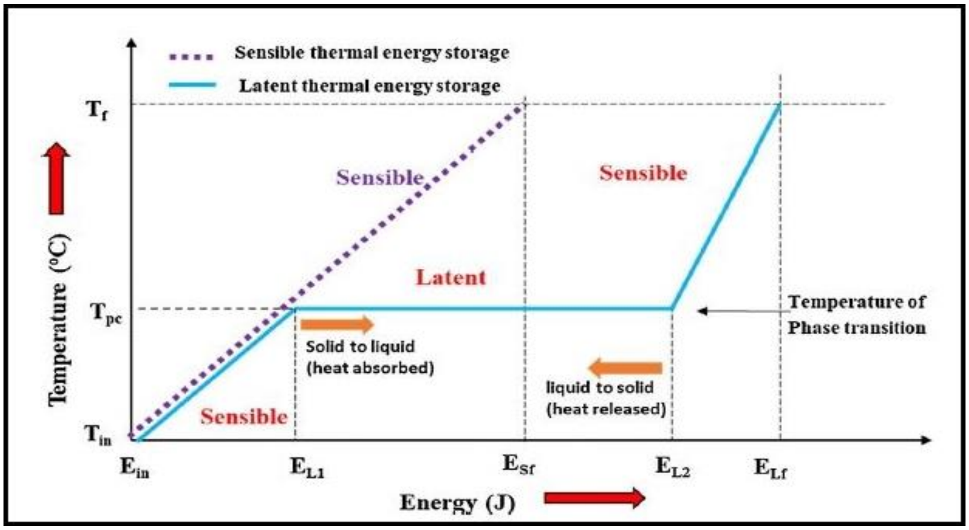

Fig 1.11) Comparison of energy storage of SES and LES [8]

LES has many applications but first the selection of materials is quite necessary. The material recommended for LES should have high thermal conductivity and latent heat of transition. It should be friendly with the environment and should not be hazardous for the people too. Moreover, it should have some economic benefits like low cost, easily available in market etc.

Now coming towards the materials, LES is divided into two main types, e.g. organic PCM's which contains paraffin wax and fatty acids and inorganic PCM's which includes salt hydrates and metallics.

Organic PCM's have great storage density even with small boiling and melting point. Paraffin wax is a soft solid with the carbon and hydrogen chains and is extracted generally from petroleum or coal. It is a colorless or white solid with the carbon atoms ranging from 20-40 (C_nH_{2n+2}). Its heat of fusion and melting temperature increases with the increase in its chain. In LES, paraffin wax is supported in many applications as it has high specific heat of fusion due to which it undergoes excellent energy storage capacity.

Inorganic PCM's are also not behind the organic PCM's. They have high thermal conductivity, latent heat of fusion, energy storage capacity and are most researched TES materials. Salt hydrates especially plays promising role for such energy storage. They have water of crystallization and are the cheapest PCM's. They include charging and discharging processes by a reversible chemical reaction. In charging, the hydrated salt is given the heat which dehydrates it and forms dehydrated salt along with water molecules. These water molecules are then stored for discharging process. Charging reaction is given as.

$$\textbf{Salt.nH}_2\textbf{O + Heat} \quad \rightarrow \quad \textbf{Salt + nH}_2\textbf{O}$$

While in discharging process this dehydrated water is again combined with the salt which again produces salt hydrate and releases heat in return. In this way we get back that heat which we provided earlier and heat is stored for a medium time limit. The discharging reaction is given as:

$$\textbf{Salt + nH}_2\textbf{O} \quad \rightarrow \quad \textbf{Salt.nH}_2\textbf{O + Heat}$$

Thermo physical properties of some salts are given below which proves salt hydrates to be excellent PCM's.

Salts	**Melting Points (°C)**	**Heat of fusion (kJ-kg^{-1})**	**Density (kg-m^{-3})**
$CaCl_2.6H_2O$	29.3	208	1802 at 24°C
$Na_2SO_4.10H_2O$	33.1	254	1485 at 24°C
$Zn(NO_3)_2.6H_2O$	36.4	147	1828 at 36°C
$Ba(OH)_2.8H_2O$	78	267	2070 at 24°C
$Mg(NO_3)_2.6H_2O$	88	163.1	1636
$NaC_2H_3O_2.3H_2O$	137	172	1450

Table 1.1) Thermo-physical properties of some salt [8]

Disadvantages: Along with benefits, there are also many disadvantages of LES which urges us to think about thermo-chemical energy storage (TCES). The disadvantages of using such storage are given below.

- Corrosion
- Lack of thermal stability
- Under-cooling
- Phase separation
- Storage duration is not long.

Such disadvantages lead us to think about TCES as it promises us to have long time storage duration.

c) **Thermo-Chemical Energy Storage:** Now a days the attention of scientists is on this area which, up till now was the least researched energy storage field. TCES ensures us to have high energy density which can be stored for a long period. If scientists become able to make it applicable, it will have ability to change the world. It has more energy storage capacity than that of LES and SES and also has ability to store energy for a larger period than that of others. That's why it intrigues the developers to work on this area and make it applicable. The difference between SES, LES and TCES is given below in table 1.2.

Storage Type	**SES**	**LES**	**TCES**
Gravimetric energy density (kWh-kg^{-1} of material)	~0.02-0.05	~0.05-0.1	~0.05-1.00
Maturity	Industrial scale	Pilot scale	Laboratory scale
Storage period	Limited (Heat loss)	Limited (Heat loss)	Theoretically unlimited
Transport	Small distance	Small distance	Theoretically unlimited distance
Technology	Simple	Medium	Complex
Disadvantages	Consequential heat loss, large volume needed	Heat loss, corrosives the material, low heat conductivity	High cost, technically complex

Table 1.2) Difference between SES, LES and TCES [9]

What is Thermo-chemical Energy Storage?

We had been studying chemistry since we were children, we studied some thermo-chemical-reactions in which heat is absorbed or released. As clear from the word, “Therm” means heat and “chemical” represents the chemical reaction. So, the chemical reactions which absorb or evolve heat during the reactant product conversion are known as thermo-chemical-reactions. For example:

$$A_{(s)} + B_{(g)} \quad \leftrightarrow \quad AB_{(s)} + \text{Heat}$$

These are the reversible reactions and using these reactions, scientists came up with an idea to store heat energy. There are two processes, charging and discharging.[10]

Charging: In charging, a solid is given heat so that it may store it and transforms itself into another solid with the emission of a gas.

$$AB_{(s)} + \text{Heat} \quad \rightarrow \quad A_{(s)} + B_{(g)}$$

Then this $A_{(s)}$ is stored or preserved which can be used later to gain that heat again by discharging process while the emitted gas can be used with further beneficial ideas.

Discharging: The discharging of the system is nothing else but the other side of the reaction. When the solid and the gas produced as the products of the above charging process are again reacted together, they release heat, which we call as the discharging of the reaction.

$$A_{(s)} + B_{(g)} \quad \rightarrow \quad AB_{(s)} + \text{Heat}$$

This is the main principle of TCES.

There are many solid gas reactions like this which can help us to store energy which includes metal sulfates, metal hydroxides, metal carbonates and pure metal oxides etc. List of many of these compounds is given below in tables one by one, which can help us to store energy [9] [11] [12].

Metal Sulfates are researched a lot in this field as they have highest enthalpies as compared to metal carbonates or metal hydroxides. In metal sulfates, there are some compounds like ASO_4 which are heated to excrete SO_3 to produce AO (metal oxide). Some examples of metal sulfates are given below in the table.

Chemical Materials	**Temperature (°C)**	**Reaction Enthalpies (kJ/mol)**	**Gravimetric Energy Density (kJ/kg)**
$MgSO_4/MgO$	1360	248.7	2066.2
$MnSO_4/MnO$	1215	257.04	1702.2
$FeSO_4/FeO$	1165	247.5	1629.3
$CuSO_4/CuO$	1130	230.1	1485
$CoSO_4/CoO$	930	202.3	1267.5

Table 1.3) Important metal sulfates for TCES[9]

Metal Carbonates are other important candidates to TCES. Their reaction enthalpies are lower than sulfates but they are really useful for some conditions where we can negotiate large energy storage density. In metal carbonates, ACO_3 is provided with the required heat to produce metal oxide similarly but with the excretion of carbon dioxide gas. This carbon dioxide gas is then again reacted with metal oxide to gain heat stored before. Some important metal oxides are given below.

Chemical Materials	**Temperature (°C)**	**Reaction Enthalpies (kJ/mol)**	**Gravimetric Energy Density (kJ/kg)**
$CaCO_3/CaO$	885	165.83	1656.8
$SrCO_3/SrO$	1220	1370.6	1370.6
$MgCO_3/MgO$	300	1174	1174
$BaCO_3/BaO$	1555	836.6	836.6
$CdCO_3/CdO$	290	560.1	560.1

Table 1.4) Some important metal carbonates[9]

Metal Hydroxides are other useful TCES materials which are most researched and easy to manage with the benefit of friendly to the environment. Most of these are easily available. In metal hydroxides a hydroxyl group is attached with the metal which on heating, breaks the bond and gives water (steam) with metal oxide. This metal oxide is then stored and again reacted with steam to get heat back. Following are the metal hydroxides given below in the table.

Chemical Materials	**Temperature (°C)**	**Reaction Enthalpies (kJ/mol)**	**Gravimetric Energy Density (kJ/kg)**
$Ca(OH)_2/CaO$	515	104.4	1352
$Mg(OH)_2/MgO$	265	77.7	1333
$Be(OH)_2/BeO$	70	51.2	1191
$Mn(OH)_2/MnO$	190	67.07	754
$Ba(OH)_2/BaO$	1005	93.4	545.4

Table 1.5) Some important metal hydroxides[9]

Pure Metal Oxides are one of the important TCES materials. They are important mainly because of cobalt oxide and manganese oxide as they have high enthalpies and high energy storage density. But cobalt oxide also has some disadvantages as it is costly and has potential to cause cancer. These reactions are also reversible and they work by oxidation reduction process.

$$\mathbf{AO_{(OX)} + Heat \quad \leftrightarrow \quad AO_{(Red)} + \tfrac{1}{2}O_2}$$

Some important pure metal oxides with their temperature of reaction, enthalpies and gravimetric energy densities are shown below in the table which proves its importance on research scale.

Chemical Materials	**Temperature (°C)**	**Reaction Enthalpies (kJ/mol)**	**Gravimetric Energy Density (kJ/kg)**
Co_3O_4/CoO	935	196.5	816.1
Mn_3O_4/MnO	1700	194.6	850.6
CuO/Cu_2O	1115	64.4	810.2
Li_2O_2/Li_2O	145	34.2	745.9
Fe_2O_3/Fe_3O_4	1360	232.6	485.6

Table 1.6) Some important pure metal oxides for TCES[9]

These were the important candidates for TCES and one can see that they have high enthalpies and high energy storage densities so they can help a lot for storing energy. Moreover, if we take table 1.2 into account we see a clear difference between SES, LES and TCES. TCES is far better than others in many aspects even if it has some disadvantages also. So in the coming chapters we will try to understand TCES better, sort out problems and will show how to solve those problems with the help of literature review.

1.3) Motivation:

Out of all the types of energy storage, thermo chemical energy storage is of great interest as it has many benefits and if applicable, has the ability to make a gigantic change in industry. It has greatest energy storage density and temperature range as compared to the thermal energy storage techniques. One of the other important benefits of this energy storage type is its transport ability.

1.4) Objective:

Main objective of this thesis is to work on thermo chemical energy storage, screen out the best suitable material for this type of energy storage and enhance its thermal properties and ability to store energy.

Chapter 2

Literature Review

While doing any research work, literature is something that helps us intensify the effort we put into our work. It guides us; gives us direction, concepts and learning related to any previous work done on that field. By literature, we basically mean the research papers published in journals, books, conference papers or reports which help us discover new things. Talking about the energy storage, many papers have been published in this area over the past few decades which can help one a lot.

2.1) Selection of Materials:

Energy storage is the most fascinating field now a days so it intrigues one to think over it. But the problem is to select a specific energy storage field out of many types which are elaborated earlier in first chapter. For electrical and mechanical energy storage, many papers can be found and a lot of work has already been done. Moreover, many applications have already shown their importance for such storage systems as batteries and capacitors have already taken their place in market while flywheels have also been applied in advanced non-polluting sustainable power supplies [16]. These energy storages are expensive and complex too. But, trying to think about something new and cheap with great energy storage gives us no choice other than to think about the sun, which provides us great energy on daily basis, of course for free. So TES is a preferable area of research that gets attention of many researchers in this era.

TES is not a new field; a lot of work has been done in it but review of all the types of TES like SES, LES and TCES, gives preference to TCES as it shows great importance. By comparing these entire types one can have an intriguing power to select TCES as it is cheap, new as not applied on industrial or domestic scale, safe for environment and have great energy storage capacity if compared to others. Yet it also has some disadvantages of being complex system, as it is not much researched, so it takes attention of the researchers. Basic review on the comparison of these three types is given below in the table 2.1.

Important selective criteria basis.	**SES**	**LES**	**TCES**
Energy storage density	Smaller than LES and TCES	Greater than SES but smaller than TCES	High energy density
Range of Temperature	110°C for water tanks. 50°C for aquifers. 400°C for concrete	20-40°C for paraffin. 30-80°C for salt hydrates.	Have range of more than 1000°C
Capacity duration to store energy	Short time storage capacity	Short time storage capacity, but still greater than SES	Can store for long duration
Maturity	Applied on industrial and domestic scale	Applied on pilot scale	Not applied, on initial stages
System complexity	Simple	Average	Complex system
Applications	Hot water tanks, underground storage	Heat and cold storage units, building walls, PCM shutters	Not applied yet.
Advantages	Easiest way to store energy, can be applied easily at domestic level, low cost, reliable.	Economically abundant, available and cost effective, high density, good heat transfer.	Highest energy density, better heat transfer, highest storage duration period, minimum heat losses
Disadvantages	High volume required for storage, notable heat loss	Material becomes corrosive, small heat conductivity, notable heat losses.	Costly, complex system.

Table 2.1) Comparison of SES, LES and TCES for selection [17][18][11]

The reviews on SES, LES and TCES can help making the above table to draw some conclusions. By comparing, TCES shows a better temperature range, it is not yet applied and a lot of work is needed to be done in this field. So, one can take part to put its efforts in TCES.

As stated in the previous chapter, TCES is based on thermo-chemical reactions, so the selection of materials is a major part for everyone. Selection of a material is always difficult when there are a lot of options. While selecting a material, a lot of things have to be considered like thermal conductivity, friendly behavior with environment, cost of the material, safeness of the material for skin and temperature range which can be easily achievable. For this, literature can help us on the screening of materials [9] for TCES in which information about all the materials is given. Selection of some of the materials on the basis of cheapness, lab scale achievable temperature range, good enthalpy and storage density is necessary. So, one can manage to screen some materials which are considerable and are given below.

Material	**Temperature Range (°C)**	**Enthalpy (kJ/mol)**	**Energy storage Density (kJ/kg)**
$Ca(OH)_2/CaO$	515	104.4	1352
$CuSO_4/CuO$	930	202.3	1267.5
$CaCO_3/CaO$	850	165.8	1656.8

Table 2.2) Selected Candidates for TCES [9]

These three were the mainly selected candidates as they have good energy storage density and their temperature range is easily achievable on lab scale.

First of all comparing $Ca(OH)_2/CaO$ and $CuSO_4/CuO$ one can see that first system has more energy storage density than that of second one even if less heat is provided. Providing 515°C of temperature is giving us 1352 kJ/kg energy storage density while in the other case providing more heat to the $CuSO_4/CuO$ system yields less energy storage density. Secondly, considering the second system, i.e

$$\mathbf{CuSO_4 + Heat \leftrightarrow CuO + SO_3}$$

One can see that SO_3 gas is emitted in that reaction and properties of SO_3 gas are not very friendly as it is a pollutant, and primary agent of acid rain. Moreover, it is highly corrosive and hygroscopic gas so it can cause significant burns on inhalation. So $Ca(OH)_2/CaO$ system is preferable over $CuSO_4/CuO$.

But using the third system, i-e, $CaCO_3$/CaO, can also have some considerable disadvantages. Our Earth is already facing a lot of problems due to global warming caused by CO_2 gas. It is playing a dangerous role for us. Now, the system reaction is given as,

$$\mathbf{CaCO_3 + Heat \leftrightarrow CaO + CO_2}$$

One can see that a large amount of CO_2 will be emitted from the following reaction which has a bad impact on the atmosphere. It will increase earth's temperature and will play a role to enlarge global warming. Moreover, it is more time taking than that of our first system because on lab scale, 515°C is easily achievable than that of 815°C which we usually achieve at the rate of 5°C/min. That's why it will also take more of our time.

Hence, selection of material for energy storage was done by encountering literature review. Now is the time to study and make understanding of this system.

2.2) $Ca(OH)_2$/CaO System:

As an application of TCES, a lot of work has been done on this system. First step is to know about its cycling stability, de-hydration, re-hydration, reaction kinetics and reactor. For this, F. Schaube has done a lot of work in which a sample of 60g has been experimented with 200-520°C temperature and appropriate mixture of steam and nitrogen [19], while final results from experiments are investigated with the help of theoretical models [20]. To check the cycling stability of the system, a test system has been constructed which includes a steam generator to generate steam out of water, nitrogen as HTF, mixing chamber in which steam and nitrogen is mixed and mainly a reactor in which de-re hydration is occurred.

Using this test system, cycling stability of the reaction was confirmed up to 25 cycles which was a good sign for TCES but there were still many problems. In the conclusion by F Schaube [19], one of the main problems was the agglomerations of the powder bed. After each cycle agglomerations are produced in the powder and they keep on increasing from cycle to cycle. The figure below shows us the condition of the reaction bed due to agglomeration after four cycles on laboratory scale.

Fig 2.1) Agglomeration after four cycles [24]

Other main problem was the low thermal conductivity of the system. In her another paper she reported thermal conductivity of $Ca(OH)_2$ to be less than 0.1 W/mK which greatly effects the rate of reaction[21]. This paper also concluded that there are a lot of limitations due to such low thermal conductivity as transport of heat from the powder bed become really challenging. To understand the importance of these problems we first need to understand the solid gas reactions in porous materials.

2.3) Solid-Gas Reactions:

Solid gas reactions in porous materials basically occur in three stages [22]:

- Mass Transfer
- Heat Transfer
- Structural changes

2.3.1) Mass Transfer:

Mass flow usually happens in three stages. First of all the gas phase mass is transferred from the bulk of the gas stream to the solid powder. After that, the process of diffusion takes place between the reactants. The gas molecules start diffusion through the pores of the solid material and adsorb on the surface of the solids.

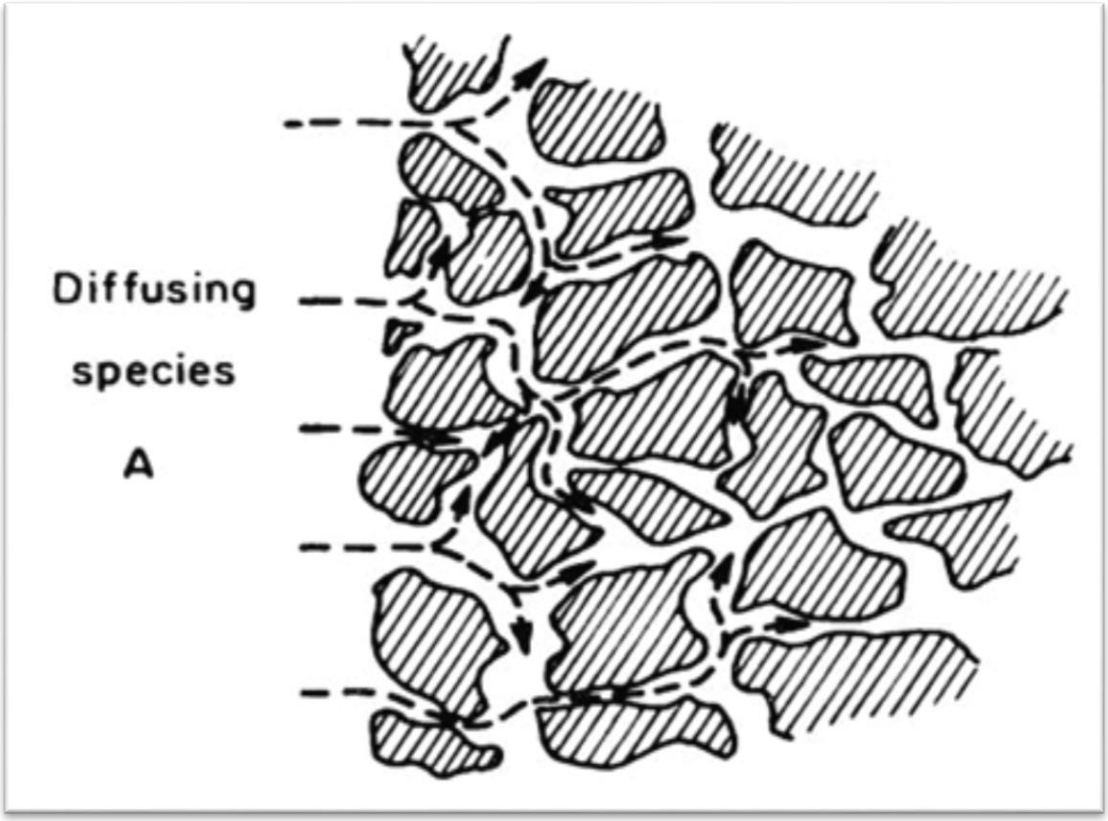

Fig 2.2) Diffusion of gas molecules [22]

Here on the surface, they start the chemical reaction and formation of reactants into products happens. After the reaction, again diffusion takes place and the un-reacted gas molecules diffuse themselves out of the solid matrix again to recombine into the gas stream. In this way mass transfer takes place in solid-gas reactions. Here the diffusion of the gas molecules is mainly of our concern.

2.3.2) Heat Transfer:

Heat is usually exchanged in all exothermic or endothermic reactions. Here in our applications of TCES, we see that our reaction is also endo and exothermic. In porous materials, heat is transferred in two ways.

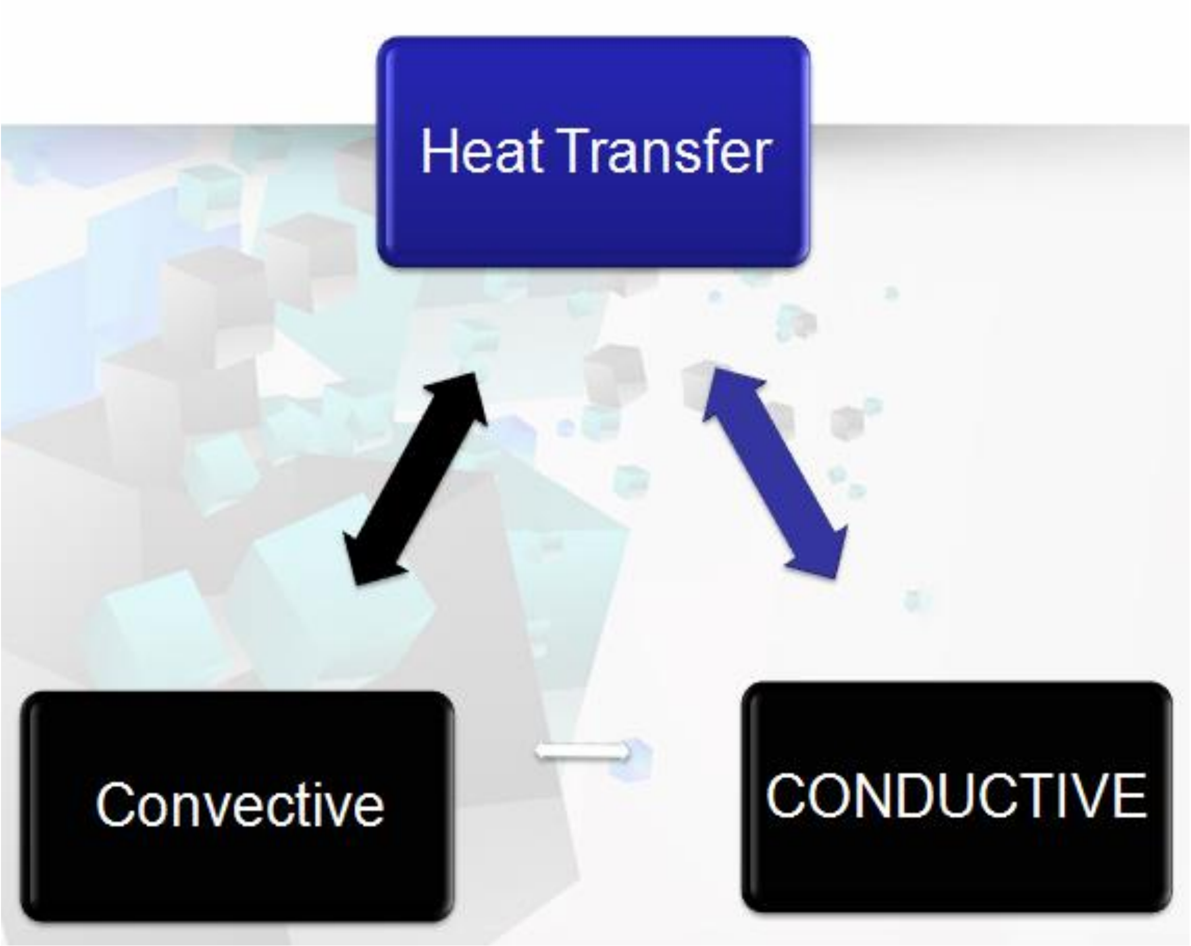

Fig 2.3) Heat Transfer Methods

First one is convection of heat from gaseous stream to the solid or from solid product to the HTF and when heat is transferred from gas to solid, second way of heat transfer begins, which is the conduction of heat from the reactant product matrix.

2.3.3) Structural Changes:

Different types of structural changes can happen in such reactions. These are for example sintering, swelling, softening or change in porosity etc. But our concern is with sintering which is a phenomenon by which porous compact increases its density at elevated temperature before melting point which results in the decrease of the pore size. Sintering occurs in different steps which can be shown below.

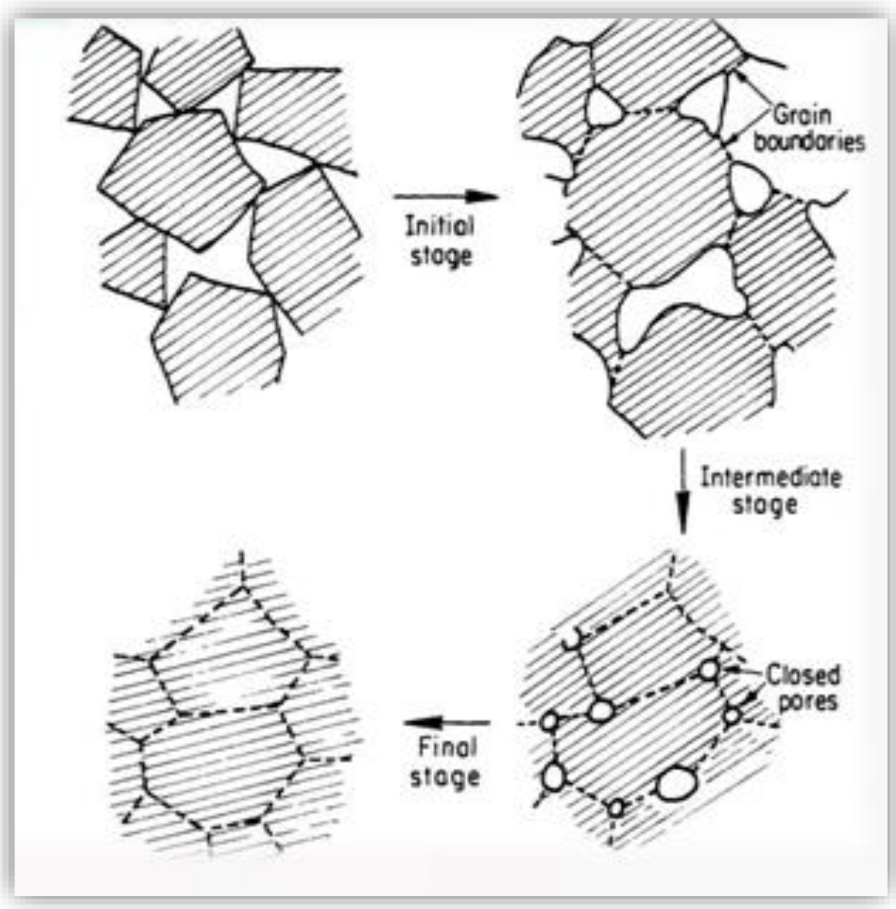

Fig 2.4) Sintering of material [22]

Now we see that this mass transfer, heat transfer and structural changes make our better understanding on the problem of agglomerations and importance of good thermal conductivity of powder to gain maximum heat. Problem of agglomeration is much researched and solved to some extent but improving thermal conductivity is still very challenging and literature can help one to give some ideas to solve this problem.

2.4) Improvement of Thermal Conductivity:

From above discussion, we have seen that heat transfers by conduction of solid matrices which shows us the importance of conductivity of the material. If material has low thermal conductivity, it means we will have to suffer from great heat loses during both charging and discharging process. During charging process, we provide heat to $Ca(OH)_2$, which conducts heat from the surface to the inner part of the matrix. Whereas during discharging process, when steam reacts with CaO, it converts itself to $Ca(OH)_2$ and this conversion results in the production of heat. In order to get this heat back for further use heat transfer fluid is normally used. To provide maximum heat to the heat transfer fluid the powder should have good thermal conductivity otherwise there will be great thermal losses. From both charging and discharging process a conclusion can be drawn that thermal conductivity of $Ca(OH)_2$ is playing a key role in the reaction kinetics but unluckily thermal conductivity of $Ca(OH)_2$ is very low which is reported to be 0.1 W/mK[21]. It means during both charging and discharging processes, the system has to suffer from great heat loses and slow reaction rate due to low thermal conductivity so there should be ways to improve thermal conductivity of $Ca(OH)_2$.

Method of doping metals is widely used to enhance thermal properties of materials in many applications [23]. This defect engineering is playing a vital role in industry to change properties of the materials. The idea of enhancing thermal conductivity of $Ca(OH)_2$ was mainly conceived from a study in which different metals are doped in $Ca(OH)_2$ to improve its thermal properties and it was seen that doping metals in $Ca(OH)_2$ greatly impacts the thermal properties of $Ca(OH)_2$ powder [23]. So, in our work, we have doped 5% Nickel (Ni), Zinc (Zn) and Strontium (Sr) in $Ca(OH)_2$ to enhance thermal conductivity of the material and the impact is seen in the thermal properties of $Ca(OH)_2$ which we will discuss in results section. Now the question arises that why we are doping Ni, Zn and Sr instead of any other metals? There are different solid reasons for that which is explained below.

First of all there exists Hume Rothery rule for doping of the materials which tells us that we cannot dope every element in any materials. There are some requirements for both substitutional and interstitial doping of the elements.

- **For substitutional doping**, the difference in atomic radii of both solute and solvent must not be greater than 15%.
- Both solute and solvent should have similar crystal structure.
- Solute and solvent should have same valency in order to complete solubility, otherwise higher valency metal will dissolve in the lower one.
- Parent and dopant element should have similar electro negativity otherwise metals form inter metallic compounds if electro negativity difference is too large.

- **For interstitial doping,** parent atomic radii should not be greater than 59% of that of dopant atomic radii.
- Electro negativity should be similar.
- Both should have wide range of composition.

Second reason to dope Ni, Zn and Sr was to study their effect in the improvement of thermal properties. Ni and Zn are pure metals and they are good conductors of heat while Sr is not a pure metal, it is basically an alkaline earth metal just like calcium. So the idea was to study the impact of replacing one alkaline earth metal with the other. So, we doped these three atoms in $Ca(OH)_2$.

Some of the properties required relatively are given below in the table:

Sr.No	**Element**	**Thermal Conductivity (W/mK)**	**Valency**	**Crystal Structure**	**Atomic Radii (Å)**	**Electro negativity**
1	Calcium	200	+2	Face centered cubic	1.94	1
2	Nickel	91	+1,+2,+3,+4	Face centered cubic	1.49	1.9
3	Strontium	35	+2	Face centered cubic	2.19	0.95
4	Zn	120	+2	Simple hexagonal	1.42	1.65

Table 2.3) Properties of Ca, Ni, Sr and Zn

Experimental technique of simple $Ca(OH)_2$ and doped $Ca(OH)_2$ is shown in the next chapter along with the used characterizing techniques by which we will discuss our results further.

Chapter 3

Experimental setup

3.1) Methods for synthesis:

All the methods have their own importance depending upon the final desired product. Any material can be synthesized with more than one method but usually cheapest and easiest method is preferred to use. A basic and short review on such methods is given below to make a better understanding towards our way of synthesis used in this research.

All these methods are divided into two main types:

3.1.1) Bottom Up Approach:

Bottom up approach is a way of synthesizing any material from even smaller particles. As clear from the name “Bottom Up” we start from the bottom and go further by building up the material; atom by atom or molecule by molecule. We start from a single atom or molecule and add them to make our required product. This approach includes many methods like:

- Sol-gel Method.
- Co-precipitation method.
- Hydro-thermal method.
- Double solvent sol-gel method.

3.1.2) Top Down Approach:

Top down approach includes the breakdown of the atoms or molecules. We have bigger particle and we make smaller particle by this method. These particles are obtained by using methods such as cutting, carving, calcinations or molding. A variety of machinery and electronic devices have been fabricated using these techniques. Some of the main methods of top down approach are given below.

- Thermal decomposition
- Lithography

- Laser ablation
- Ball milling

Our first task was to synthesis $Ca(OH)_2$ powder for which we have used sol-gel method as it is an easy method which do not require any high temperature and it also saves time.

3.2) Sol-gel Method:

As mentioned above, sol-gel method is a way of manufacturing solid particles from tiny particles. It is one of the most used methods, especially for the manufacturing of metal oxides. As from the word “sol-gel” sol refers to the colloidal solution and gel refers to the precipitant that appears like a gel. In this method, there is a monomer which basically acts as a precursor and produces colloidal solution and a precipitant which makes a gel like material. The formation of final product undergoes in few steps like hydrolysis, condensation and finally drying [25].

In our research, we have first synthesized $Ca(OH)_2$ powder by sol-gel method and then we have doped this $Ca(OH)_2$ powder with Ni, Sr and Zn with the 5% doping to get the final product of the form $Ca_{1-x}A_x(OH)_2$ where x=5 and A is doping element. These doping are also governed by sol-gel method.

3.3) Synthesis:

In our research, as mentioned above, we have first synthesized $Ca(OH)_2$ powder and then we doped Ni, Sr and Zn. Materials used for these syntheses are mentioned below.

3.3.1) Materials:

To get best results, it was made sure that all the materials were of research grade and there was no compromise taken on the quality of the materials. For the synthesis of $Ca(OH)_2$, ethylene glycol 99.9% (Merck) as medium, calcium nitrate tetrahydrate $Ca(NO_3)_2.4H_2O$ (Merck) as precursor, sodium hydroxide NaOH 99% (Merck) as precipitant and Distilled water were used. After synthesis of $Ca(OH)_2$, $CaCl_2$, $ZnCl_2$, $SrCl_2$ and $NiCl_2$ were used for doping along with ethylene glycol as medium and NaOH as precipitant.

3.3.2) Synthesis of $Ca(OH)_2$:

Synthesis of $Ca(OH)_2$ is governed by the following chemical reaction:

$$Ca(NO_3)_2(aq) + 2NaOH(aq) \rightarrow Ca(OH)_2(s) + 2NaNO_3(aq)$$

We see that one mole of $Ca(NO_3)_2$ reacts with 2 moles of NaOH and produces 1 mole of $Ca(OH)_2$ so we did it with the same ratio of moles. 41g (0.25 mol) $Ca(NO_3)_2.4H_2O$ (precursor) was first added in 90ml ethylene glycol which acted as a medium. 20g (0.5 mol) NaOH (90ml) was then added to the above solution under vigorous stirring which proved to be a precipitant. This solution was kept on stirring for 15 minutes. After this, the gel solution was kept untouched on static position for about 5 hours. This gel solution was then washed by centrifugation under 4000 rpm for 6 min of duration. The obtained particles were then dried in vacuum oven at 50°C for 5 hours. After drying, the powder was collected and it appeared to be 16.14g which is about 0.22 moles while theoretical yield was of 0.25 moles. Obviously, this loss must be happened in handling and washing. [26]

3.3.3) Synthesis of doped $Ca(OH)_2$:

For doped $Ca(OH)_2$, $CaCl_2$ was used as a precursor instead of calcium nitrate tetra hydrate. 20g $CaCl_2$ and 5% $NiCl_2$ (1.16g), $SrCl_2$ (1.42g) and $ZnCl_2$ (1.22g) were mixed respectively in the presence of ethylene glycol [23]. Then 14.4 g (65ml) NaOH was added in it drop by drop and gel formation was observed. These solutions were kept on stirring for 20 minutes and after that it was left static for 5 hours. The obtained solution was mixture of all the products and some non reacted reactants so it was then washed with distilled water by centrifugation. Gained particle solution was then dried at 50°C to get powder.

These prepared samples were passed out from different tests to get attested for our system. X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF) were done to confirm doping. FTIR was done to study bonds and then samples were passed through TGA and hot plate method of thermal conductivity to study thermal properties of all the samples.

3.4) Characterization Techniques:

One main part of the experimentation is the characterization of the item made in the lab. These characterizations give us different knowledge about our final product depending on the type of characterization. So far, science has made some outclass achievements and hence there are plenty of characterization techniques available for us. These characterization techniques can provide us the knowledge about crystal structures, phase purity, morphology of the surface, composition of elements, surface area, porosity of the powder, magnetic and electric properties, thermal conductivity and cycling stability of the reactions etc. These techniques are used with accordance to the required results. In our research we have done XRD to know crystal structures, phase purity and composition of our materials, XRF to know presence of elements in the powder, FTIR to study bonds, TGA to study thermal properties like weight loss with temperature and lastly hot plate method to find thermal conductivity of the powders.

3.4.1) X-Ray Diffraction: (XRD)

XRD is not that simple as it seems to be. It has two main parts; one is which we can see as it exists in real space while other is which we cannot see due to the fact that it is in momentum space and that is the main portion we need to know to have better grip in understanding this technique. So we need to explain it thoroughly to know what basically is happening there in the characterization technique.

The figure given below is D8 advance XRD machine placed in CAS-EN NUST from which we had our samples got characterized. This is one of the advance machines for XRD characterization with a lot of modifications to get better results and it has its own software to generate result.

Fig 3.1) D8 Advance XRD Machine

It has a moveable source from which X-Rays are emitted. These rays are directed towards the powder or crystals by using slits. The powder is placed in the sample holder. The X-Rays coming from the source strikes with the powder or crystal and are diffracted. These diffracted X-Rays are directed towards moveable X-Ray detector with the help of slit again. According to that detection of X-Rays in the detector, a graph is constructed with the help of software between 2ϴ and intensity. This is the first part which we can just observe during characterization. The schematic diagram is given below.

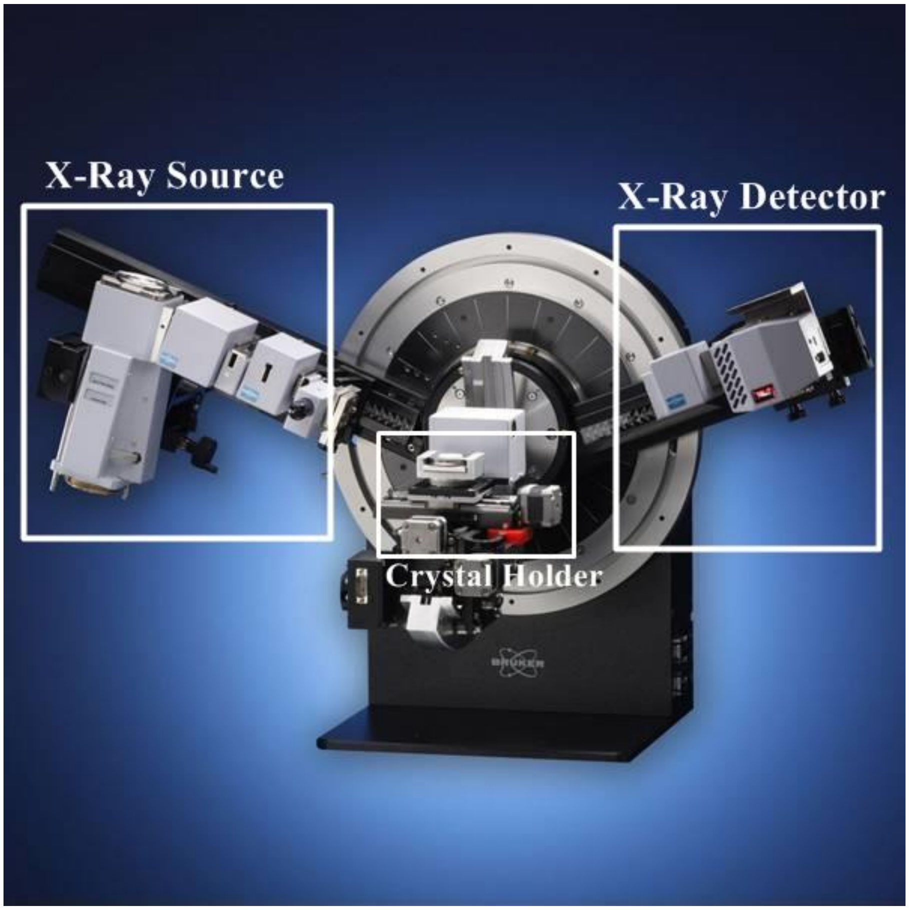

Fig 3.2) Source, sample holder and detector in XRD Machine

There are a lot of things to understand during this. Main thing is to understand what basically is happening when X-Rays strikes with the powder. To understand this we need to go in the history of XRD.

X-Rays were first discovered by Rongten and he gave two theories about X-Rays which he could not prove experimentally.

- X-Rays behave like electromagnetic waves of very high frequency and they get reflected like an ordinary wave.
- X-Rays are very high energy particles having great penetrating power.

After this, numbers of experiments were performed to better know the behavior of X-Rays. In 1913, William Henry Bragg along with his son William Lawrence Bragg did his experiments on X-Rays in which they fell X-rays on different crystalline solids and they discovered that every crystal shows a surprisingly different pattern on the reflection of X-Rays from it. They observed that, on some specific wavelength and angle, these crystalline solids produce intensive peaks of reflected rays [27]. We know that in any crystalline solid, the atomic planes are usually considered to be semi-transparent which allows X-rays to pass from it. Distance between atomic planes is denoted by d. These X-Rays interact with the electrons in the atoms and are reflected back to the detector as the angle of incidence is equal to the angle of reflection. Now the peaks we get in the final result depends upon the constructive or destructive interference. Waves given by source cover equal distance as long as there is no electron in the path of the wave because waves have same wavelength. Suppose two waves are applied to the powder constructively from which one wave strikes with the atom and get reflected while the other wave passes through inter-atomic space and strikes the atom in the second plane. Obviously second wave will cover extra distance and will reach the detector after wave one. If the extra distance covered by the wave is integral multiple of λ then both the waves will remain constructive in the detector and we will get intensity peaks on the output as

$$n\lambda = 2d\sin\theta \quad \text{(Bragg's Law)}$$

If that extra distance is not integral multiple of λ, then there will be a destructive interference due to which there will be no peak in the output. In this way we get different peaks for different elements depending upon their arrangement of atoms. For this work, they got a Nobel Prize in 1915. Schematic diagram to understand it better is given below.

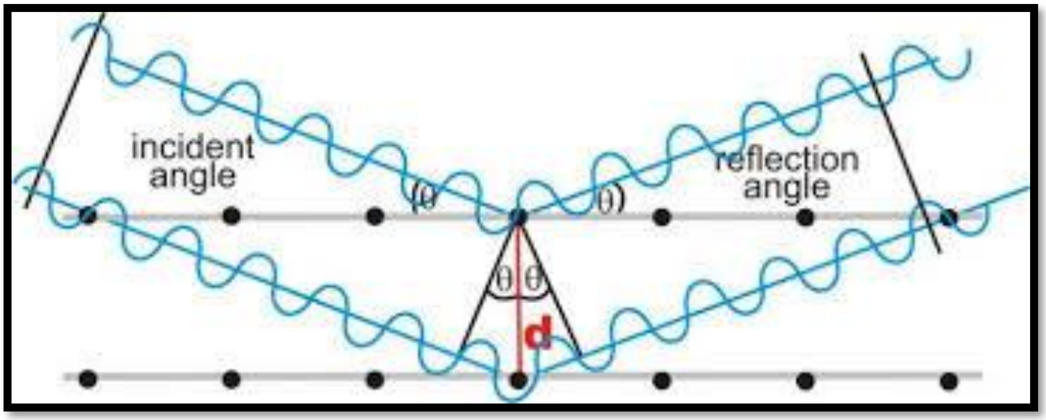

Fig 3.3) Braggs Law [28]

Uses of XRD are in identifying crystalline phase and orientation, analyzing crystal structure, determining structural properties, atomic arrangements, crystalline size and the presence of impurities. Crystalline size is determined by Scherer formula which is given by:

$$\tau = \frac{K\lambda}{\beta cos\theta}$$

Where τ is the grain size, K is the dimensionless shape factor which is which is about 0.9 and β is full width half maxima of the highest intensity peak. Hence, peaks of XRD also give us information on grain size.

3.4.2) X-Ray Florescence (XRF):

XRF is a very handy technique to find the elemental presence in a sample under consideration. Is has an x-ray source which generates x-ray of 20-60 keV, a sample holder and detector which detects emitted photons. Physics behind XRF is not that difficult to know. It is based on Moseley's law in which energy of photon emitted from an atom depends upon atomic number Z. In this technique, high energy X-Rays of short wavelength, having energy greater than the ionization energy of the material are fallen upon the material which knocks out the electron from the innermost shell of the atom of the material and ionizes it. Atom becomes unstable and this instability of an atom causes the electron from higher orbit to fall upon the empty space generated by the incident x-ray by emitting x-ray photon. This photon has some specific energy and wavelength of which can be calculated by Planck's Law [29]

$$\lambda = \frac{hc}{E}$$

where λ is wavelength, h is Planck's constant, c is speed of light and E is energy. Energy of the photon is calculated by the detector and hence atom can be recognized by using Moseley's Law as this emitted energy depends upon atomic number Z by the equation [30]

$$E = \frac{m_e q_e^4}{8h^2\varepsilon_o}(Z-1)^2\left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right]$$

where m_e is mass of electron, q_e is charge on electron, n_f is the the number of orbit in which upper electron transitions and n_i is initial orbit number of electron. So in this manner presence of the atom is recognized in the sample by the detector and graph is plotted between energy dispersion or wavelength dispersion on x axis and intensity or the number of counts in the y axis, where intensity depends upon the number of photons striking with the detector from any atom. Some of the calculated values of wavelengths of Kα emission of different atoms used in research is given below in the table.

Element	**Line**	**Wavelength (nm)**
Ca	$K\alpha_{12}$	0.3359
Ni	$K\alpha_1$	0.1658
Sr	$K\alpha_1$	0.08753
Zn	$K\alpha_1$	0.1435

Table 3.1) List of wavelengths of different atoms used [29]

3.4.3) Fourier-Transform Infrared Spectroscopy (FTIR):

Spectroscopy is basically a technique in which we discuss the interaction of electromagnetic waves with matter. In this technique we observe the absorption or emission of light. FTIR is also a type of spectroscopy in which we fall electromagnetic waves of mid region infrared having different wavelengths (2.5-25μm) rather than monochromatic light on our sample from which it absorbs or emits energy. These infrared waves make the bonds in the sample to vibrate on the basis of which we recognize the presence of bonds in the sample. The basic physics behind this technique is in Michelson interferometer which is shown below in the diagram.

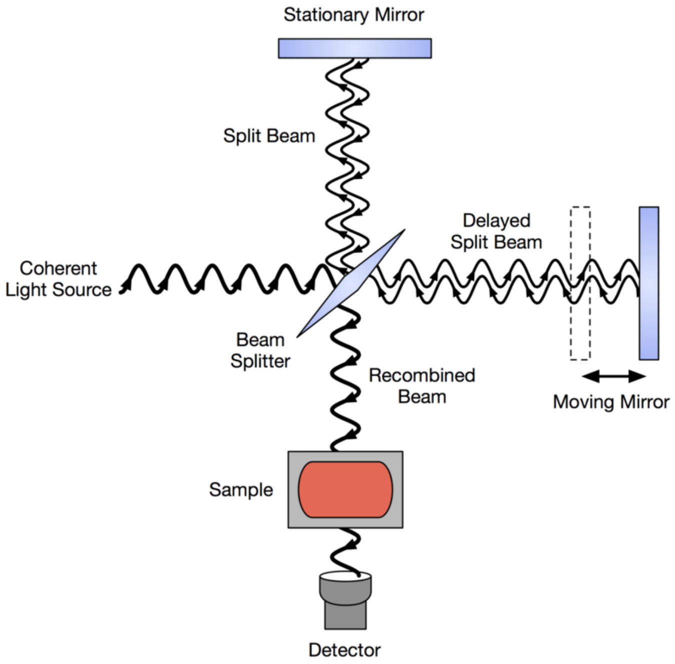

Fig 3.4) Michelson Interferometer [31]

In the figure above we can observe a light source, beam splitter, two mirrors one of which is moveable and one is fixed, sample holder and then detector. The moveable mirror moves a round trip distance of 21cm. When silicon carbide element is heated up to 1200K, it emits light which acts as a source wave. This source wave strikes with the beam splitter made up of potassium bromide coated with germanium to make it semi reflective so that it reflects 50% of the light and transmits remaining 50%. Reflected wave then strikes with the stationary mirror while transmitted wave strikes with the moveable mirror and again these radiations are reflected back to the beam splitter. From the beam splitter it is transmitted through the sample and reaches to the pyro-electric detector which responds to the temperature as the intensity of infrared waves falling on the detector varies. When the difference between the stationary and moveable mirror from the beam splitter is same, the condition is called zero path difference and constructive interference is made on the output which means that maximum signal is reaching to the detector. But when moveable mirror reaches to a point of half λ then destructive interference is made due to which no signal reaches the detector. So this moveable detector is responsible for changing the wavelength of the source. In practice, with such in phase, out of phase and partial interface patterns, the net signal falling on the detector is sinusoidal. The detector gathers the data with all the different wavelengths and combines them to give a final interferogram in time domain which is again with the help of Fourier transformation converted to the frequency domain. Hence a final graph is plotted between transmittance on y axis and wave number on x axis. Every bond present in a compound gives a different range of transmittance on some specific wave number by which presence of bonds is recognized.

3.4.4) Thermo Gravimetric Analysis (TGA):

Thermo gravimetric analysis is usually done by an apparatus generally known as thermo gravimetric analyzer, which consists of a pan in which sample is held, temperature sensor and mass recorder which are further attached with a computer to be controlled by a program. It basically provides us the knowledge of the decrement or increment of mass with the increase in temperature in which mass percentage is held at y-axis and temperature is held at x-axis by the software which plots the result. Schematic diagram of TGA is given below:

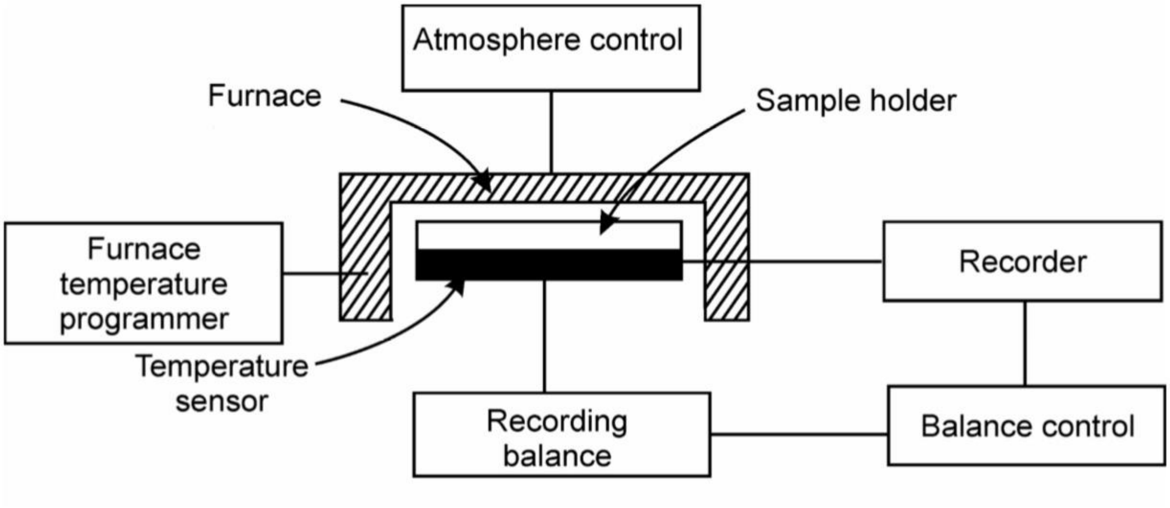

Fig 3.5) Schematic diagram of TGA [32]

Here in the diagram, we can see a sample holder in which we place the sample. Temperature is given to the sample by the furnace with the desired constant rate and this temperature is recorded by the temperature sensor (thermocouples). This rise in temperature may cause an increase or decrease in mass of the sample. This increase or decrease of the mass is then recorded by the balance recorder and this recorded mass is then plotted as a function of temperature by the software.

There are three types of TGA analysis.

- **Dynamic TGA** is the most used TGA analysis. We change the temperature of the system with a constant rate and analyze that at which temperature range our sample is changing its mass. This gives us the knowledge about physical or chemical transition of the sample at any temperature.
- **Static or isothermal TGA** is the other type. From the word "isothermal" it is clear that temperature is constant in this type of analysis. This TGA is basically measure of mass changes with respect to time. In this analysis we give a constant temperature and observed whether in how much time our sample is changing its mass.
- In **Quasi static TGA** we increase the temperature of the system and go to the maximum point up till the further change in mass of the sample stops. It gives information of all the phase changes of the mass. Some time there is a scenario where mass is dropped at certain temperature and if we keep on increasing the temperature, further mass is dropped at some other point. So in this type of analysis we keep on increasing the temperature of the system until mass of the sample becomes constant.

The question is why does this mass change with temperature? There are many possible reasons for that change in mass which are mainly divided into two types.

Physical Transition	Chemical Transition
Adsorption	Oxidation
Desorption	Reduction
Sublimation	Chemisorptions
Evaporation	Water of crystallization
Vaporization	Loss on drying

Table 3.2) Reasons for change in mass in TGA

3.4.5) Hot Disk Method for Thermal Conductivity:

Measuring thermal conductivity is one of the most important points in case of our application as our main target is to enhance thermal conductivity of $Ca(OH)_2$. There are two types of methods to measure thermal conductivity. One of which is transient or non steady technique while other is steady technique. Hot disk method is basically a transient technique and this method to find thermal conductivity was first discovered by Gustafson in 1967 [33]. This is one of the most efficient techniques to find thermal conductivity just in few seconds even in the range of 0.005-500W/mK. This hot disk apparatus just consists of double spiral shape wire made of Nickel with the thickness of 10µm which acts as temperature source and change in temperature sensor. This nickel wire is embedded between a metal to make it stiff. During measurement, hot disk sensor is placed in a bridge circuit which is further connected with the potentiometer to control the resistance of the circuit as shown in figure below.

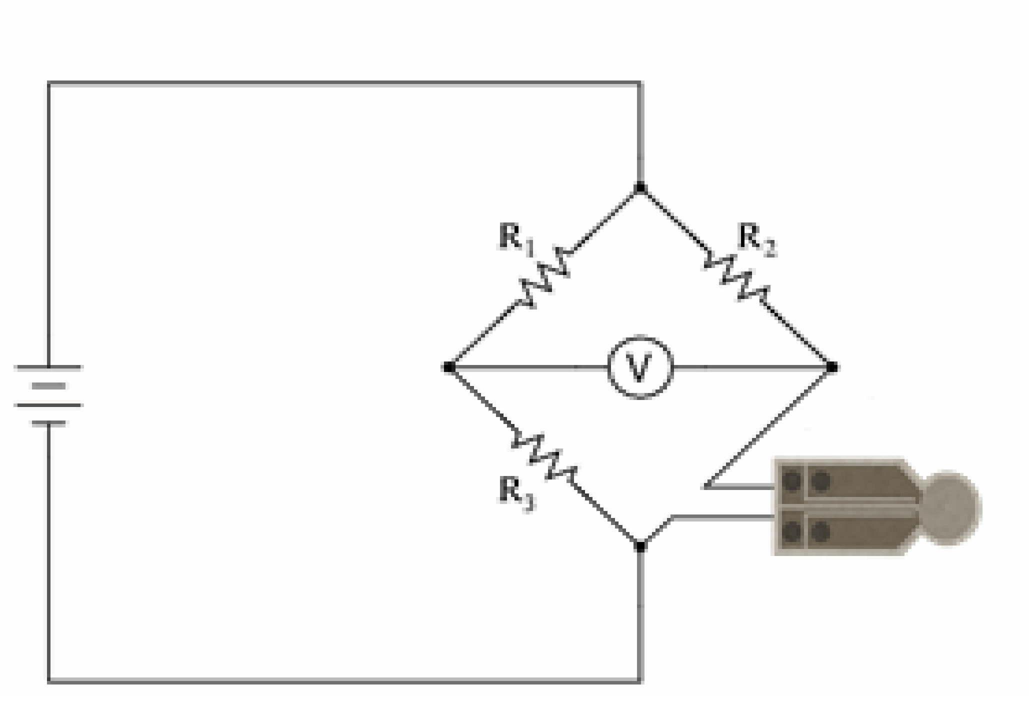

Fig 3.6) Bridge Circuit for Conductivity measurement

Then the sensor is placed between the sample and a small current is provided which increases the temperature of the wire and hence acts as a temperature source. Now the sample will affect this temperature increase in wire according to the thermal transport properties of the sample and hence there will be a change in temperature of the wire. This change in temperature can be measured experimentally by the resistance of the wire which is given as:

$$R = R_o(1 + \alpha\Delta T)$$

Where R is the measured resistance of the wire, Ro is the initial resistance, α is the temperature coefficient of resistance which is 0.00641/°C for nickel [34] and ΔT is the change in temperature. Hence in this way this wire also acts temperature sensor and we can get to know about the thermal properties of the sample. This whole method is governed by an equation which is given as:

$$\Delta T = \frac{P_o}{\pi^{\frac{3}{2}} a K} D(\tau)$$

Where P_o is the power output of the hot disk sensor, a is the radius of the largest ring, K is thermal conductivity and D(τ) is the dimensionless time function which includes Bessel Function. Hence, from the equation we can simple observe that change is temperature is directly proportional to the time function so we plot a graph between change in temperature (measured by resistance) and time function through a software which collects experimental data of both. By the software, we get a straight line between both the quantities, having a slope $P_o/\pi^{3/2}aK$ through which we calculate thermal conductivity of the material.

There are many advantages of using this hot disk method as a tool of measuring thermal conductivity. One of the main advantages is that this hot disk method has much more higher resistance than other techniques due to which measure of temperature due to resistance is quite accurate as compared to others. Second main advantage is that it can measure the conductivity of compact samples as compared to other techniques in which length to width ratio should be 20:1 which is too much. Hence, much less sample can be treated by hot disk method.

By using all these techniques the results are discussed in detail in the next chapter.

Chapter 4

Results and Discussion

In this chapter the results are presented and discussed with reference to the aim of study.

4.1) Sample Detail:

Sample details are given below to distinguish between the samples.

Sr. No	Sample ID	Composition
1	CS	$Ca(OH)_2$
2	C/Ni	$Ca_{1-x}Ni_x(OH)_2$
3	C/Sr	$Ca_{1-x}Sr_x(OH)_2$
4	C/Zn	$Ca_{1-x}Zn_x(OH)_2$

Table 4.1) Sample Description

4.2) X-Ray Diffraction:

XRD pattern of all the samples is obtained from D8 advance XRD machine. XRD pattern of synthesized $Ca(OH)_2$ powder is obtained to confirm its formation. After that $Ca(OH)_2$ is doped with different elements and further tests are performed.

4.2.1) XRD Result of $Ca(OH)_2$:

Fig 4.1 shows the XRD pattern of $Ca(OH)_2$ powder.

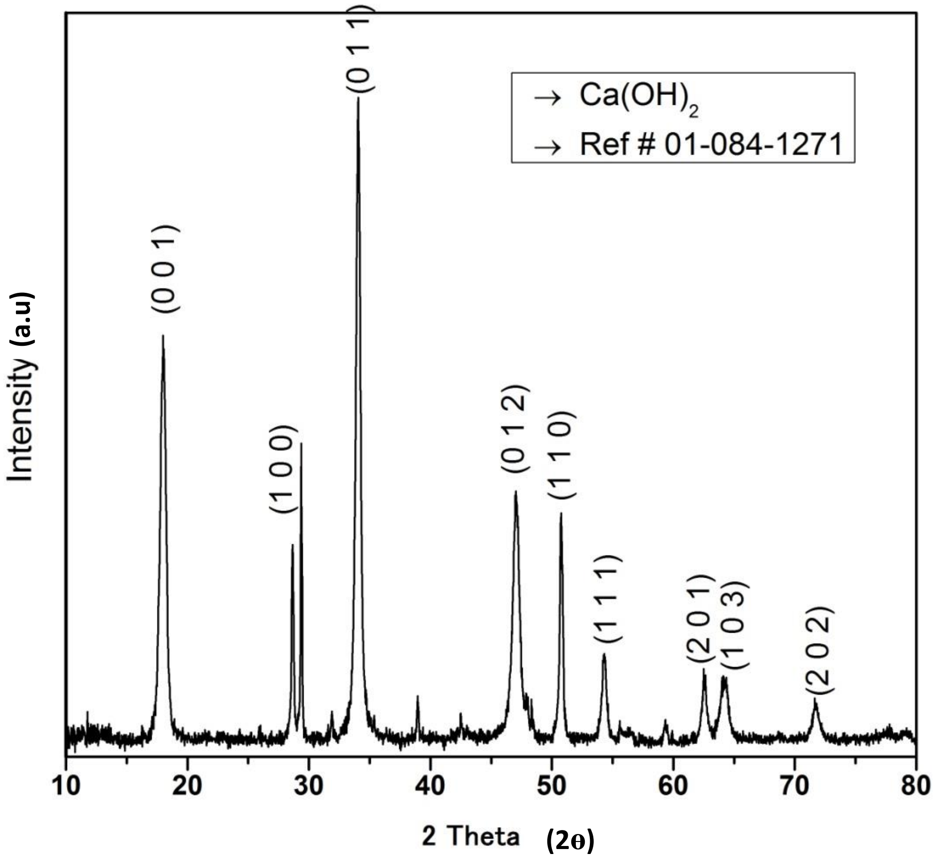

Fig 4.1) XRD pattern of $Ca(OH)_2$

The XRD pattern of $Ca(OH)_2$ powder is matched with the reference number 01-084-1271. It has a hexagonal structure with the crystallite size of 17.3 nm calculated by Scherrer formula. Each plane (001), (100), (011), (012), (110), (111), (201), (103), and (202) corresponds to the crystal structure of $Ca(OH)_2$ and is mentioned in the figure while a peak at 29° is not mentioned as it is $CaCO_3$ with phase (104) as an impurity which is due to the absorbed CO_2 from the atmosphere [35].

4.2.2) XRD Result of Doped Materials:

XRD pattern of all the doped materials is combined in a single graph and is given below in fig 4.2.

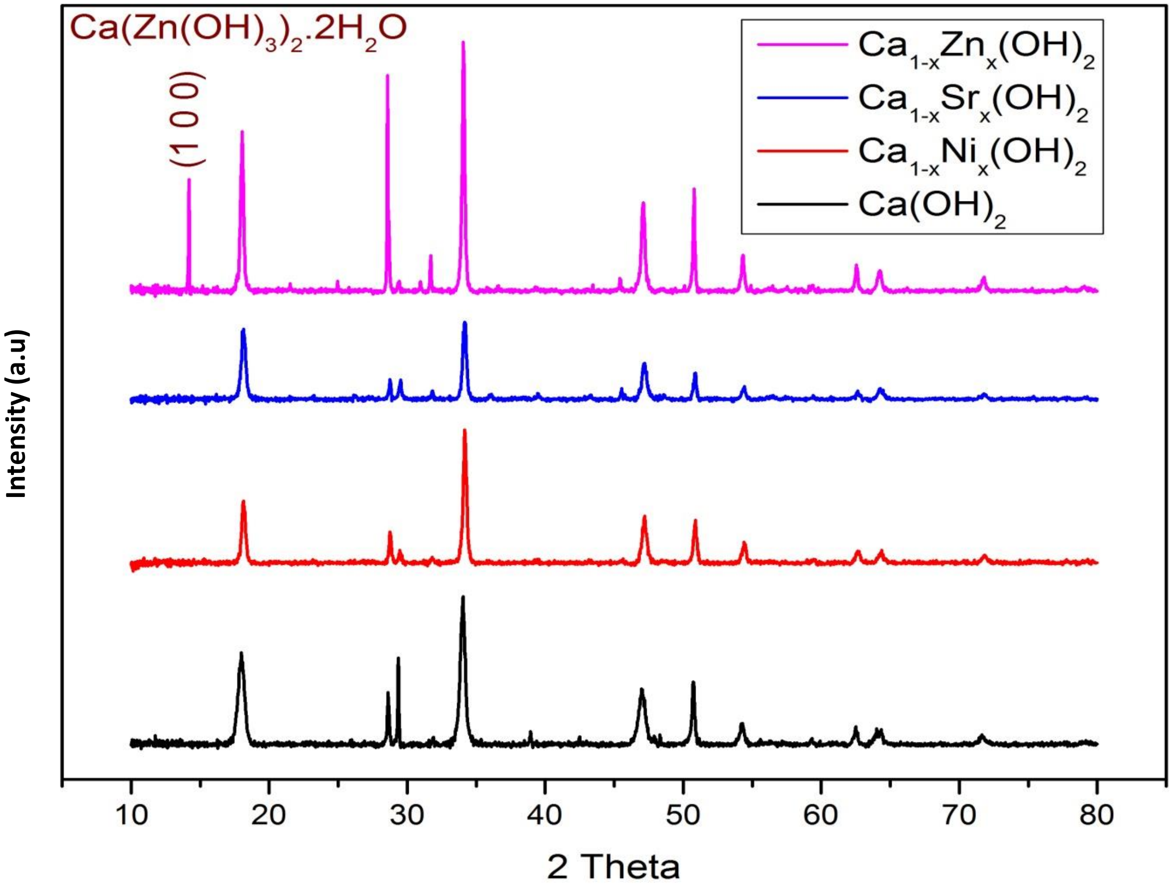

Fig 4.2) XRD Pattern of doped materials

Taking $Ca(OH)_2$ patternas a reference pattern to compare with, some significant changes can be seen, although most of the peaks resembles with $Ca(OH)_2$ but the peak at 29 is of $CaCO_3$ which appears as a result of CO_2 absorbance, an extra peak at 14 in case of zinc, a small increase of peak at 32, a peak at the 64 of 2ө which was a duplet first and after doping, became a singlet and lastly broadening or shortening of peaks are the main differences. For having most of the peaks at same angles one can suggest that there are no structural changes after doping which provides an evidence of substitutional doping. But there is a noticeable difference between the peaks width which suggests the change in crystallite size. Crystallite sizes of CS, C/Sr, C/Ni and C/Zn are 17.3nm, 29.4nm, 35.5nm and 49.5nm respectively. An increase in the crystallite size of the doped material even after having same external conditions of number of moles and temperature etc is observed. This increase can be because of difference in atomic radii which causes the increase in tendency of forming agglomerations and hence increase crystallite size. Moreover, considering the peak of $CaCO_3$, one can see a clear difference in C/Ni and C/Zn where carbonate peak is compressed a lot which shows that doping Ni or Zn causes $Ca(OH)_2$ to be more stable and do not form $CaCO_3$ [36][37]. While CS and C/Sr have clear peak of carbonate impurity which is because they are naturally not much stable and react with CO_2 present in atmosphere [38][39]. An extra phase of impurity can be observed in Zn doped $Ca(OH)_2$ which is identified as $Ca(Zn(OH)_3)_2.2H_2O$ with the phase (100). In case of C/Ni and C/Sr, we can see that there is no extra phase and a common thing between Ca, Ni, and Sr is that they have simple cubic structure while zinc has hexagonal structure. This difference of structure may account for an extra phase and step towards more stability. Taking into account the peak of CS at 64 which is duplet, we can see that after doping, this duplet is converted into a fine single peak which is because of different atomic radius of the doped material that causes little phase distortion due to change in cell volume. [40]. A small increase of a peak at 32 in the figure 4.2 is nothing but calcium and it can be removed by more washing.

4.3) Elemental Analysis (XRF):

To provide another evidence of doping, elemental presence of all the doped materials is shown by XRF. The elemental presence of zinc, nickel and strontium along with calcium is confirmed by XRF. Fig 4.3 shows the elemental analysis of C/Sr and the elements of strontium and calcium are identified in it while there is no other element present confirming the doping of strontium in $Ca(OH)_2$. Similarly fig 4.4 shows presence of Ni and Ca confirming its doping while fig 4.5 is showing us the elemental presence of Zn and Ca. In these three pictures, no other elements are found except for the doped one and keeping in mind the results of XRD one can say that these metals are successfully doped in $Ca(OH)_2$.

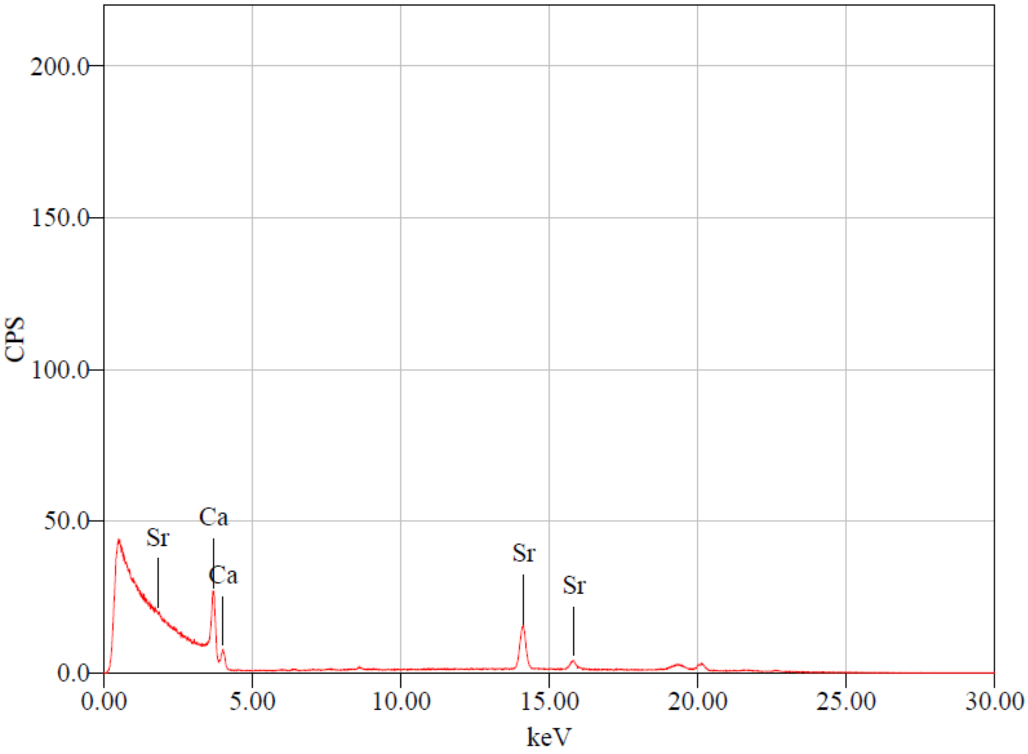

Fig 4.3) Elemental presence of C/Sr

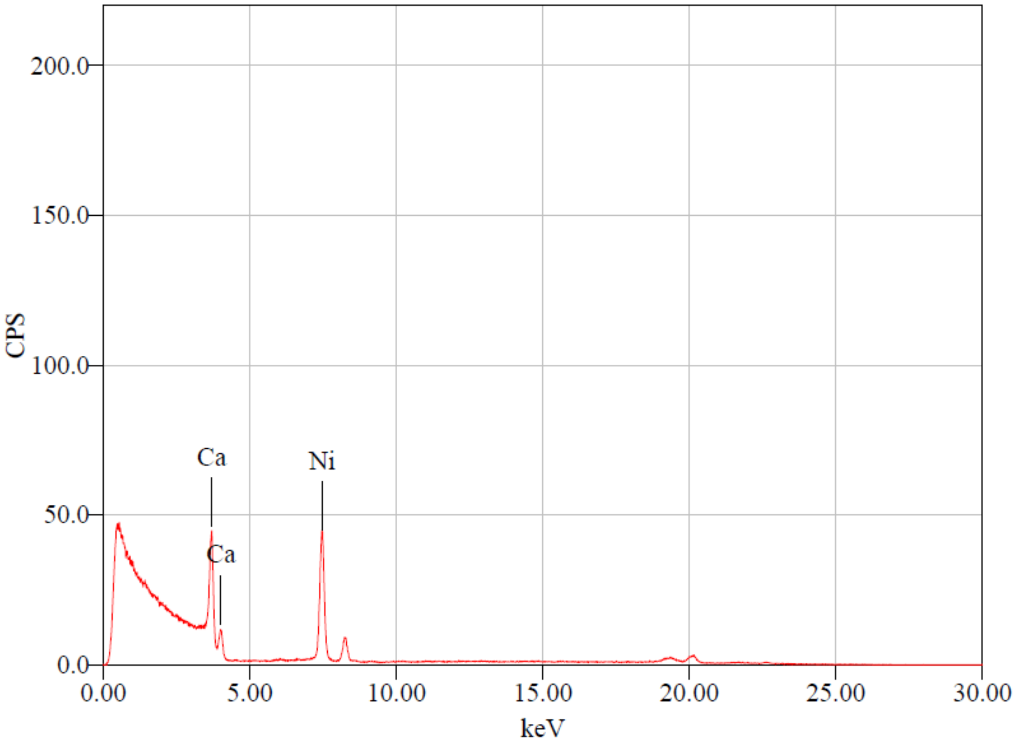

Fig 4.4) Elemental presence in C/Ni

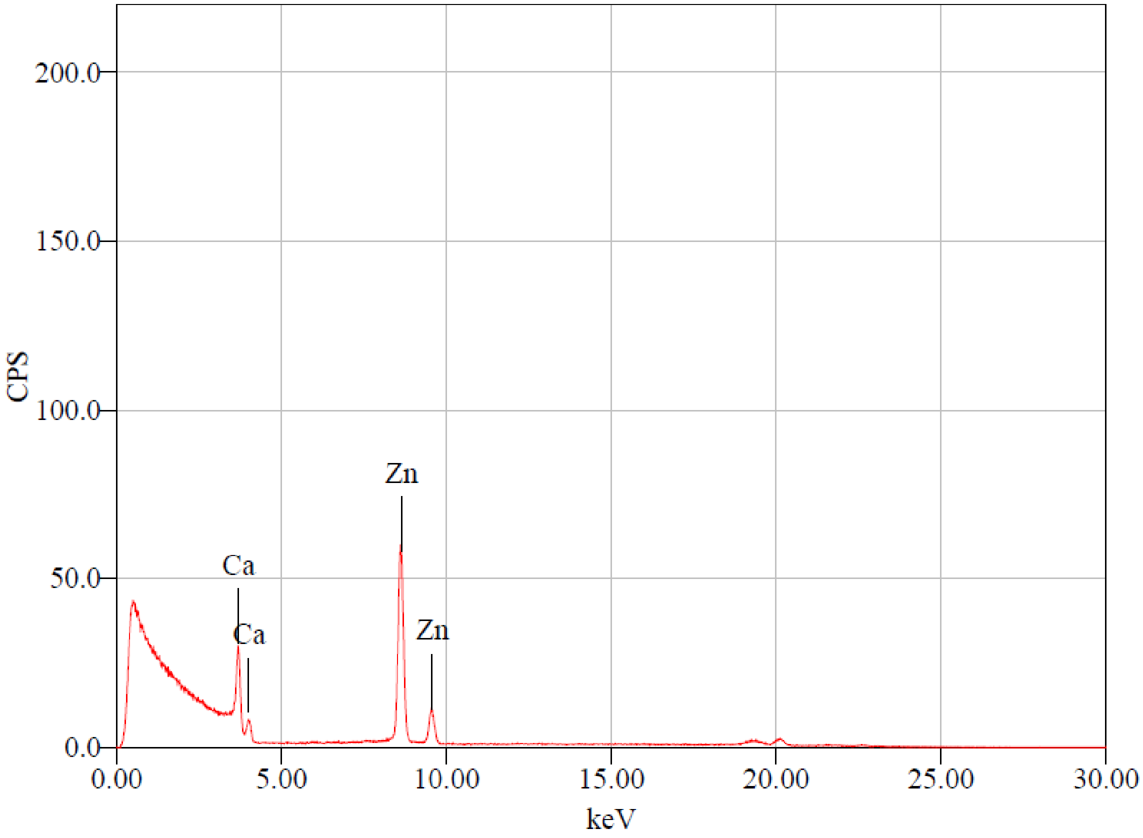

Fig 4.5) Elemental presence in C/Zn

4.4) Fourier Transform Infrared Spectroscopy:

Study of bonds through absorbance or transmittance of infrared radiation is carried out by FTIR. Fig 4.6 confirms the presence of functional group OH bond and impurity of $CaCO_3$. Fig 4.7 shows the comparative study of doped and pure $Ca(OH)_2$. The sharp peak at 3642 cm^{-1} represents the O-H stretching of $Ca(OH)_2$ while O-H bending could only be seen in plain $Ca(OH)_2$ from 3250- 3580 cm^{-1}, showing that doping has suppressed the O-H bending. Peak at 2800 cm^{-1} shows the presence of CO_2 which is more visible in plain $Ca(OH)_2$ and C/Sr while it is suppressed in C/Ni and C/Zn. This is mainly due to the adsorbed CO_2 from atmosphere while peak at 1420, 1040 and 872 cm^{-1} represents different modes C-O of calcium carbonate [41].

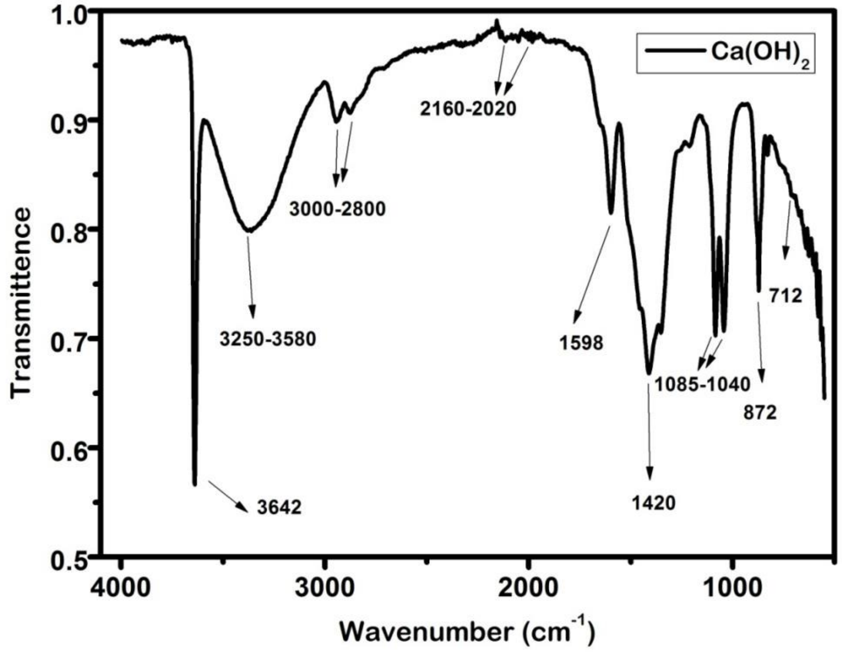

Fig 4.6) FTIR of simple Ca(OH)$_2$

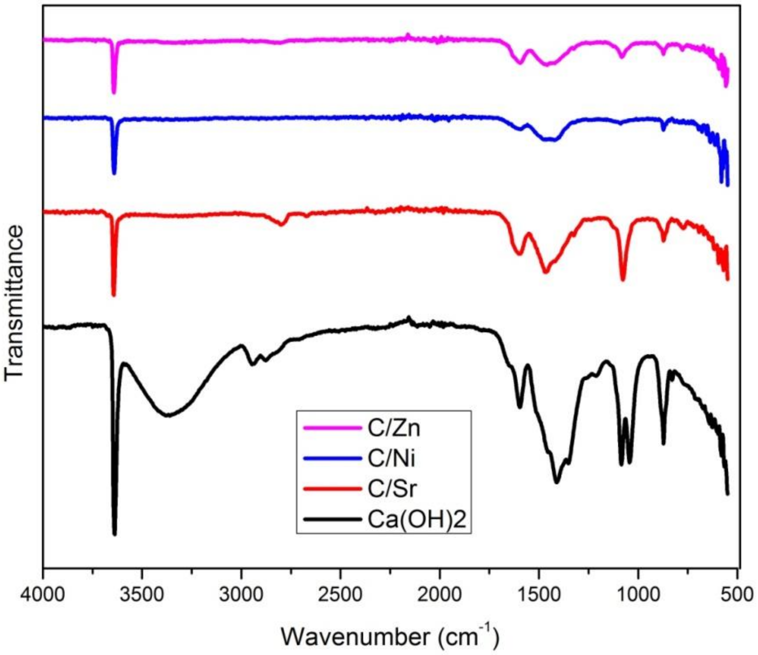

Fig 4.7) FTIR analysis of Doped Ca(OH)$_2$

4.5) TGA Results:

TGA gives us the effect of temperature on mass of the material. By analyzing TGA, we can deduce much information such as removal of adsorbed water, thermal decomposition or removal of CO_2 from the sample. From fig 4.8, one can see that C/Ni has least amount of adsorbed water and CO_2 which is a good sign. First decrease of mass from the start up to 200°C is representing the mass loss due to adsorbed water. Second sharp decrease in mass from about 350°C corresponds to the thermal decomposition of hydroxides into oxide while third mass loss from about 530°C represents removal of CO_2. From the XRD results we saw that CS and C/Sr has the most formation of $CaCO_3$ which we can confirm from TGA by quantitative analysis on the graph. Table 4.2 gives us the information deduced from TGA.

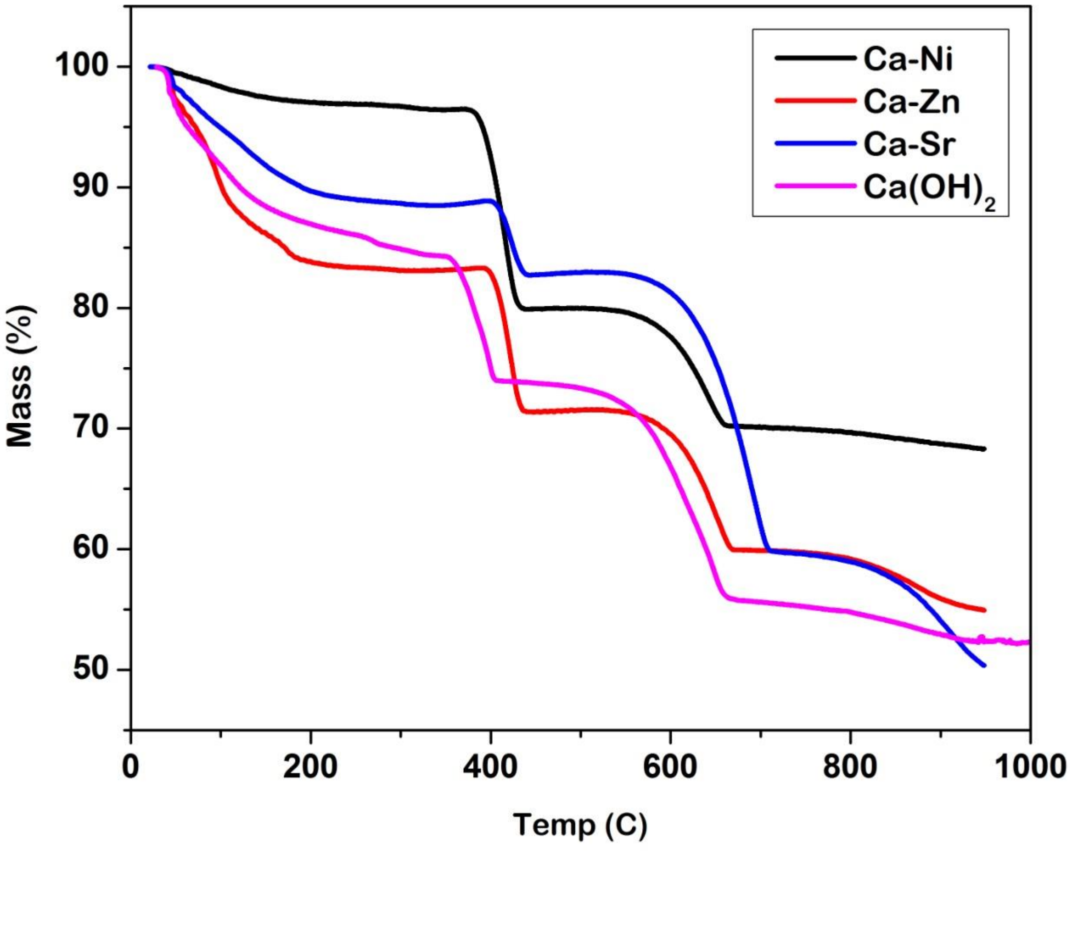

Fig 4.8) TGA of simple and doped $Ca(OH)_2$

No of Samples	Mass loss due to adsorbed water	Mass loss due to decomposition	Mass loss due to CO_2 removal	Decomposition temperature difference (°C)
$Ca(OH)_2$	15.67%	10.19%	18.32%	56.3
C/Sr	11.20%	6%	23.08%	37.33
C/Ni	3.63%	16.51%	9.51%	56.2
C/Zn	16.64%	12.16%	11.07%	43.80

Table 4.2) Quantitative TGA details of sample.

From the table given above we can see that maximum water was absorbed by C/Zn and hence it had maximum weight loss due to adsorbed water while minimum water was absorbed by C/Ni. Further we can see that C/Ni gave us the maximum decomposition of hydroxide into oxide which is also a good sign for dehydration. Similarly adsorbed CO_2 behavior can also be observed from the table 4.2 as C/Ni and C/Zn have minimum adsorbed CO_2 while simple $Ca(OH)_2$ and C/Sr have maximum adsorbed CO_2.

4.6) Thermal Conductivity:

One of the main task of this research was to increase thermal conductivity of $Ca(OH)_2$. As reported before, thermal conductivity of $Ca(OH)_2$ at room temperature is 0.010W/mK which is very low. Doping of $Ca(OH)_2$ with metals has proved itself to be a good candidate by improving thermal conductivity. Thermal conductivity of all the samples at 20, 50, 80, 110 and 140°C is given below in the table 4.3) and it is then plotted below in the figure 4.9.

No of Obs	Temperature (°C)	C/Ni (W/mK)	C/Sr (W/mK)	C/Zn (W/mK)
1)	50	0.1749	0.21845	0.205
2)	80	0.1853	0.2212	0.20925
3)	110	0.1996	0.22545	0.20895
4)	140	0.2063	0.22535	0.22365

Table 4.3) Thermal conductivity of doped materials

From table, one can see that thermal conductivity of the doped materials is increased and it even increases with the increase in temperature which is due to the fact that thermal conductivity has direct relation with specific heat of the material which according to Debye's law further has T^3 dependence on it. This data is plotted below in the figure 4.9 to get better understanding of the behavior.

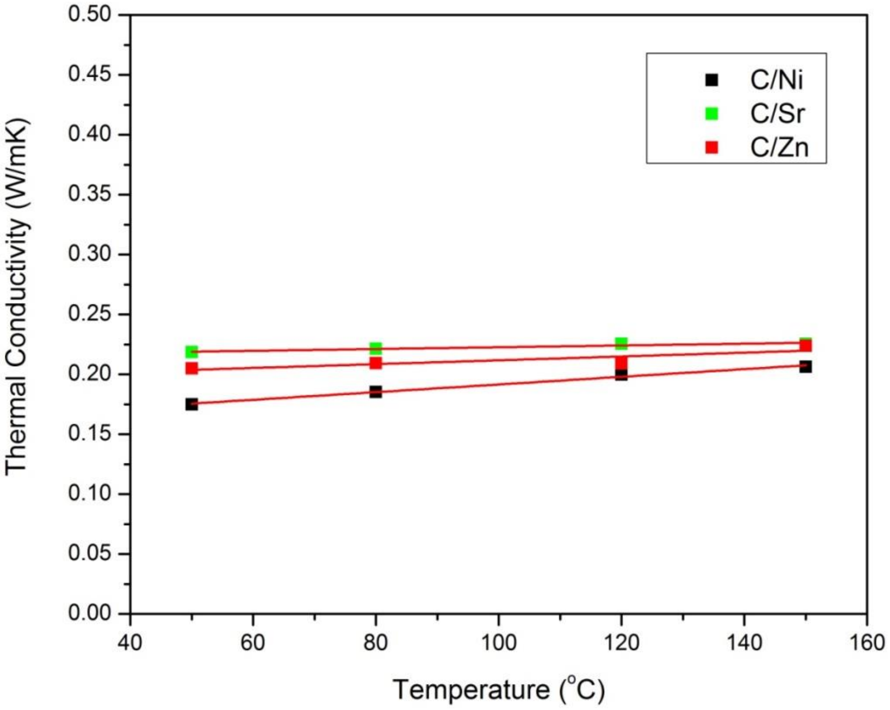

Fig 4.9) Behavior of thermal conductivity with temperature

Doped materials have shown a clear increasing behavior of thermal conductivity with temperature. However, C/Ni showed maximum increase with temperature. Although thermal conductivity of C/Sr is high but its increment with temperature is less than others which is may be due to the fact that it is alkaline earth metal just like calcium while others are pure metals which show more increase in thermal conductivity. C/Zn has shown a little deviation at 120 which is due to the removal of water from the sample and hence thermal conductivity due to hydrate has dropped.

Chapter 5

Conclusion

Keeping in mind all the results and discussion in the above chapter, following conclusions can be drawn.

- From XRD we could observe that there were no secondary phases in C/Ni and C/Sr while C/Zn made a secondary phase.
- There was no difference in crystal structure but there were very minor peak shifts due to change in lattice parameters after doping.
- Elemental analysis by XRF showed us the presence of Nickel, Strontium and Zinc in their respective doped material which also proved to be an evidence of doping.
- OH stretching was seen by FTIR in all the samples.
- Presence of $CaCO_3$ was compared by FTIR and it was seen that $Ca(OH)_2$ and C/Sr had maximum carbonate peaks in FTIR which also satisfied the results of XRD.
- Dehydration was shown by TGA and it showed that C/Ni had greatest mass loss due to dehydration and C/Sr had minimum mass loss due to dehydration.
- C/Ni showed minimum adsorbed water which proved it to be water repellant while C/Zn showed maximum water which also satisfied XRD result in which it produced extra phase with hydrate.
- Thermal conductivity was improved after doping. C/Sr, C/Zn and C/Ni had thermal conductivities at room temperature to be 0.203, 0.181 and 0.158.

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