

EXPERIMENTAL STUDY OF QUATERNARY NITRATE/NITRITE MOLTEN SALT
AS ADVANCED HEAT TRANSFER FLUID AND ENERGY STORAGE
MATERIAL IN CONCENTRATED SOLAR POWER
PLANT

by

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April 17, 2015

Abstract

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The University of Texas at Arlington, 2015

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Solar energy is used to produce electricity by two methods namely photovoltaic and concentrated solar power plant systems. Concentrated Solar power plants hold a distinct advantage over photovoltaic, which is that of energy storage. Energy can be stored in thermal energy storage system during day time and can be used to dispatch energy during peak demand and during raining or cloudy days to produce electricity. All concentrated solar power plants in operation use sensible heat storage method to store energy. Sensible heat storage system have been used in industry owing to ease of dispatch ability. Currently a binary mixture of NaNO_3 and KNO_3 (Solar Salt) is being used in industry owing to advantages such as, environmentally safe, low vapor pressure, relatively low cost and easy availability, low viscosity and compatibility with plant piping system. Heat is transferred to energy storage material through heat exchanger by high temperature fluid using forced convection. One of the disadvantages of this salt is low energy storage density, which in turn requires large storage tanks to store the material adding to the cost of the plant. Another drawback of using this mixture is its freezing point being too high. Temperature tends to drop at

night and as a result salts tend to freeze. Along with freezing of the salt being an issue, other issue is the salt tends to expand on being heated to reuse again, which may lead to significant damage to Heat transfer fluid pipe system. Auxiliary equipment are required to keep the salt from freezing which increases the cost of the plant. To mitigate the thermodynamic losses because of the presence of the heat exchanger, it has been suggested to use HTF and TES as same substance, which would result in elimination of heat exchanger and reduce thermodynamic losses. From energy point of view, the efficiency of TES is considered high.

A new Quaternary nitrate/nitrite mixture has been developed whose melting is 100°C. However, the major drawback of the salt to be used as TES/HTF is its poor thermos-physical properties such as lower specific heat capacity. Earlier there have been reports of substantial improvement in thermal properties of organic/inorganic salts on being doped with nanoparticles in minute concentration. Nanoparticle, on being doped in base salt tend to induce nanostructure, which due to its high surface area and high surface energy increase the heat transfer property. In this work, silica nanoparticle of various sizes are doped in the base eutectic salt to increase its specific heat capacity. After doping the base salt with silica nanoparticle it was observed, that there is anomalous enhancement in the specific heat capacity of the eutectic mixture.

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Chapter 1

Introduction

1.1 Introduction to Solar Energy

Crude oil, coal and gas are world's main resources of energy. There have been econometric model developed to estimate when the fossil reserves would be depleted. According to a model developed by Klass it is estimated that coal reserves are available up to 2112 and coal would be the only fossil fuel available after 2042 [1]. Wind Energy, Solar Energy, Geothermal Energy, Biomass Energy, Hydropower, Biodiesel and Advanced Biofuels are some of the example of renewable energy on the surface of earth. Renewable Energy now accounts for 40% of all domestic power supply installed in 2013. Currently 190GW of energy is produced by renewable sources. Out of all, Solar Energy stands out. 400, 000, 000, 000, 000, 000, 000, 000, 000 watts of energy is produced by sun [1] and it is estimated that it will last for another 5 billion years. Photovoltaic and Concentrated Solar Power systems (CSP) are namely 2 types of technology that uses sun's energy produce electricity. However, it is important to understand that both the technologies are very different from one another. Concentrated Solar Power Plant (CSP) is a technology where Sun's energy is used to create heat and that heat is used to run a heat engine. The heat, which is produced, is used to raise the temperature of working fluid, which could be anything like water, synthetic oil etcetera. The heated fluid is used to run steam turbine generator, which produces electricity. On the other hand, Photovoltaic directly converts the Sun's light to electricity, which is in form of DC and is converted to AC with the help of inverter. One of the technical challenges with Photovoltaic is that it only produces electricity during daytime, which implies that they are ineffective during nighttime as solar panels cannot produce electricity at that time of the day.

Whereas in concentrated solar power plant heat can be store at daytime and can be used to produce electricity at nighttime. Thus energy storage is easy and way more efficient method, which is what makes concentrated solar power plant (CSP) far more favorable when it comes to production of electricity on large scale basis. Energy storage capacity can result in radical improvement in bringing down the cost of electricity produced by solar energy and can also help in reducing the overall cost of plant installation.

1.2 Concentrated Solar Thermal Energy Technology

At present Concentrated Solar Power technology has 4 technologies that are used to produce electricity. Parabolic Trough Systems, Concentrated Solar Power, Fresnel Linear Technology and Parabolic Dish Collector. Parabolic Trough System and Concentrated Solar Power are 2 most mature technologies that are mostly employed to harness sun's energy. Solar energy concentrator i.e. solar tracker, electricity generator, steam turbine are few components that form the CSP plant system.

1.2.1 Parabolic Trough System

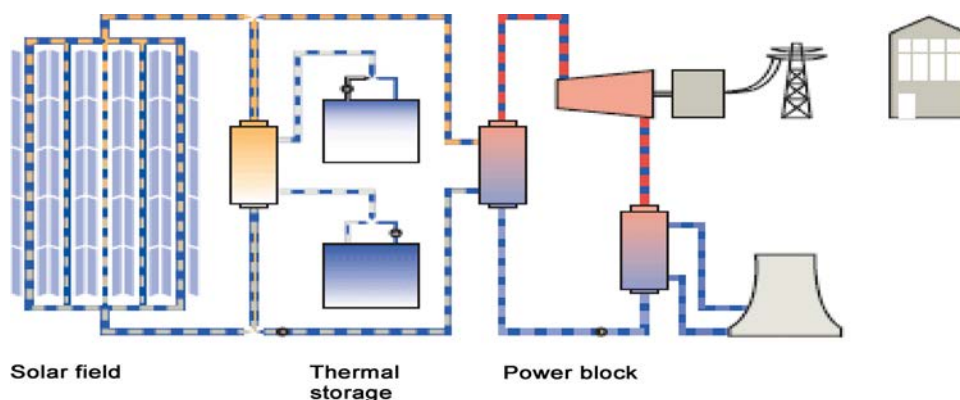


Figure 1.1 parabolic trough plant [2]

Parabolic Trough System has cylindrical and parabolic reflector, which focus all the sun's radiation on to a vacuumed glass tube. An absorption tube is placed inside a Vacuum glass tube. The Absorption tube has high absorptivity and low emissivity resulting in low heat losses of the whole system. There is high temperature fluid or heat transfer fluid is flowing in the absorption tube, which gets heated up by absorbing heat, which is reflected by the reflectors. In parabolic trough Systems, the heat transfer fluid used is mineral oil. This system has capability to reach up to temperature of 400°C. The heated fluid is transferred to heat exchanger by pumps and there it is used to convert the heat to steam, which in turn is used to produce electricity.

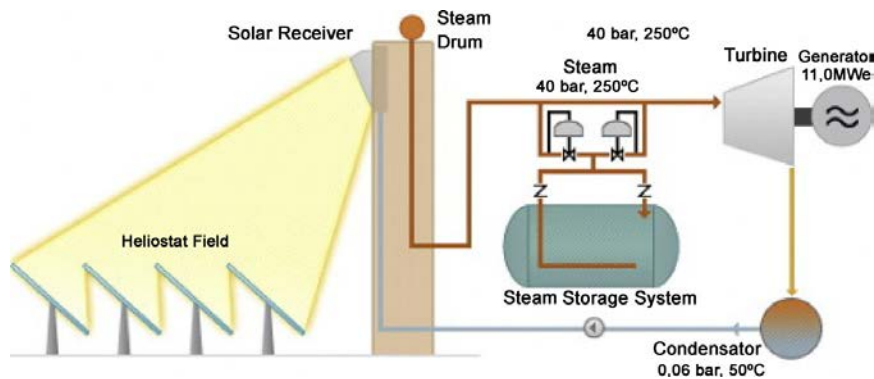


Figure 1.2 power tower system [2]

Solar power tower system composes of several reflecting mirrors also known as heliostats. These heliostats have a surface of 100m² on average. Heliostats are placed around a central receiver in which there is high temperature fluid is flowing which could be a molten salt, liquid sodium, water or air. The heliostats are incorporated with its own sun tracking system along two axis. Heliostats are usually flat, but on being concave they could reflect more sun's irradiation on to the receiver. The receiver is usually placed on to a tower, which is about 80m – 100m in height. The prime advantage of having a solar power tower is that it is point focus system

rather than line focus as in case of Parabolic Trough System. A large amount of radiation is focused on a single receiver as much as of 200-1000 kW/m² which is helpful in increasing the efficiency of the whole system and minimizing the heat losses. The other advantage of solar power tower could be that if large numbers of heliostats are employed, they could reflect tremendous amount of solar flux towards the receiver and increase the operation temperature which in turn can increase the efficiency of the Rankine cycle.

1.2.3 Fresnel Linear Technology

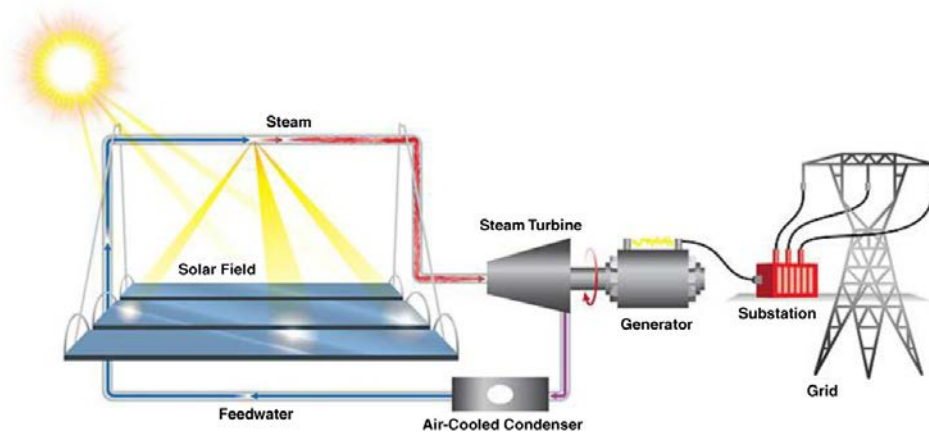


Figure 1.3 linear fresnel system [2]

Fresnel Linear Technology has mirrors, which are slightly parabolic or flat in shape. The mirrors reflect the sun's irradiation on to towards the tube. The tubes have water running in it. The water is heated and converted to steam. The pressure created by the steam helps it to move towards the turbine and helps the generator to produce electricity.

1.2.4 Dish Stirling Technolog

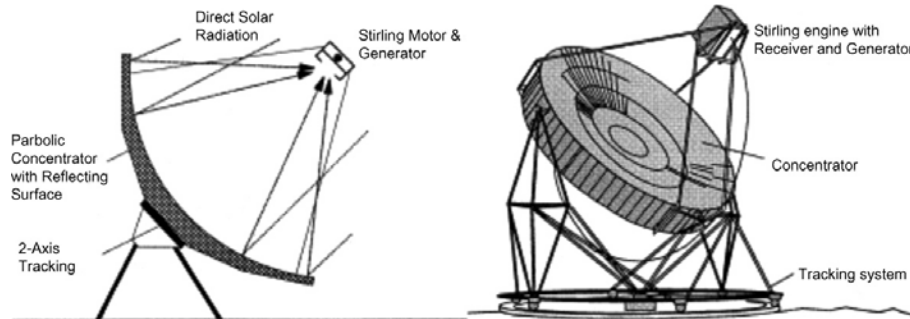


Figure 1.4 dish sterling system [2]

Dish Stirling System is point focus system. In this system, a parabolic shaped dish is used to reflect sun's radiation on to a single receiver, which in this case is a Stirling engine, which is nothing but a heat engine. The Stirling engine absorbs the heat energy and converts the same in to mechanical work. An alternator attached to the engine converts this mechanical work to electricity. In Dish Stirling systems temperature up to 1500°C could be achieved attributing to point focus collector system. Parabolic dishes used in Dish Stirling System are usually coated with reflective material such aluminum, glass, plastic. Mirrors made up of silver on glass with iron have high reflectance of 90% -94%.

1.3 Thermal Energy Storage System and energy storage systems

As the sun is not available throughout the day or when the conditions are cloudy, this is one of the Complications associated with the use of solar thermal energy as source to produce electricity. To counter the effect of variable solar flux available throughout the day, there needs to be energy storage systems, which can storage energy during day time and supply energy when needed. Energy storage systems can basically be divided in to 3 categories namely sensible heat storage system, Latent heat storage system and chemical energy storage.

1.3.1 Sensible Heat Storage system

Sensible heat energy storage employs heating of solid or liquid energy storage material. In sensible heat storage system the material does not undergo any phase change and only temperature of the medium is increased. Solid material like silica firebricks, solid NaCl, reinforced concrete can be used for energy storage purpose. However, while employing solid material as energy storage material, indirect method to storing energy is used where high temperature fluid is allowed to get in thermal contact with solid energy storage material, and then solid energy storage material absorbs heat from high temperature fluid convectively. Liquid material like mineral oil, synthetic oil, silicone oil, carbonate salts, nitrate salts can also be used for energy storage material. One advantage of using liquid material, as energy storage liquid is, that they can also be used as high temperature heat transfer fluid. They could be stored in an insulating tank, which could maintain them at high temperature. Carbonate salts, nitrate salts are nothing but molten salts, which could be used as energy storage material. These molten salts have some desired properties such as low cost, high specific heat capacity, high thermal conductivity, stability at high temperature, less reactive etcetera. The amount of energy storage in sensible heat storage is given by $Q = m C_p \Delta T$ [3], where m is mass of the storage medium in which energy stored, C_p is the specific heat capacity of storage medium, ΔT is temperature change during the whole process.

1.3.2 Latent Heat Storage

Latent heat is heat released or absorbed during melting or solidification of the material. Phase change materials generally have higher densities than sensible heat energy storage materials. For this phenomena material, which fall under the

temperature of solar field, can be looked up on. Phase change could be solid – liquid, liquid – gas, solid – solid. Due to low volumetric expansion, solid – liquid is preferred over liquid – gas and due to high enthalpy over solid – solid respectively. The energy stored for solid – liquid over phase change transition is given by the following equation $Q = m [C_{ps} (T_m - T_s) + h + C_{pl} (T_l - T_m)]$, [3], where Q is the energy stored, C_{ps} and C_{pl} are average specific heat capacity in solid and liquid phase respectively of phase change material, T_s is temperature of solid, T_l is the temperature of the liquid and T_m is melting temperature [3]. Materials that comply with latent heat storage system have low thermal conductivity during freezing or during the time when energy is released. As a result, it has poor heat transfer performance.

1.3.3 Thermochemical Energy Storage

The greatest advantage offered by thermochemical storage system is of high-energy storage density with heat of reaction [7]. However, it is still not used in industry because of its drawbacks. Reactants undergo decomposition over a longer period of time. This decomposition of the reactants results in reduction in the ability to store energy and heat transfer.

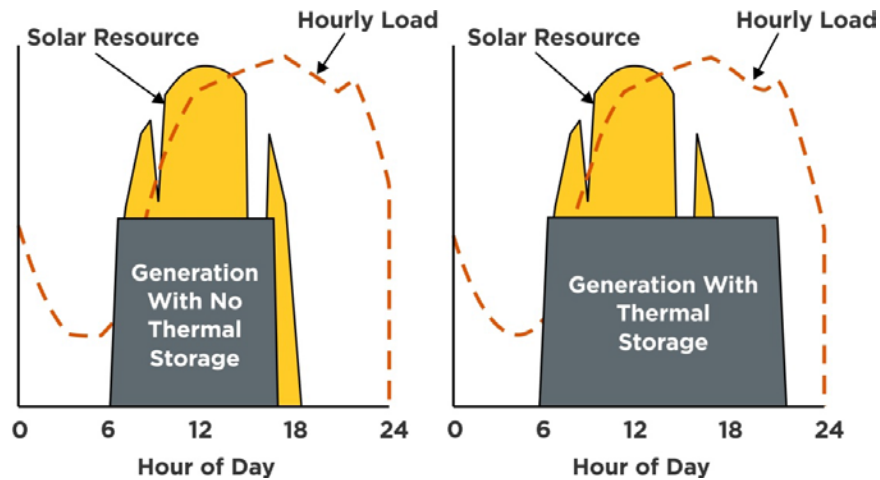


Figure 1.5 advantage of thermal energy storage system [6]

1.4 Introduction to nano eutectic salt

Colloidal suspension of nanometer-sized particle in a solvent material is termed as Nano fluid. It has been reported that Nano fluid possess superior thermal properties when compared to conventional heat transfer fluid and to that of fluids containing micrometer sized particle in solvent. Since surface area to volume ratio of 1000 times larger of particle with Nano meter dimension, a high anomalous enhancement in thermal property of the overall liquid.

1.5 Eutectic nitrate/nitrite mixture

Eutectic mixture of LiNO_3 , KNO_3 , KNO_2 and NaNO_3 are used here attributing to their low melting point. At present the industrial energy storage material, which is binary mixture of KNO_3 and NaNO_3 also known, has solar salt, has freezing point of 222°C . Various methods such as circulating heat transfer fluid during the night time through solar field and using auxiliary heater to maintain certain temperature are used to prevent freezing of salt.

1.6 Nanomaterial

A nanomaterial substance is defined as a substance whose one dimension is less than 100nm [9]. A nanometer is 1 millionth of a millimeter. Quantum dots, Fullerenes, dendrimers and nanotubes are some example of nanomaterial. Nanomaterial for properties such as unusual electrical, mechanical, optical and magnetic properties has gained more interest in recent decade. Many researches have reported on the use of silica nanoparticles anomalous enhancement in thermal properties. Here silica nanoparticle is selected for the experimental investigation

1.7 objective of this study

The objective of this study is to investigate quaternary nitrate/nitrite molten salt for as advance thermal energy storage material by doping the base molten salt with silica nanoparticle in minute concentration. Earlier results have been reported that doping alkali halide salts with silica results in enhanced thermal properties of the overall mixture.

1.8 Significance of study

Here a novel energy storage material is fabricated for the purpose of storing energy with low melting point. At present the current energy storage material, which is a binary combination of KNO_3 and NaNO_3 , is being used in industrial application. Its melting point is 220°C . Lot of investment goes in to prevent the freezing of the salt. Besides there is enhancement in energy storing capability i.e. specific heat capacity of the salt, which would result in reduction of the physical size of the tank, storing energy storage material.

Chapter 2

Experimental setup

2.1 Material information and synthesizing procedure

A quaternary eutectic mixture of $\text{LiNO}_3 - \text{KNO}_3 - \text{NaNO}_3 - \text{KNO}_2$ is considered here for purpose of study attributing to its low melting point of 100°C [6]. The Eutectic mixture is selected based on the experimental findings by [6]. The composition, which forms the eutectic mixture of $\text{LiNO}_3 - \text{KNO}_3 - \text{NaNO}_3 - \text{KNO}_2$ by mixing is (9 - 33.6 - 42.3 - 15.1) in mass fraction (wt. %). The salts used in procedure were procured from Alfa Aesar Corporation. LiNO_3 , KNO_3 , NaNO_3 procured were 99.0 % pure and KNO_2 was 96.0 % pure. Silicon Dioxide (SiO_2) nanoparticles used were procured from Meliorum Technology. Different sizes of nanoparticles were used (5, 10, 30, 60 nm). 17.57 mg of LiNO_3 , 66.56 mg of KNO_3 , 83.75 mg of NaNO_3 , 29.89 mg of KNO_2 and 2mg of SiO_2 were mixed using a microbalance (Sartorius, CPA225D). The mixture is prepared in 25 ml glass vial. The glass vial is filled with water approximately up to 20 ml and allowed to sonicate for 240 minutes in an ultra sonicator (Branson, 1510), procured from Branson Ultrasonic Corporation. The purpose of the sonication is that all the five elements are mixed homogenously, which implies that there is uniform dispersion of the nanoparticles and minimum agglomeration. The sonicated vials were evaporated on hot plate at temperature of 200°C for 8 hours. After complete removal of water, the remaining solution is allowed to solidify and heated at lower temperature of 50°C to remove any trace of moisture from the sample.

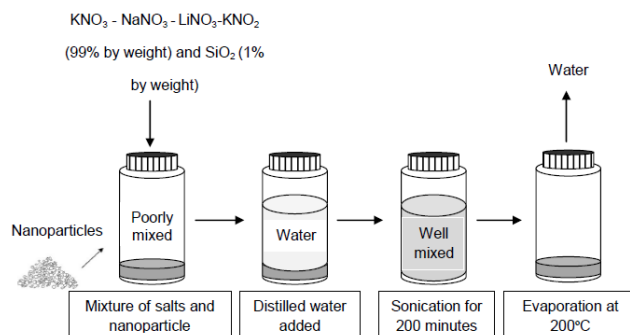


Figure 2.1 synthesize protocol [14]

2.2 Properties of quaternary nitrate/nitrite salt

Table 2.1 Individual properties of salt used in quaternary mixture

Properties	Sodium Nitrate	Potassium Nitrate	Lithium Nitrate	Potassium Nitrite
Molar Mass	84.99gm/ mole	101.1gm/ mole	68.95gm/ mole	85.10gm/ mole
Melting Point	306°C	400°C	251°C	387°C
Boiling Point	380°C	334°C	600°C	N/A
Decomposition Temperature	>400°C	380°C	>600°C	N/A
Flash Point	Non-Flammable	Non-Flammable	Non-Flammable	Non-Flammable

2.3 Preliminary Testing of Quaternary salt

In preliminary testing the sample is tested for safety purpose. The stability of the salt at higher temperature is tested along with decomposition of the salt. The salt for this purpose is tested using Tzero Aluminum pan. Corrosion of the pan is also tested to check whether the salt has any corrosion effect on the pan. For this purpose, sample between 10mg – 15mg is sealed inside a pan, which is sealed hermetically. The sealed pan is kept on hot plate for 4 hours on hot plate at 300°C. As per experiment, the weight of the sample and color change was tested. It was observed that neither there is any weight change of the sample nor there is any color change of the sample. Thus it was decided, that the samples safe and could be tested further.

2.4 Modulated differential scanning calorimeter

A Modulated Differential Scanning Calorimeter (MDSC; Q20, TA Instruments Inc.) was employed to measure the specific heat capacity of the compound salt. In Modulated Differential Scanning calorimeter (MDSC), two pans are used, one pan is filled with sample whose specific capacity is to be measured and other pan is empty, which is a reference pan. Both the pans are placed on the holder under which a thermocouple is placed which is responsible for increasing the temperature of the pan. The MDSC records the heat flow signal, which is nothing but the difference in thermal energy of empty pan and sample pan. Basically there are 2 methods to get the specific heat capacity to be obtained base on above information namely ASTM 1269E and MDSC. In Differential Scanning Calorimeter, there are 2 ways data can be obtained i.e. standard DSC and Modulated DSC. In traditional DSC, during various processes such as heating, cooling or while the sample is at isothermal state difference in heat flow rate is measured between sample pan and reference pan. The

resulting heat flow signal is plotted versus temperature or time. In standard DSC the temperature always changes linearly. Here only a single heat flow rate is produced which is sum of all heat flows occurring during that temperature or time. The operating principle for Modulated Differential Scanning Calorimeter (MDSC) is that it produces 2 heat signals i.e. 2 heating rate simultaneously. First Heating rate is similar to that produced by standard DSC which is linear heating rate, Second heating rate produced is sinusoidal or modulated which gives the capability to measure the sample's specific heat capacity. A modulation period (seconds) and modulation temperature ($^{\circ}\text{C}$), which is required in order to create sinusoidal heating rate. Apparently MDSC holds advantage than standard DSC because the MDSC measures Total heat flow, specific heat capacity and kinetic component whereas the standard DSC only measure single signal heat flow which sum of all thermal events at a particular temperature/time.

2.5 Testing procedure in MDSC

A modulated protocol is employed in the Differential Scanning Calorimeter (DSC) to measure the specific heat capacity. Two pans are loaded in MDSC i.e. empty pan, which is the reference pan and sample pan. Initially the samples are maintained at a temperature of 40°C and then the temperature is ramped up to 300°C at the rate of $5^{\circ}\text{C}/\text{min}$. The samples are maintained at that temperature for 5 minute i.e. the samples are at isothermal state. Gradually the samples are allowed to cool down. Specific heat capacity results are obtained from software from TA Universal Analysis (TA Instruments) [17], which is connected, to DSC and a computer. The plot of specific heat capacity versus temperature observes a

significant amount of enhancement. The samples tested are doped with 5nm, 10nm, 30nm, and 60 nm size nanoparticles.

Chapter 3

Result and discussion

3.1 Specific heat capacity results

The MDSC gives us the result of specific heat capacity in solid state as well as the liquid state. Here the specific heat capacity is measured versus temperature. Initially, pure samples are tested to make sure the results obtained from DSC are correct and nanoparticle doped samples could be tested so that whether there is enhancement or not is detected. For this purpose, pure samples are prepared first followed by Nano fluid. According to literature average specific heat capacity of pure sample in liquid state is 1.4 J/g °C. The experimental value obtained from the DSC is in good agreement with the literature. For repeatability purpose the samples are tested from the sample bottles or vials. The experimental tests are followed by testing of nanoparticle doped samples i.e. Nano eutectic of different sizes of nanoparticle were used for doping the base material. 5 nm, 10 nm, 30 nm and 60 nm were the sizes used for doping the base sample.

3.1.1 5nm SiO₂ doped in base salt

Table 3.1 Comparison Table of pure salt v/s 5nm nano eutectic

Heat Capacity	Pure	Nano Eutectic Mixture (5 nm)
Repeat # 1	1.42	1.52
Repeat # 2	1.40	1.56
Repeat # 3	1.39	1.42
Average	1.40	1.51
Enhancement (%)	-	7.85
Standard Deviation	0.02	0.05

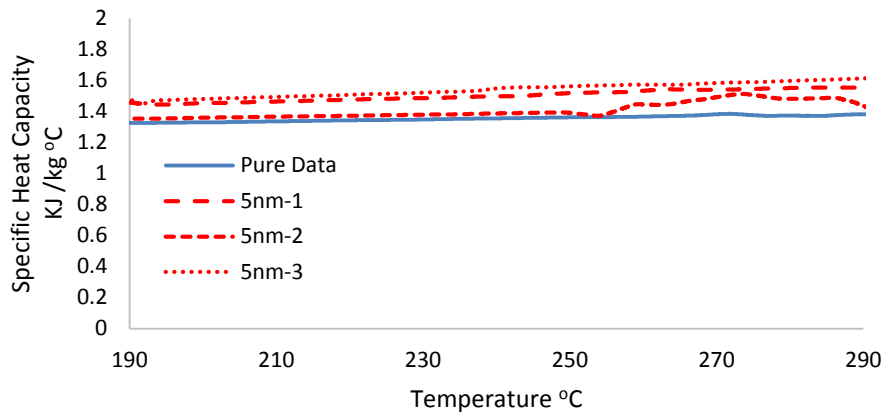


Figure 3.1 comparison of specific heat capacity of pure salt v/s 5nm nano eutectic

Enhancement of 7%-8% in specific heat capacity is achieved by embedding 5nm nano particle in pure quaternary mixture

3.1.2 10nm sio2 doped in base salt

Table 3.2 Comparison Table of pure salt v/s 10nm nano eutectic

Heat capacity	Pure	Nano Eutectic Mixture (10 nm)
Repeat # 1	1.42	1.73
Repeat # 2	1.40	1.76
Repeat # 3	1.39	1.81
Average	1.40	1.76
Enhancement (%)	-	25
Standard Deviation	0.02	0.04

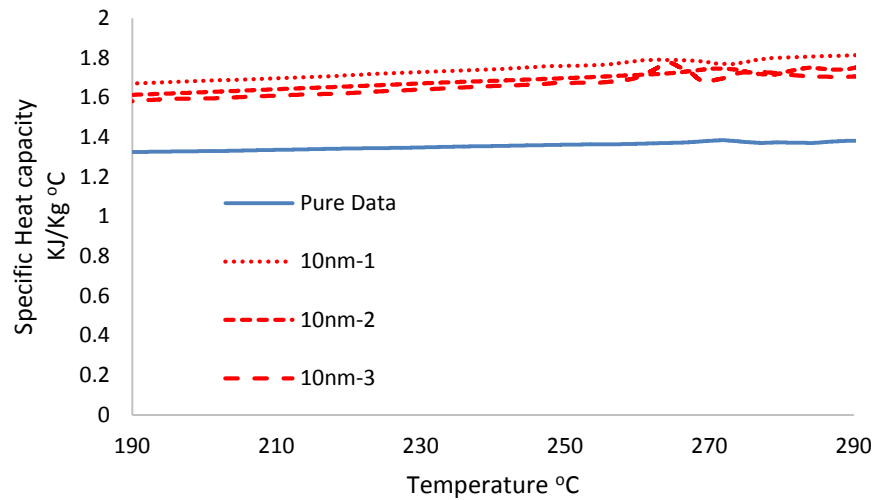


Figure 3.2 comparison of specific heat capacity of pure salt v/s 10nm nano eutectic

Enhancement of 20%-25% is achieved in specific heat capacity by embedding 10nm nanoparticle in pure quaternary mixture

3.1.3 30nm sio2 doped in base salt

Table 3.3 Comparison Table of pure salt v/s 30nm nano eutectic

Heat Capacity	Pure	Nano Eutectic Mixture (30 nm)
Repeat # 1	1.42	1.57
Repeat # 2	1.40	1.60
Repeat # 3	1.39	1.65
Average	1.40	1.60
Enhancement	-	1.60
Standard Deviation	0.02	0.04

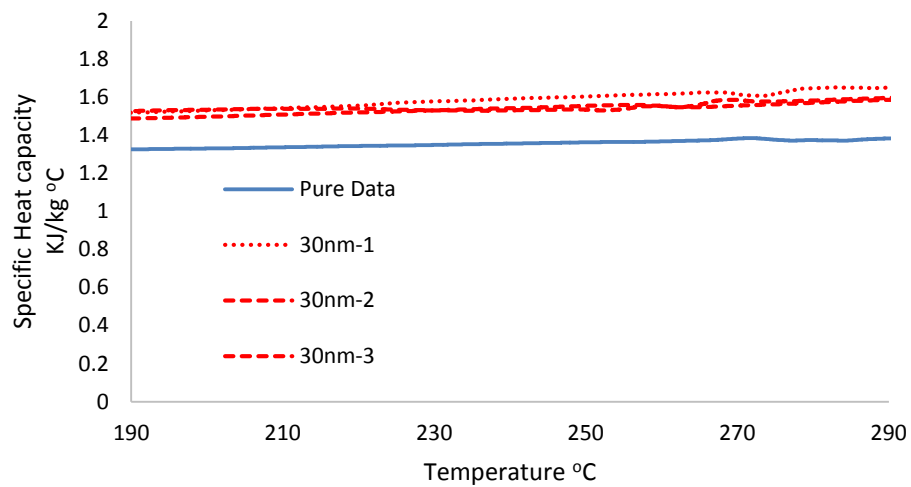


Figure 3.3 comparison of specific heat capacity of pure salt v/s 30nm nano eutectic

Enhancement of 10%-15% is achieved in specific heat capacity by embedding 30 nm Nano particle size in pure quaternary mixture

3.1.4 *Sio2 doped in base salt*

Table 3.4 Comparison Table of pure salt v/s 60nm nano eutectic

Heat Capacity	Pure	Nano Eutectic mixture (60 nm)
Repeat # 1	1.42	1.62
Repeat # 2	1.40	1.64
Repeat # 3	1.39	1.70
Average	1.40	1.65
Enhancement (%)	-	17.85
Standard Deviation	0.02	0.04

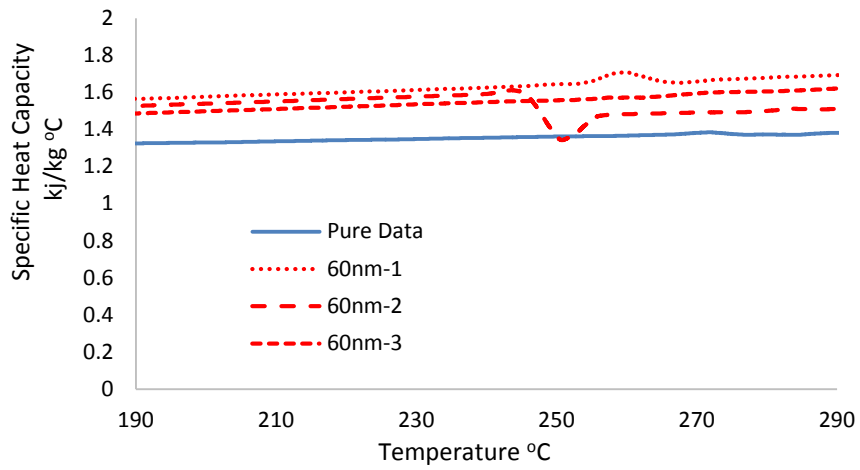


Figure 3.4 comparison of specific heat capacity of pure salt v/s 60nm nano eutectic

Enhancement of 15%-20% is achieved in specific heat capacity on embedding 60nm nano particle in pure quaternary mixture

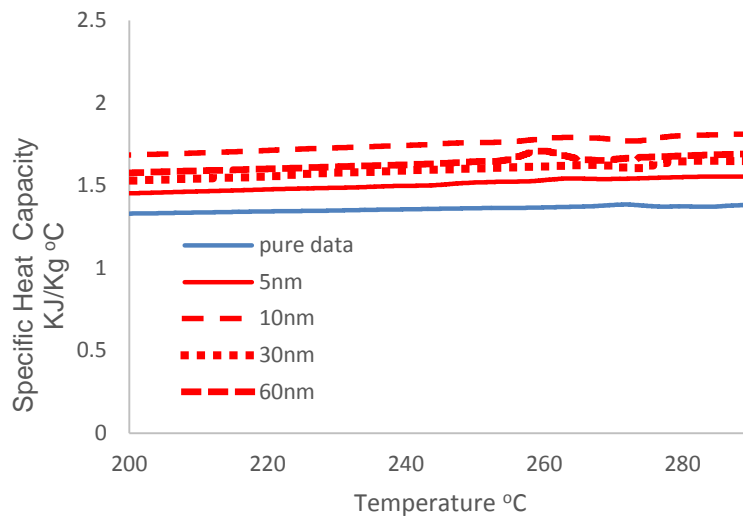


Figure 3.5 comparison of specific heat capacity of pure salt v/s effect of various sizes of nanoparticles

The above graph shows the comparison of increment in specific heat capacity of nano eutectic salt doped with various sizes of nanoparticles v/s pure base salt

Chapter 4

Material characterization

4.1 Scanning electron microscopy

In order to understand the underlying mechanism causing the enhancement in specific heat capacity, it was decided to perform material characterization. Material characterization refers to study of material in which usually internal structures and various properties are measured. Since specific heat capacity is related to internal structure of the substance, material characterization is performed here in order to understand the enhancement of specific heat capacity on structural level. Various other material characterization techniques include Energy Dispersive Spectroscopy (EDS), Back Scattering Electron spectroscopy (BSE), X-ray diffraction (XRD), and X-ray photoelectron Spectroscopy (XPS). Scanning Electron Microscopy (SEM), High resolution Scanning Electron Microscopy (HRSEM) are performed here in order to comprehend the phenomena responsible for enhancement in specific heat capacity. silica nanoparticle reacts and form nanostructures

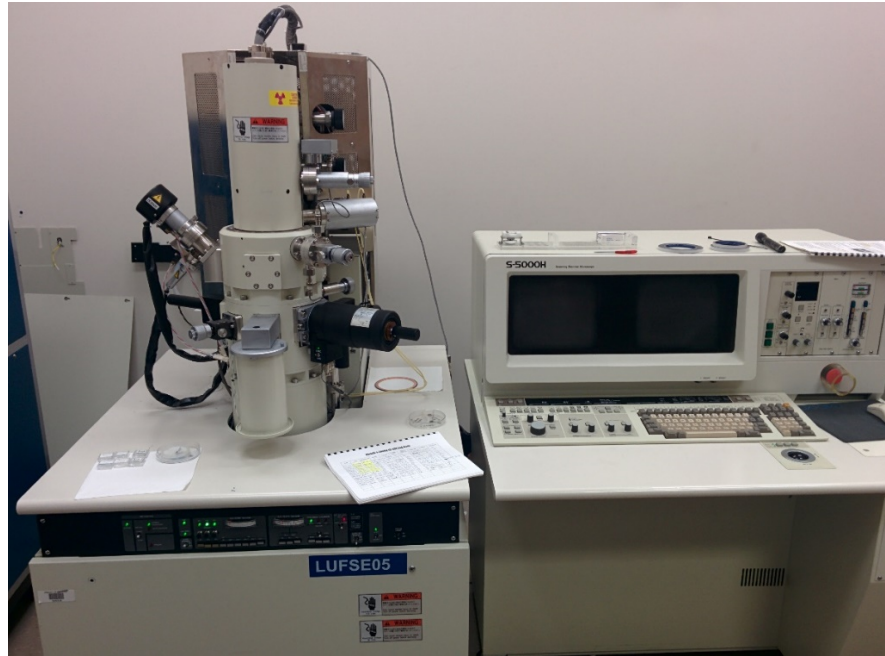


Figure 4.1 High resolution scanning electron microscopy

4.2 High Resolution Scanning Electron Microscopy Images

4.1.1 Pure quaternary salt mixture image at 3000x

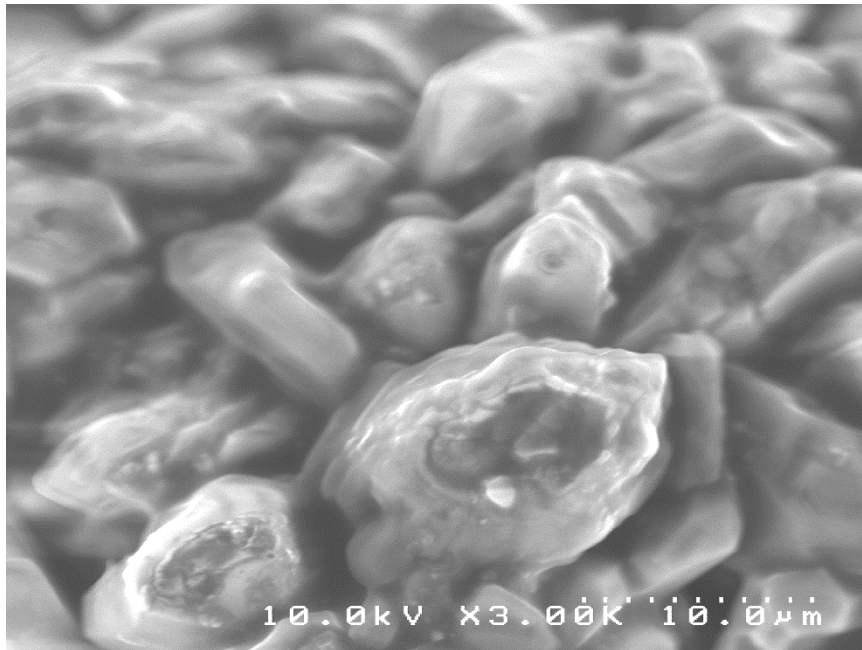


Figure 4.2 High resolution scanning electron microscopy image of pure salt

The above image is taken by high resolution scanning electron microscopy which is image of pure quaternary nitrate salt which is not doped with silica nanoparticles, hence showing no needle like structures

4.1.2 30nm SiO₂ added in base quaternary salt image taken 10000x resolution

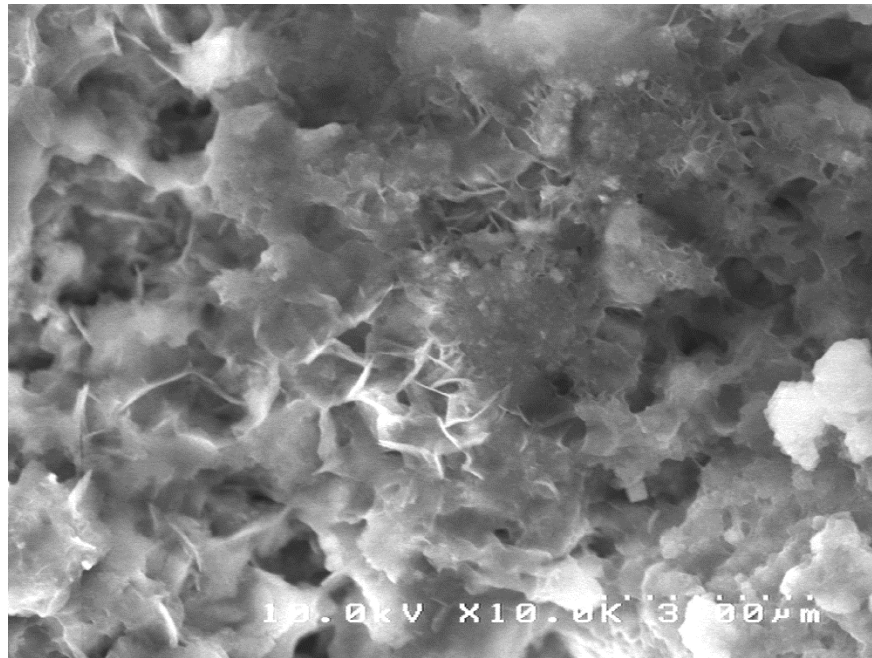


Figure 4.3 High resolution scanning electron microscopy of nanostructure - 1

The above image is taken by high resolution scanning electron microscopy which is image showing formation of needle like structure when base salt is doped with 30nm nano particle.

4.1.3 30nm SiO₂ added in base quaternary salt image taken 15000x resolution

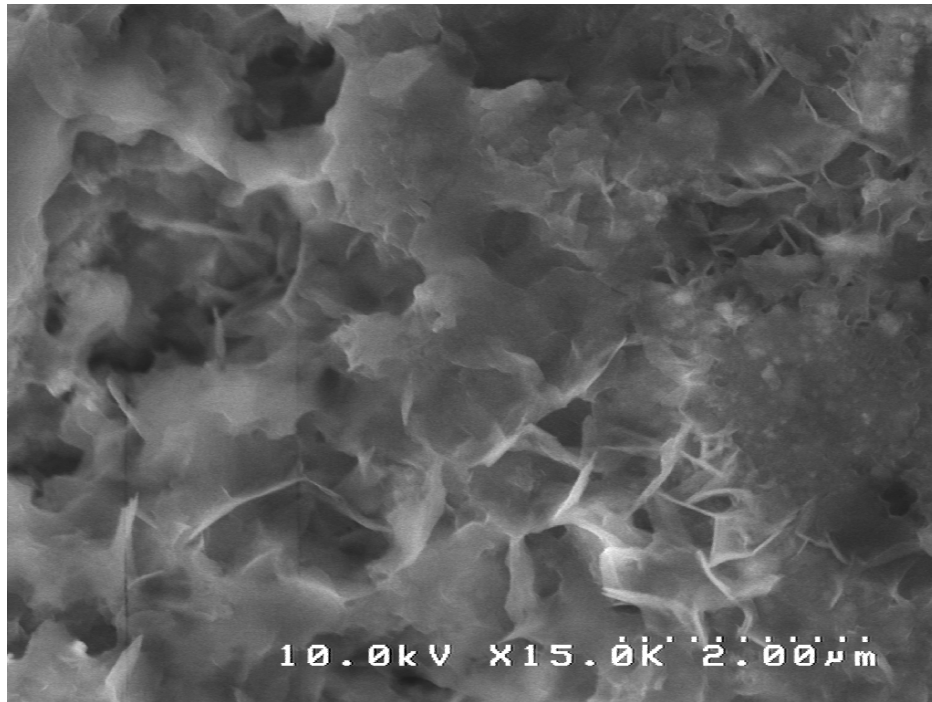


Figure 4.4 High resolution scanning electron microscopy of 30nm nanostructure -1

The above image is taken by high resolution scanning electron microscopy which is image showing formation of needle like structure when base salt is doped with 30nm nano particle

4.3 High Resolution high magnification

4.3.1 High magnification 10nm image

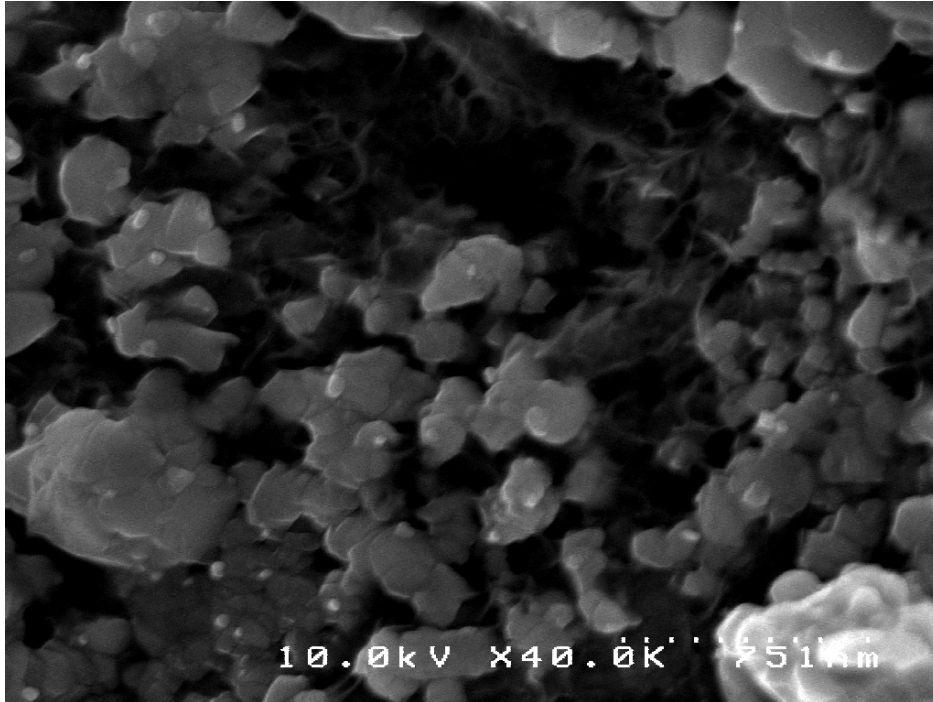


Figure 4.5 High resolution scanning electron microscopy image - 1 of 10nm nanostructure formation

This is high resolution image showing formation of nano structure when base salt is doped with 10nm size nanoparticle

4.4 Energy dispersive spectroscopy

Energy diffusive spectroscopy is one of the material characterization technique, where we can determine the element present in the specimen under consideration and quantity of those element. A spectrum of x-ray beam is generated from the scanned area of the scanning electron microscopy image of the specimen under consideration . Here Y-axis represents the number of X-rays received and processed by the detector and the X-axis represents the energy level of those X-rays. Noran System Six software, here, is used to represent the data is tabular and graphical form.

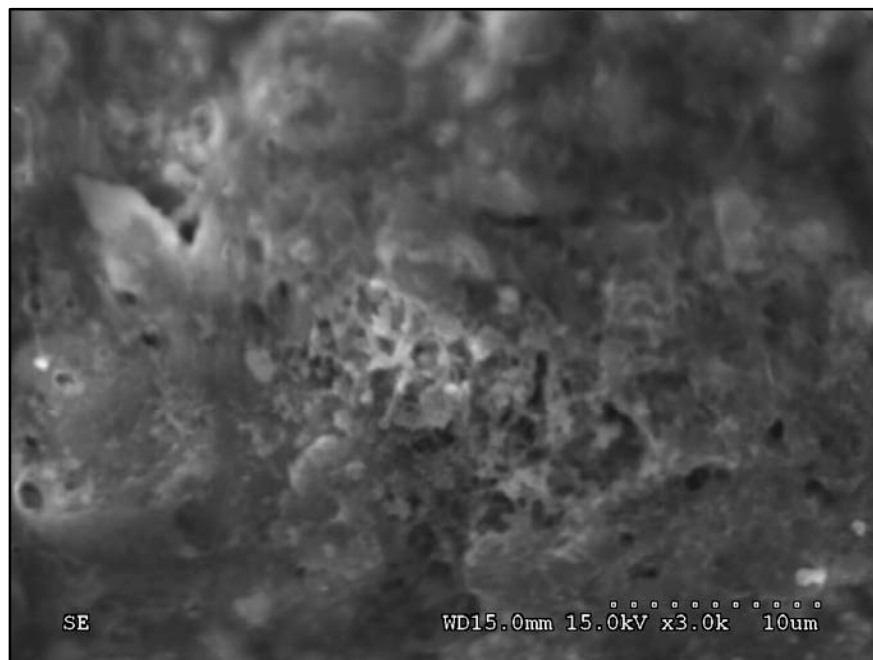


Figure 4.6 Low resolution SEM for EDS analysis

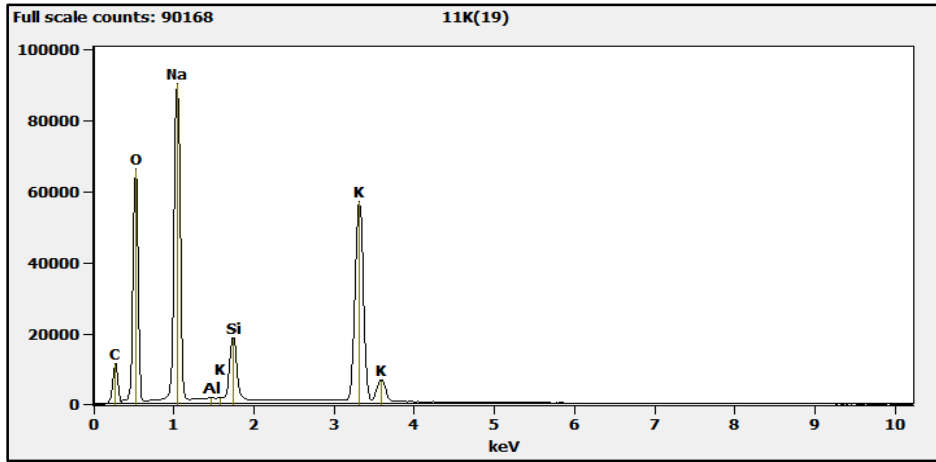


Figure 4.7 Elemental analysis of the nano structure area

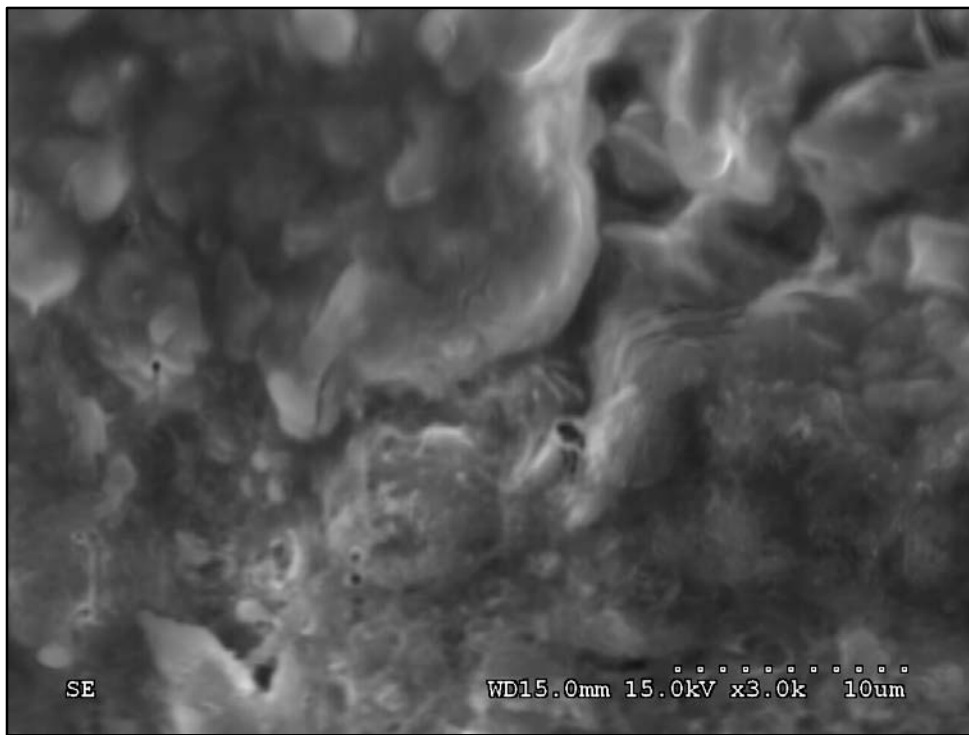


Figure 4.8 Low resolution SEM of plain area near nanostructure

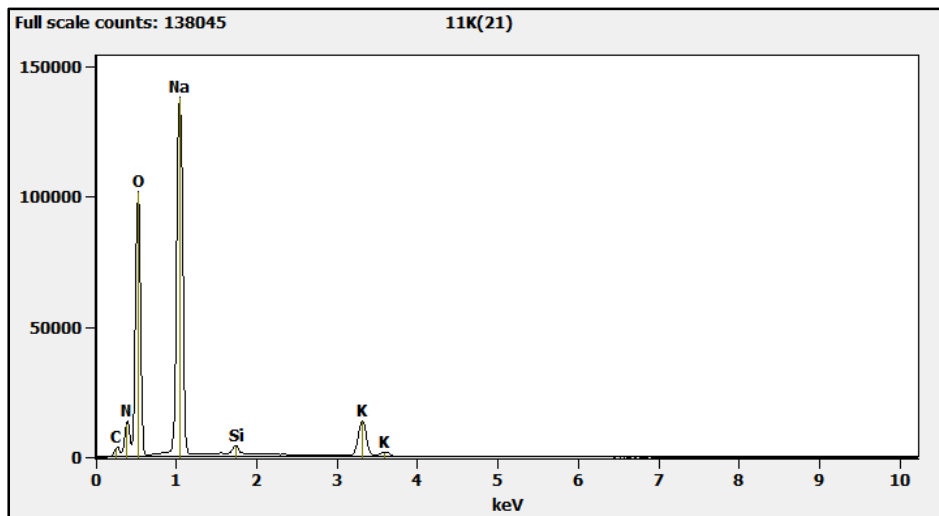


Figure 4.9 elemental analysis of no nanostructure area

Chapter 5

Conclusion and future work

In this study, a novel quaternary nitrate/nitrite eutectic mixture has been embedded with silica nanoparticle to in order to enhance its specific heat capacity. A eutectic mixture of $\text{LiNO}_3 - \text{KNO}_3 - \text{NaNO}_3 - \text{KNO}_2$ is synthesized in (9 - 33.6 - 42.3 - 15.1) in mass fraction (wt. %). The pure data was verified and it is in good agreement with the literature value. Silica nanoparticle are doped in the base eutectic mixture in small concentration. Different sizes of nanoparticles like 5nm, 10nm, 30nm, 60nm were used to embed in pure salt. It was observed that the mixture showed enhancement in specific heat capacity. Different size of Nano particle sizes showed different percentages of enhancement in specific heat capacity. Highest amount of enhancement i.e. 25% is observed when pure quaternary mixture is embedded with 10 nm sizes Nano particle. Scanning Electron Microscopy is performed in order to understand the internal structural behavior of the salt. On performing the SEM analysis it was observed that on doping the base eutectic mixture with silica nanoparticle in small concentration, dendritic or needle like structures are formed. Based on previous research results reported, It seems that these needle like or dendritic structures seemed to be a reason which causes anomalous enhancement in specific heat capacity [10-15].

Current binary nitrate molten salt used in industry as energy storage material has a disadvantage which is that of high freezing point of 220°C. The quaternary nitrate/nitrite material holds a distinct advantage of low melting of 100oC. On being used as an advanced HTF & TES in industry, a significant cost of the overall power plant could be brought down. Physical size of thermal energy storage tanks practically can be reduced which would result in reduced cost of the CSP plant.

Along with bringing down the cost of plant, the cost of electricity could also be brought down. Currently the cost of electricity produced by CSP is 0.15-0.17KWh. The cost of electricity could go down as low as 0.05-0.07 KWh [16]

The future work regarding quaternary nitrate/nitrite molten salt is to conduct testing to check thermal stability, viscosity measurements, different concentration ratio of silica nanoparticle should also be tested to measure to effect of concentration of silica nanoparticle on enhancement of specific heat capacity

References

- 1) Chu, Y. (2011). Review and comparison of different solar energy technologies. *Global Energy Network Institute (GENI), August.*
- 2) Pavlović, T. M., Radonjić, I. S., Milosavljević, D. D., & Pantić, L. S. (2012). A review of concentrating solar power plants in the world and their potential use in Serbia. *Renewable and Sustainable Energy Reviews, 16(6)*, 3891-3902.
- 3) Kuravi, S., Trahan, J., Goswami, D. Y., Rahman, M. M., & Stefanakos, E. K. (2013). Thermal energy storage technologies and systems for concentrating solar power plants. *Progress in Energy and Combustion Science, 39(4)*, 285-319.
- 4) IEA, solar thermal electricity roadmap, 2014 edition
- 5) Introduction to Nano material. Pdf
- 6) Margolis, R., Coggeshall, C., & Zuboy, J. (2012). SunShot vision study. *US Dept. of Energy.*
- 7) Glatzmaier, G. (2011). Summary Report for Concentrating Solar Power Thermal Storage Workshop. *National Renewable Energy Laboratory, Golden, CO, Report No. NREL/TP-5500-52134.*
- 8) Devaradjane, R. (2013). Utilization Of Molten Nitrate Salt Nanomaterials For Heat Capacity Enhancement In Solar Power Applications.
- 9) Eastman, J. A., Choi, S. U. S., Li, S., Yu, W., & Thompson, L. J. (2001). Anomalously increased effective thermal conductivities of ethylene glycol-based nanofluids containing copper nanoparticles. *Applied physics letters, 78(6)*, 718-720.
- 10) Alguacil, F. J. (2012). Energy technology 2012: Carbon dioxide management and other technologies. *Revista de Metalurgia, 48(5)*, 395.

- 11) Shin, D., & Banerjee, D. (2011). Enhancement of specific heat capacity of high-temperature silica-nanofluids synthesized in alkali chloride salt eutectics for solar thermal-energy storage applications. *International journal of heat and mass transfer*, 54(5), 1064-1070.
- 12) Shin, D., & Banerjee, D. (2011). Enhanced specific heat of silica nanofluid. *Journal of heat transfer*, 133(2), 024501.
- 13) Tiznobaik, H., & Shin, D. (2013). Enhanced specific heat capacity of high-temperature molten salt-based nanofluids. *International Journal of Heat and Mass Transfer*, 57(2), 542-548.
- 14) Dudda, B., & Shin, D. (2013). Effect of nanoparticle dispersion on specific heat capacity of a binary nitrate salt eutectic for concentrated solar power applications. *International Journal of Thermal Sciences*, 69, 37-42.
- 15) Shin, D., & Banerjee, D. (2013). Enhanced specific heat capacity of nanomaterial's synthesized by dispersing silica nanoparticles in eutectic mixtures. *Journal of Heat Transfer*, 135(3), 032801.
- 16) Tiznobaik, H., & Shin, D. (2013). Experimental validation of enhanced heat capacity of ionic liquid-based nanomaterial. *Applied Physics Letters*, 102(17), 173906.
- 17) <http://www.renewableenergyfocususa.com>
- 18) http://www.tainstruments.co.jp/application/pdf/Thermal_Library/Technical_Papers/TP006.PDF

Biographical Information

Sumeet. Changla was born in Rajasthan, India on 24th December 1990. He did his schooling in St. Xavier's high school. He graduated from Gujarat Technological University in 2012 and worked as a Maintenance Engineer for K. S. Constructors Private Limited from June 2012 – June 2013. In May 2015 he completed his Master of Science degree in Mechanical Engineering from University of Texas at Arlington. He has over 1 year experience in thermal fabrication of novel molten salt for energy storage material whose application lies in concentrated solar power plant. He also holds expertise in Material characterization techniques such Scanning Electron Microscopy and Energy Diffusive Spectroscopy.

Sumeet Changla is the eldest son to Mr. Surendra Changla and Mrs. Pramila Changla. His father works as Deputy Manager in Indian Oil Company and his mother is a housewife. His sister is in 3rd year pursuing her Electrical and Electronics Engineering from Indus University, Ahmedabad.