UTILIZATION OF MOLTEN NITRATE SALT NANOMATERIALS

FOR HEAT CAPACITY ENHANCEMENT IN

SOLAR POWER APPLICATIONS

by

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ABSTRACT

UTILIZATION OF MOLTEN NITRATE SALT NANOMATERIALS

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Concentrated solar power (CSP) system use general thermodynamic cycle to produce electricity and thus the system efficiency is mainly determined by the working temperature of heat transfer fluid (HTF). Organic-based HTFs (e.g., mineral oil, ethylene glycol, etc.) were firstly used for this application. However, this has limited the working temperature of CSP around 300 °C since these organic material starts to decompose below 400 °C. Typical liquid salts are thermally stable to high temperatures (500~600 °C). Using these salts as HTF can significantly increase the working temperature and as a result the system efficiency can also be highly enhanced. For example increasing working temperature from 300 °C to 500 °C can simply increase Carnot efficiency from 48 % to 61 %. Moreover, these salts are eco-friendly and using them as HTF can reduce the potential environmental cost caused by the conventional HTF. These salts also have very low vapor pressure that can reduce the potential mechanical stress on the pipe / storage system caused by using the conventional HTF.

Recently a binary liquid salt ($NaNO_3$-KNO_3; also termed as "solar salt") has been introduced and adapted in the most recent CSP plants. This solar salt is also used as thermal energy storage (TES) medium. Extra thermal energy collected in the daytime is stored in solar salt and kept in a TES for later use. When electricity demand peaks (e.g., evening time) solar salt in TES provide thermal energy to continue electricity production. One of the major challenges to use solar salt as HTF / TES is its high freezing point at 220 °C. This has the potential risk of crystallization in a pipe / storage system in a harsh condition (e.g., rainy season) and can result in high maintenance & operation costs for extra freezing protection system (e.g., insulation, auxiliary heater, etc.).

Adding $Ca(NO_3)_2$ to solar salt can dramatically decrease the freezing point (down to 120 °C). However, this ternary salt mixture has relatively low thermo-physical properties. Doping this material with oxidized nanoparticles can improve these properties. Nanofluids are liquids doped with nanoparticles. They have been proposed for large enhanced thermo-physical properties. In this report, the low thermo-physical properties were highly enhanced by doping with nanoparticles (19 % increase by 1 % nanoparticle concentration by weight). The result of this study will be useful to develop advance HTF / TES material for CSP plants. This will also applicable for other high temperature HTF applications such as geothermal energy, nuclear energy, and other energy generation technologies using thermodynamic cycle.

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CHAPTER 1

INTRODUCTION

1.1 Introduction to Solar Energy

Solar energy is renewable energy derived from the sun. This radiant energy is being used with the modern evolving technologies. This energy derived from the sun is inexhaustible, harmless and can serve the long time benefits. Technologies utilizing solar energy can broadly be categorized into two main types, namely the Active solar and the Passive solar. Techniques which include the direct application to harness energy from the sun as in the case of thermal collectors or photovoltaic panels where the sunlight is directly used come under the active solar. The passive solar includes techniques where the energy is harnessed with the help of other favorable thermal materials which utilize the solar power for their operation such as the case with buildings orienting to the sun, selecting materials with favorable thermal mass and designing accordingly. Passive solar is constrained to certain areas with the proper climatic requirements.

Solar thermal energy (STE) is the technology for harnessing the solar energy to thermal energy as in the form of heat. Harnessing solar energy can be conducted in two different ways. Photovoltaic (PV) actively converts solar energy into electricity using semi-conductors whereas concentrated solar power (CSP) collects solar radiant energy into a small focal point to obtain high quality thermal energy. Solar thermal energy is much more efficient in converting the solar energy directly to electricity than photovoltaic [1]. Concentrated solar power plants using this solar energy are likely to produce around 14000 megawatts [2]. With the need for an alternate source of energy solar thermal energy is one of the best solutions to meet the growing demand.

1.2 Concentrated Solar Power

Solar thermal technologies are based on the concept of concentrating the radiation from the sun which produces steam or hot air by which generation of electricity is established following the thermal power cycles. Mirrors with high reflectivity or sometimes glass serve the purpose of concentration. Line focusing and point focusing are the two systems which are used in concentrating the solar power from the sun. These systems use only the direct radiation from the sun in focusing the energy.

Line focusing system has a low concentration factor and can achieve only low temperatures. They usually operate at pressure's ranging from 80 to 120 bar and the temperature of the steam that can be achieved ranges about 350 to 550 ºC. The point focusing systems considerably have a higher concentrating factor and can reach up to 600 ºC to 1200 ºC and their operating pressures are usually 1 to 20 bar [3].
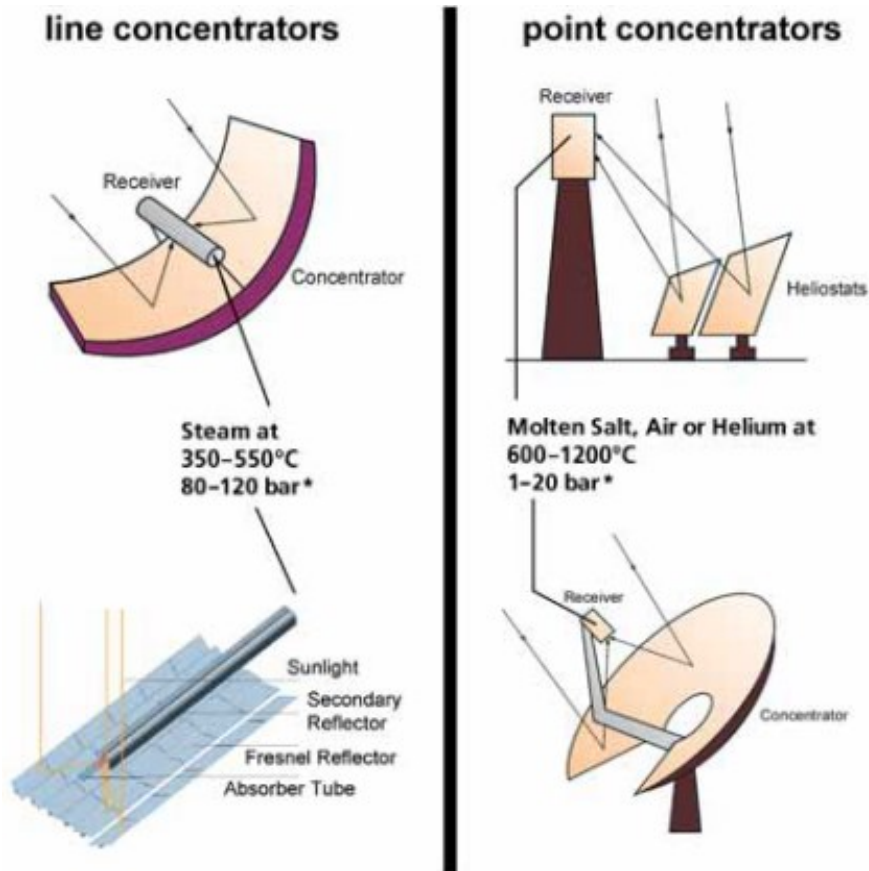
Figure 1.1 Technologies for concentrating solar radiation: Line concentrators – parabolic and linear Fresnel trough. Point concentrators – tower receiver and parabolic dish (Source DLR) [3]

The Solar thermal power plants constitute the following major parts concentrator, receiver, storage / transport system, and the power conversion device. The economic success of a thermal power plant is dependent on its storage capacity [4]. Designing a storage system is a complex part due to issues related to its design and heat transferring capacities. Storage systems that are to be considered should have the capacity to be operated between 300°C to 390°C [5]. The material to be selected for the transfer and storage hence must possess certain enhanced characteristics as in high thermal conductivity (K), good heat transfer co-efficient (Cp), less corrosive to the heat exchanger, cost efficient, high flash point, high heat of

vaporization and less thermal decomposition [6]. The selected material for the Thermal Energy Storage (TES) is to be thermally stable, less reactive with the medium, feasibility to be stored in a container, high resistance to cyclic thermal loading and low cost. A heat transfer fluid can be utilized for this application. Heat transfer fluids in conventional system may heat to ~ 500°C which can be used as a storage medium or even as a channel to store the heated fluid. The thermal energy storage medium can later be used to obtain the required electrical energy.
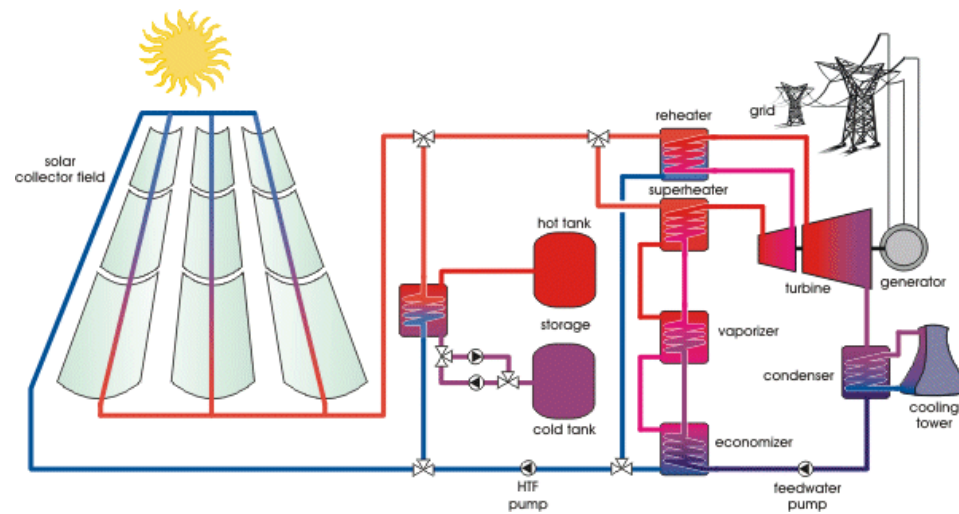
Figure 1.2 Schematic diagram of a steam cycle power plant with a parabolic trough collector and thermal energy storage (Source DLR) [3]

1.3 Molten Salts as Heat transfer Fluid

Molten salts are ionic liquids which are solid at standard temperature pressure but attain the liquid phase at elevated temperatures. Molten salts can be used as Heat Transfer Fluids (HTF) in a trough for many reasons. When molten salts can be used, the temperature of the output field nearly raises to about 450°C to 500° C, which increases the Rankine cycle efficiency of the block to about 40%. This is high as compared to the 37.6% efficiency attained by high temperature oil at 393 °C. Temperature of HTF increases nearly by a factor of 2.4 hence reducing the physical size and storage capacity of the storage system [7]. Moreover,

molten salts are cheap, environmentally friendly and are easily available. This makes molten salts a better alternative to oil. However, the freezing point of molten salts is much higher than oil. Binary salts, freeze at 220 ºC whereas ternary molten salts freeze at 120 ºC. This problem demands innovative freeze protection methods and increased operation and maintenance. By using molten salts, the thermal-fluid characteristics of the collector field are improved. The choice of molten salts is also for their diverse properties namely like their tendency to act as a chemical catalyst, property to stay stable at high temperatures.

1.3.1 Specific Heat Capacity

Specific heat capacity is the amount of heat required to raise the temperature of a unit mass substance by one degree Celsius. Specific heat capacity is the key factor of the storage/transport system in the solar thermal power plant, since this phenomenon completely controls the capacity of raise in temperature that can be stored or transported. Increasing the specific heat capacity increases the overall cycle efficiency.

<u>1.4 Heat transfer Fluid in Parabolic Trough</u>

The rising popularity for alternate energy has taken a huge step in resource management and has enhanced research work in this area. HTF which serves the purpose of thermal storage in a solar power plant is the key component and the one with complex design issues which arise in transferring the high heat. Systems that are considered to serve the storage purpose may be operated between 120 ºC to 400 ºC.

In a parabolic trough, the trapped solar energy requires suitable material to be transported to the thermal energy storage devices. The complete storage process involves three major steps – charging, storing and discharging. The HTF chosen for storage must possess some enriched characteristics. The HTF must be thermally stable, should be less reactive with the medium, feasible to be stored in a container, must have high resistance to cyclic thermal loading and cost efficient. Heat transfer fluids in conventional system may heat to

~ 500°C which can be used as a storage medium or even as a channel to store the heated fluid. The thermal energy storage medium can later be used to obtain the required electrical energy.

There are a few factors which mainly affect the performance of the plant when salts are used as HTF [7]. Compared to the synthetic oil that is currently being used, molten salts can operate at elevated temperatures. The high steam pressure that can be achieved in the Rankine cycle leads to higher cycle efficiency. When molten salts are used, the mass flow rate of the solar field is considerably low, which in turn leads to reduced loss of pressure in the piping. Reduced mass flow rate and pressure loss together lead to low pumping parameters as compared to Therminol VP-1. The average temperature in the solar field increases with increase in temperature of the outlet. This consequently leads to higher heat losses in the solar field, and the solar field efficiency decreases. Also, another negative factor up on using hitec xl, is that the freezing point is around 120°C which is high. Hence, there is additional heat loss to keep the solar field temperature well above 120°C even during nights as a freeze protective operation.

1.5 Candidate Salts

Nitrate salts are selected for the purpose to be used as HTF. Some of the favorable properties of Nitrate salts make them a better candidate than other salts like chlorides and carbonates. A few of the reasons for selecting Nitrate salts are thermal stablility at high temperatures, low corrosion rates with the materials used for heat transfer, low vapor pressures, ability to remain at elevated temperatures throughout the Rankine cycle and relatively cheap.

According to a recent study carried out by Kearney and Associates [7] under subcontract to SunLab looks in detail at the option of using inorganic molten salts as the heat transfer and thermal storage fluid for a trough system. The commercial nitrate mixture hitec xl melting at about 120°C is selected. The hitec xl is a composition of Calcium Nitrate, Sodium Nitrate and Potassium Nitrate. Compared to other heat transfer fluids, like Therminol VP-1, solar salt, Hitec and ionic liquid, hitec xl is a ternary salt which can sustain the heat collection

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particularly at high temperatures. Hitec xl can also be configured to be used with two different fluids like oil to salt heat exchanger or in other cases as storage system analysis using a thermocline system.

The only engineering issue related to using hitec xl salt is the problems associated with freeze protection methods, costing and operation at low temperatures. This usually happens at night times when the flow of the molten salt from the thermal storage tanks freezes. To combat this problem, innovative approaches like using freeze protection techniques with external heated coils, ball and joint protection, using an anti-freeze agents etc., are to be installed. Some of the operating parameters comparing Hitec, Solar salt, hitec xl and Therminol VP are enlisted in the table 1.1 [7].

Table 1.1 Operating conditions and fluid cost for storage [7]

	Steam Rankine cycle		
Power block capacity	55 MWe		
Steam inlet pressure	66bar to 100bar		
Steam inlet temperature	Around 400ºC		
Salt	Temperature raise	Cost per Kg	Storage Cost
	ºC	$/Kg	$/KWh
Hitec (Sodium Nitrate/ Nitrite and potassium Nitrate)	200	0.93	10.7
Solar Salt (Sodium Nitrate and Potassium Nitrate)	200	0.49	5.8
Therminol VP – 1	100	2.2	57.5

Table 1.1 – *Continued*

Hitec xl (Calcium Nitrate, Sodium Nitrate and Potassium Nitrate)	200	1.19	15.2
	150	1.19	20.1
	100	1.19	30.0

The table briefs the economic value and range of properties for the use of hitcec xl, the Hitec salt is also one of the candidate salts taken under consideration, but the presence of Nitrites makes it a less favorable due to higher corrosion rate. Usually the pipes are made of Carbon steel when the operating temperature is about 325ºC and Ferritic steel if the temperatures ranges between 400ºC to 500ºC. Nitrites cause a higher corrosion rate than compared with Nitrates. This gives a preference for Nitrates over Nitrites. Nominal storage cost and the ability to reach high temperatures makes hitec xl a preferred candidate than other molten salts or oil. Comparison of some key properties for hitec xl with other candidate heat transfer fluids like Therminol VP1- and the ionic liquid are scripted in the table 1.2 [8].

Table 1.2 Key properties of Therminol VP-1, hitec xl and Octylmethyl-imdazolium Tetrafluoroborate (ionic liquid) [8]

Properties @ 25ºC	Therminol VP-1	Hitec xl	Ionic liquid
Freezing point (ºC)	13	120	<25
Max applicable T (°C)	400	>500	400
Density (kg/m3)	815 (300°C)	1992 (300°C)	1400
Specific Heat capacity Cp (J/Kg K)	2319 (300°C)	1447 (300°C)	2500
Thermal conductivity k (W/mK)	0.098479 (304°C)	0.519 (300°C)	Tbd
Cost ($/kg)	3.96	1.19	4.57

Maximum temperature for hitec xl is much greater than both the ionic liquid and Therminol VP-1. Also the cost per kg of hitec xl is much lower than Therminol VP-1 and ionic liquid. These important parameters initiate the advantage of using the molten salt as a HTF.

1.6 Composition and Properties

Hitec xl is a composition of Calcium Nitrate ($Ca(NO_3)_2$), Sodium Nitrate ($NaNO_3$) and Potassium Nitrate (KNO_3). The mole fractions of the respective salts are as follows - 49% $NaNO_3$, 30% KNO_3 and 21% $Ca(NO_3)_2$ possessing a molar mass of 85.0g/mole, 101.1g/mole and 164.09g/mole respectively. The individual thermal and physical properties of the eutectic are discussed in Table 1.3 [9].

Table 1.3 Physical and Thermal properties of Calcium Nitrate, Sodium Nitrate and Potassium Nitrate [9]

	Sodium Nitrate	Calcium Nitrate	Potassium Nitrate
Molar Mass	84.9947 g/mol	164.088 g/mol	101.1032 g/mol
Density	2.257 g/cm^3	2.504 g/cm^3	2.109 g/cm^3
Melting Point	308 °C	42.7 °C	334 °C
Boiling Point	380 °C	132 °C	400 °C
Solubility in water	91.2 g/100 mL @ 25°C	121.2 g/100 mL @20 °C	316 g/L@20 °C
Flash point	Non-flammable	Non-flammable	Non-flammable

Hitec xl as a eutectic has enhanced characteristics than the individual components. The Specific heat capacity, which is the amount of heat that can be stored or transported parabolic trough as a HTF can be enhanced, by the addition of nanoparticles. Research has shown that nanoparticles of the right material, size and quantity can enhance some properties. Suspension of nanoparticles in a base fluid can result in unique transport properties which do not block the flow or settle under gravity. Enhanced functions and properties can be achieved by combining

and controlling the interactions using different mixing methods, flow conditions and thermal conditions.

1.7 Nanomaterial Properties

Nano fluids are nothing but suspensions of nanoparticles in a base fluid. Nano fluids have a wide range of applications as in heat transfer nanofluids, chemical nanofluids, medical nanofluids, coating and surfactant nanofluids etc. In the research work carried by Dr. Choi [10] and his team, Nanofluids are classified as a new class of advanced heat transfer fluids, engineered by dispersing nanoparticles smaller than 100nm in diameter in conventional heat transfer fluids.

The original concept of dispersing solid nanoparticles in a fluid dates back to the time of Maxwell in the 19th century where the enhancement of thermal conductivity is witnessed on the addition of solid nanoparticles to fluidic base medium. Various studies on particle suspensions to the base medium have been confined to millimeter sized particles. When such small particles are dispersed in the liquid medium there are several challenges that ought to be addressed. The major challenge in using particle dispersion is the rapid settling of these particles in the base fluid. When nanoparticles are used for suspension, they remain suspended for a longer time and if the quantity of the suspended particles is greater than the threshold level, these particles remain suspended almost for an indefinite period. Proportionate addition in the amount of nanoparticles to the base fluid can be used for enhanced flow rate, heat transfer and other characteristics.

Some of the common materials that can be used for nanoparticles include ceramic oxides like Al_2O_3, CuO, SiO_2, Nitrides like AlN, SiN, Metals like Ag, Al, Cu, Carbides like SiC, Nonmetals like carbon nanotubes, Graphite etc. Materials that are widely used as base fluids include water, ethanol, methanol, oil and some polymer solutions. The specific heat capacity (C_p) can be enhanced by the addition of nanoparticles of right composition at the right

temperature with right proportions. Studies by Debjyoti Banerjee and Donghyun Shin [11] have shown an enhancement of about 22% in the solid phase and 74% in the liquid phase for the carbonate salts doped with SiO_2 nanoparticles.

<div align="center">1.8 SiO₂ and Properties</div>

Silicon dioxide is one of the commonly found substances in nature. It is mostly found as sand or quartz. The tetrahedron structure with four oxygen atoms makes it more stable. Silicon oxide Nanopowder also known as nanodots are particles with high surface area. On the nano scale these silicon oxide nanoparticles widely range from 5 to 100 nanometers (nm) with their specific area ranging from 25 m^2/g to 50m^2/g. Silica nanoparticles are chosen for their ability to withstand very high temperatures (600ºC), which is precisely the operating temperature of the CSP. The other important reason for the selection of silica is their high solubility in water at room temperature (12mg in 100ml of water at 20ºC). Some of the thermal and physical properties of silica nanoparticels are discussed in table 1.4.

<div align="center">Table 1.4 Physical and Thermal properties of Silica Nanoparticles</div>

Properties	
Appearance	White powder
Molecular weight	60.09
Exact mass	59.9668g/mol
Charge	0
Melting point	1600ºC
Boiling point	2230ºC

Table 1.4 – *Continued*

Density	2533Kg/m^3
Thermal conductivity	0.014W/cm-K
Thermal diffusivity	0.006cm^2/s
Specific heat	1.0J/g-K
Refractive index	1.46
Coefficient of thermal expansion	5×10^{-7}/K

<u>1.9 Nomenclature</u>

ρ_p - density of nanoparticle

ρ_f - density of base material

V_f - volume fraction of base material

V_p - volume fraction of nanoparticle

$c_{p,f}$ - specific heat capacity of base material

$c_{p,t}$ - specific heat capacity of nanomaterial

$c_{p,p}$ - specific heat capacity of nanoparticle

Cp – specific heat capacity measured at a particular temperature

T – Temperature at which the specific heat capacity is measured

<u>1.10 Theoretical Investigation</u>

The specific heat capacity measurements are compared with the classical heat capacity

model based on thermal equilibrium for a mixture as discussed by Buongiomo [12] as

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$$c_{p,t} = \frac{V_p\, \rho_p\, C_{p,p} + V_f\, \rho_f\, C_{p,f}}{V_p\, \rho_p + V_f\, \rho_f}$$

We find that the specific heat capacity of the nano fluid mixture to be slightly lower than the specific heat of the pure eutectic. The specific heat of the nanoparticle is known to be 1.0J/g-K and that of the pure eutectic is 1.4J/g-K. by the theoretical approach, the specific het capacity of the nanofluids should be slightly lower than that of the pure hitec xl. On contrast this does not happen experimentally, the specific heat is enhanced up on doping of nanoparticles to the base eutectic. Hence this observed enhancement in specific heat capacity cannot be explained by the conventional macro scale heat transfer and the theoretical model fails here.

Based on the Solar Advisor Model, developed by the National Energy Renewable Laboratory [13], the specific heat equations are used to calculate the difference in temperature between the solar field inlet and outlet when the solar field output is zero for a concentrated solar plant. In correspondence to the hitec xl eutectic, the heat capacity equation is given be

$$C_p = (-1.139 \times 10^{-4} \cdot T^2) - (2.624 \times 10^{-1} \cdot T) + (1.536 \times 10^3)$$

As per our considerations taking 'T' to be 300ºC, we can draw the specific heat capacity of the pure hitec xl to be 1447.03 J/Kg- ºC.

1.11 Objective of the Study

The aim of this study is to investigate the effect of nanoparticle dispersions on a ternary nitrate molten salt on their thermal properties and in utilizing them for high temperature heat transfer applications.

1.12 Significance of the Study

The significance of this study is to develop advanced nanomaterials for heat transfer and thermal storage applications at high temperatures to be used in CSP. The results from this study support the use of nanomaterials for heat capacity enhancement and a potential

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substitute to the existing heat transfer fluids with a great reduction in cost. Some of the details from this study are –

- Method of synthesis for molten salt nanomaterials.

- Effect on heat capacity enhancement of nanomaterials with nanoparticle dispersions.

- Effect of molecular change due to doping of nanoparticles.

- Parameters of cost reduction due to enhanced thermal properties.

CHAPTER 2

EXPERIMENTAL PROCEDURE

2.1 Synthesis of Nanofluid

Hitec xl considered here for the experimentation is based on a recent study carried out by by Kearney and Associates[14] under subcontract to SunLab looks in detail at the option of using inorganic molten salts as the heat transfer and thermal storage fluid for a trough system. The hitec xl with a melting point temperature of about 120ºC, was chosen as the commercial nitrate mixture for the study. The study by Daniel M. Blake, et al [15], summarizes the properties of the current working fluid in the Luz plants in California, hitec xl, the nitrate salt with the lowest freezing point, and an organic salt of the type termed ionic liquids in the chemical community discussed. The considerations for the experiments were such that – 49% $NaNO_3$, 30% KNO_3 and 21% $Ca(NO_3)_2$ by mole fractions for the hitec xl salt mixture. The eutectic of sodium nitrate, potassium nitrate and calcium nitrate were procured from Spectrum Chemical Mfg. Corp. Silicon dioxide nanoparticles of four different sizes namely 5nm, 10nm, 30nm and 60nm were used in the experiments. The silicon dioxide nanoparticles were procured from Meliorum Technologies, Inc. The pure samples were prepared with a mass balance of the molar fractions and are well dispersed. To prepare a 200mg of nanofluid sample having 1% concentration by weight of the nanoparticles, 198mg of the eutectic mixture has to be prepared with 2mg of the respective SiO_2 nanoparticle. With considerations of the molar mass of KNO_3 to be 101.10, $NaNO_3$ to be 85 and $Ca(NO_3)_2$ to be 164.09, calculations for the weight fractions are done. The corresponding weight fractions with regards to the mole fractions considered are found to be 56.45mg of $NaNO_3$, 77.53mg of KNO_3 and 64.10mg of $Ca(NO_3)_2$ respectively. Water is used as the base liquid here. The corresponding weight fractions are measured accurately with a microbalance

(Sartorius CPA225D). To prepare a pure sample just the eutectic mixture in their respective weights are measured and are filled in a glass container. In order to prepare a nanofluid, the eutectic mixture along with the respective nanomaterial with the particular size is chosen and 2mg of the same is added to the eutectic. 20ml of distilled water is added to the mixture. Agglomeration is a serious problem that can occur in case where the nanoparticles are not dispersed properly in the liquid medium. Agglomeration is nothing but the formation of the cluster, when the nanoparticles are not properly dispersed in the nanofluid and get adhered to the molten salts. This problem may affect the experimentation. In order to avoid agglomeration, the nanofluid is made to undergo another process called the ultra-sonication.

2.2 Ultra-sonication

The eutectic with the nanoparticle mixture is well dispersed in 20ml water and is completely sealed. The glass container with the sample is now introduced into the ultra-sonicator. Ultra-sonication ensures homogeneous dispersion of the nanoparticles with the base fluid. The sonication is carried out for about 200 minutes in the Branson 1510, procured from Branson Ultrasonics Corporation. This ensures uniform dispersion and minimal agglomeration of the nanoparticles. The nanofluid solution after ultra-sonication is placed on a hot plate procured from Fisher Scientific, isotemp and is maintained at a temperature of $200^{\circ}C$ for about 8 hours for the complete evaporation of the water. The nanomaterial and the molten salt are now completely dispersed. The temperature of the hot plate is then increased to about $250^{\circ}C$ for less than an hour so that any remaining moisture gets evaporated.

KNO$_3$ - NaNO$_3$ - Ca(NO$_3$)$_2$

(99% by weight) and

SiO$_2$ (1% by weight)

Water

Nanoparticles

| Poorly mixed | Water | Well mixed | |

| Mixture of salts and nanoparticle | Distilled water added | Sonication for 200 minutes | Evaporation at 200°C |
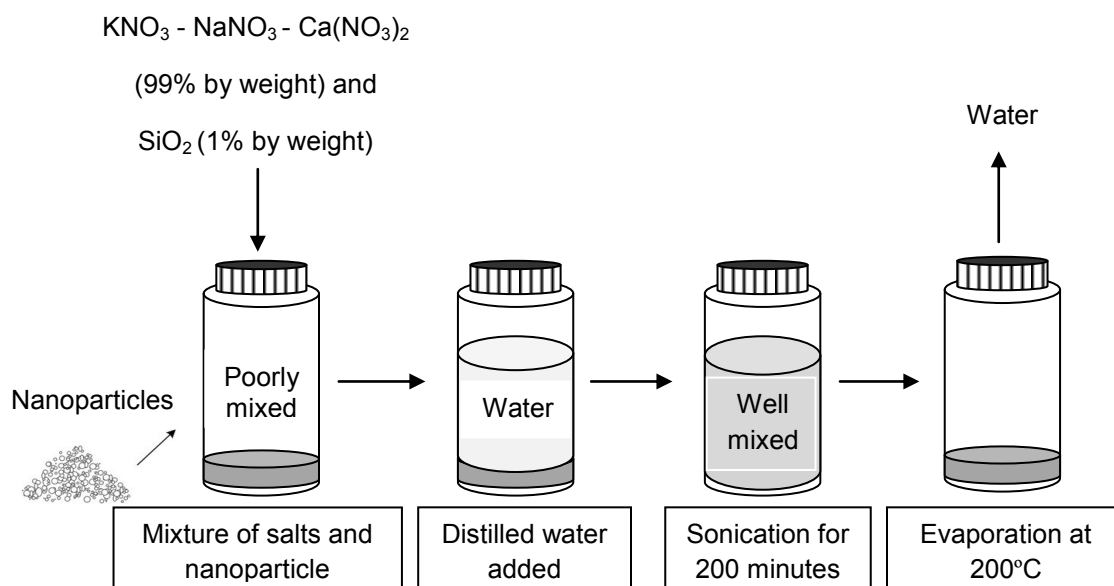
Figure 2.1 Synthesis of nanomaterial [23]

2.3 Decomposition Test

The decomposition test is a verification test to check the stability of the compound at very high temperatures. For the hitex xl eutectic, the normal working temperature is less than 400°C, but in order to ensure stability of the compound the composition is subjected to very high temperature of about 520 °C on the hot plate for about 8 hours. The reason behind this test is to find out whether there are any distinct color changes or disintegration of the hitec xl composition.

The decomposition test is usually done once to ensure the safety and physical stability of the compound at high temperatures. The hitec xl salt composition, when tested does not undergo any distinct color change or there is no evident disintegration of the salt. The test was confirmed when a small quantity of the pure sample was placed, in a Tzero pan weighted first with the microbalance and then placed on the hot plate for 8 hours. The sample was weighed

again after 8 hours and was verified to have the same quantity and no change in color was noticed.

2.4 Measurement of Specific heat capacity

The differential scanning calorimeter can be used to measure the specific heat capacity. The calorimeter works on the principle of differential scanning calorimetry. The technique involved in this process is that the difference in amount of heat required to raise the sample and the reference is measured as a function of temperature. The sample to be measured and the reference sample are almost maintained at the same temperature throughout the experiment. An inbuilt program is used to analyze the sample with respect to the reference and the difference with the increase in temperature is measured linearly with respect to time. The heat capacity of the reference sample is defined to be specific along the temperature range of the sample to be measured.

A Modulated Differential Scanning Calorimeter (MDSC) Q20, procured from TA Instruments Inc, New Castle, DE is used in the experiment to measure the specific heat capacity. The difference between a modulated DSC and a conventional DSC is that, in an MDSC different heat flow can be applied to the sample and the reference. Also, the method of ramping the heat in each varies. In a DSC, the increase in temperature is linear specific to the ramp, whereas oscillations are overlaid to the linear heating ramp to yield a heating profile where the increase in temperature with respect to time is in a non-linear fashion [16].

The testing procedure in an MDSC is such that, a fraction of the dry sample is put into a Tzero hermetic pan and placed on a hot plate to remove any moisture that may be present. The Tzero pan is then fixed and sealed with a Tzero hermetic lid procured from TA Instruments Inc. The empty pan that is placed acts as the reference sample. Besides the reference sample, the sample whose specific heat is to be measured is placed. A fraction of the sample usually 10%, weighing between 17.5mg to 22.5mg is measured and placed in the Tzero pan. The sample is

in the pan is heated at 200°C for about 10 minutes to remove the moisture and to improve the accuracy of the result. The sample in the pan is then sealed with the lid and weighed again. The readings are noted and entered in the program.

The Tzero pan with the sample is placed alongside the reference sample (empty pan). At the beginning of the test temperature is held at 40°C. Temperature is then ramped from 40°C for 5mins to 400°C at the rate of 20°C/min and held for 5mins. The system is gradually cooled down to 40°C again at the rate of 2°C/min. The results of the experiment are then observed which gives the characteristic phase change in a plot with the rise in specific heat capacity along the increase in temperature for the pure eutectic sample.

The procedure is followed with the addition of 1% weight of the Silicon-di-oxide nanoparticles in the synthesis of the nanofluid. This nanofluid sample is tested with MDSC following the same test procedure. In the experiment, 5nm, 10nm, 30nm and 60nm nano materials are tested. The results are again plotted and compared with results from pure eutectic. A typical enhancement can be observed after the nanoparticle is doped with the eutectic sample. Specific heat capacity as a measure of raise in temperature in the pure sample is studied and variations with regards after addition of nanomaterials are compared and the results are discussed.

Figure 2.2 Modulated Differential Scanning Calorimeter

<u>2.5 Material Characterization (SEM)</u>

Material characterization refers to the procedure in which the internal structure of a material is studied with the probe of external techniques. The phenomenon used here is to magnify the specimen under study to visualize the internal structures or any change in the internal structures. Material characterization is greatly useful in comparing the interactions between the molecules, changes in shape and dimensions of the specimen under study and to validate the physical properties to a great extent. Some of the material characterization techniques involve optical microscope, scanning electron microscope, transmission electron microscope, X-ray diffraction topography etc.

Scanning electron microscopy is used in this experimentation to analyze the hitec xl characteristics and the nanoparticles. The SEM uses a focused beam of high voltage electrons to generate a variety of signals, which derive the information from the specimen – electron interactions. Information about the structure, chemical composition and orientation of the

specimen under study is revealed. A two-dimensional image is generated which displays a spatial variations in properties. The range of a Scanning electron microscope may vary from 1cm to 5microns. In some cases the range may be as high as a few nanometers. The magnification ranges approximately from about 50X to about 30,000X.

The scanning electron microscopy works on the principle where accelerated electrons carrying significant amount of kinetic energy. The electron beam with the high energy is incident on the sample after passing through a pair of scanning coils, deflector plates and a final lens. The electron beam interacts with the specimen and loses its energy by repeated random scattering and absorption within the specimen on its surface. The landing energy of the electron depicts the volume of interaction. The exchange of energy between the sample and the electron beam results in the refection of high energy electrons, electromagnetic radiation and the emission of secondary electrons. These emissions are detected with the help of specialized detectors by which the images are created. Electronic amplifiers are used to amplify these signals and the resulting output is displayed as variations on computer's monitor as an output. The essentials parts of the SEM are the electron source, lenses, stage, detectors, display unit, proper power supply and a vacuum environment.

The scanning electron microscopy used for the study is ZEISS Supra 55VP. The pure eutectic is first tested in a clean room environment and then the nanomaterials with various nanoparticle sizes are tested to study the variation in internal structures owing to the results acquired from the MDSC.
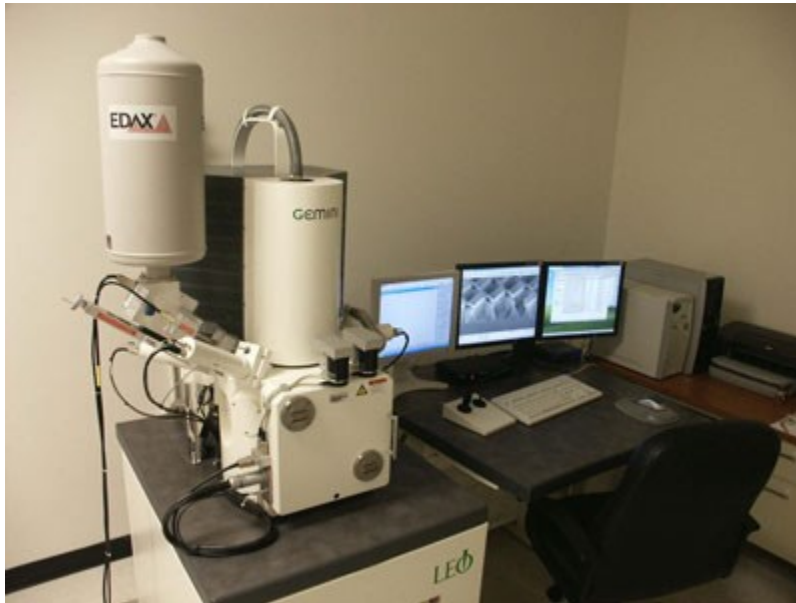
Figure 2.3 Scanning Electron Microscope

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Specific Heat capacity results

The result from the MDSC gives the specific heat enhancement for the particular sample. The specific heat capacity is measured directly with variation in temperature. The pure sample are tested first followed by the nanoparticles. Hitec xl has a low melting point at 120°C, so the comparison is completely evaluated in the liquid state. Pure samples are prepared in large number and are tested individually. The mean of the specific heat capacity that is measured is fixed to be the standard and it is close with the literature value from earlier experiments. The mean obtained from the experiments is close to about 1.3 J/g°C and the literature value for the hitec xl is close to 1.4 J/g°C. The standard deviation is measured for the values obtained with repeated testing of the pure hitec xl. The standard deviation gives the measure of the deviation between the mean and the expected value.

The experiments are repeated with each nanoparticle sizes and in each case, the mean and the standard deviation are calculated. The   and the enhancements or detractions in the specific heat capacity are measured. The methodology from previous studies involving the technique of enhancing the specific heat capacity upon addition of nanoparticles discussed by D. Shin and D. Banerjee [17] with their study on Carbonate molten salts is verified with the ternary nitrate salts and hitec xl gives an enhancement in the specific heat capacity upon the doping of nanoparticles.

The following were the results obtained from MDSC upon comparison with pure eutectic and the nanofluid samples measured at 350°C.

3.1.1. 5nm SiO_2 Nanoparticles with base salt

Table 3.1 Comparison of Pure hitec xl v/s 5nm Nanofluid

Heat Capacity (kJ/kg°C)	Pure	Nanofluid
Repeat # 1	1.31	1.69
Repeat # 2	1.31	1.71
Repeat # 3	1.31	1.68
Repeat # 4	1.30	1.66
Average	1.31	1.67
Enhancement	-	28 %
Measurement Uncertainty	0.4 %	1 %

Enhancement in Specific heat capacity of about 28 % on the doping of 5nm nanoparticls to the base fluid is achieved.
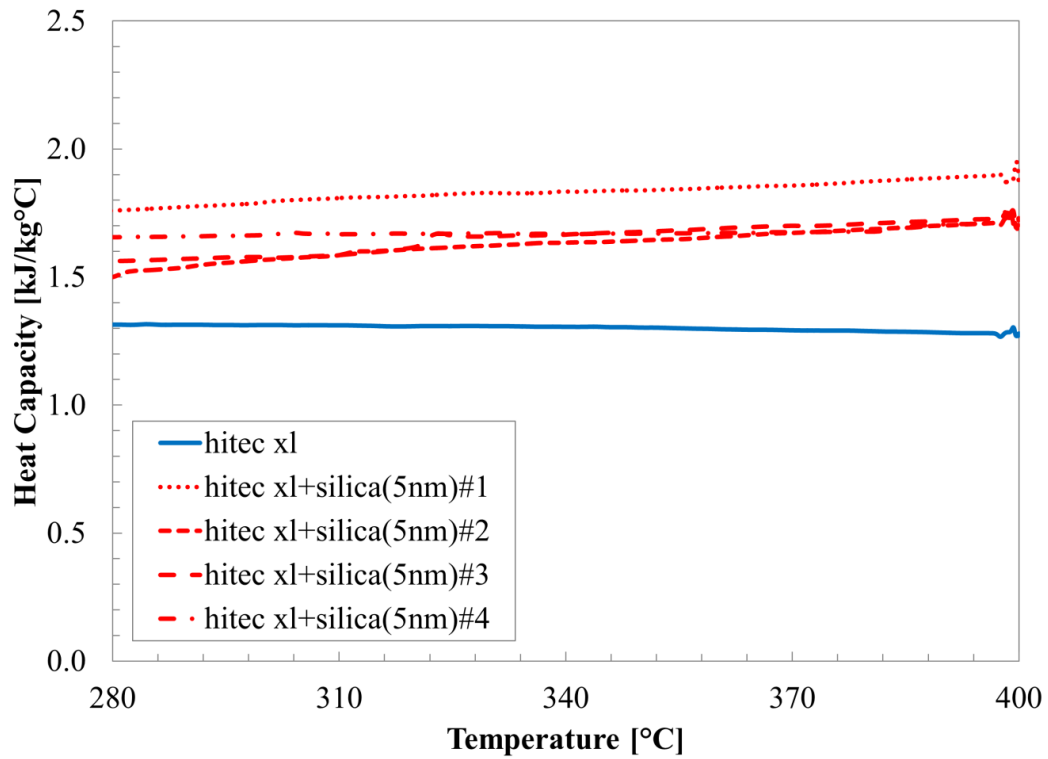
Figure 3.1 Variation of Specific Heat capacity - Pure Eutectic and 5nm nanofluid against

Temperature

The graph explains the enhancement achieved each time upon addition of the nanoparticles to the base eutectic. The average enhancement here is about 28 %.

3.1.2. 10nm SiO$_2$ Nanoparticles with base salt

Table 3.2 Comparison of Pure hitec xl v/s 10nm Nanofluid

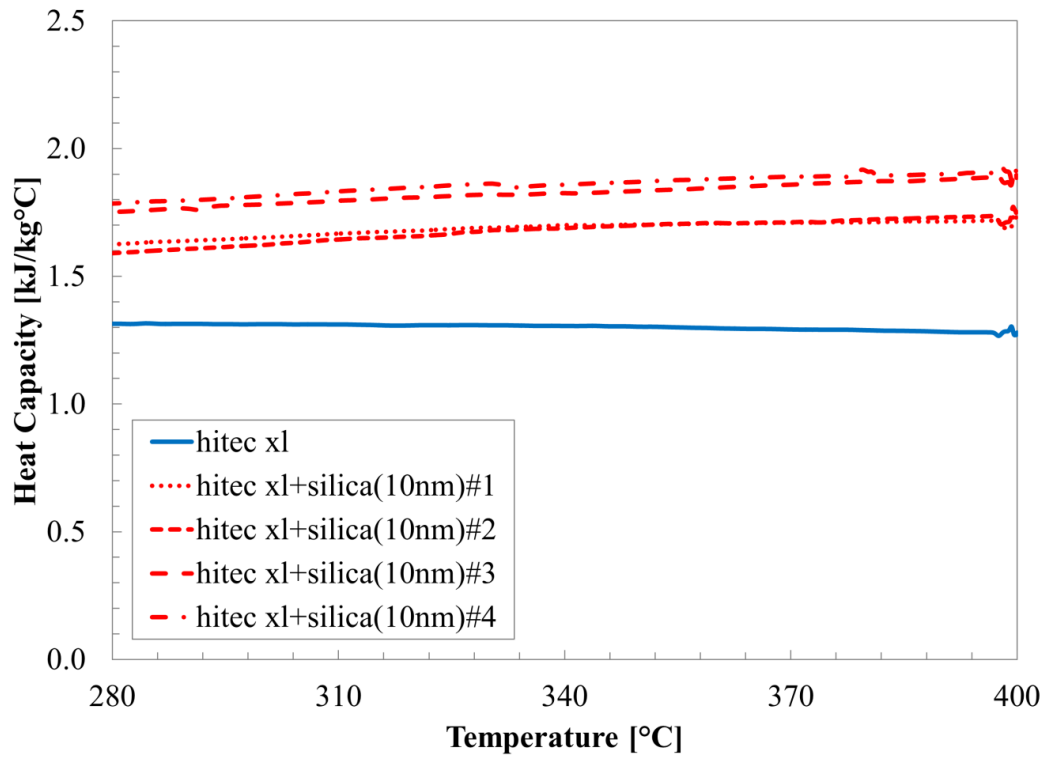| Heat Capacity (kJ/kg°C)	Pure	Nanofluid
Repeat # 1	1.31	1.71
Repeat # 2	1.31	1.70
Repeat # 3	1.31	1.80
Repeat # 4	1.30	1.78
Average	1.31	1.75
Enhancement	-	34 %
Measurement Uncertainty	0.4 %	2.5 %

Figure 3.2 Variation of Specific Heat capacity - Pure Eutectic and 10nm nanofluid against

Temperature

The average enhancement achieved after repeated testing of 10nm nanoparticles is found to be about 34 %.

3.1.3. 30nm SiO_2 Nanoparticles with base salt

Table 3.3 Comparison of Pure hitec xl v/s 30nm Nanofluid

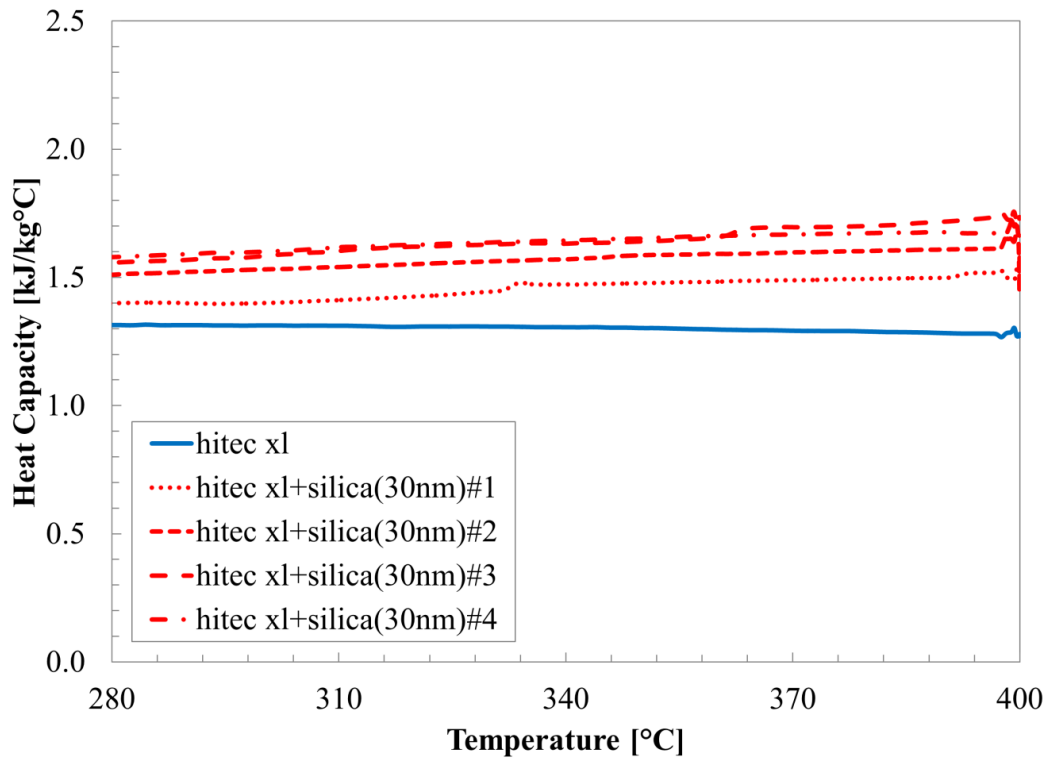| Heat Capacity (kJ/kg°C)	Pure	Nanofluid
Repeat # 1	1.31	1.61
Repeat # 2	1.31	1.60
Repeat # 3	1.31	1.49
Repeat # 4	1.30	1.51
Average	1.31	1.55
Enhancement	-	19 %
Measurement Uncertainty	0.4 %	3.2 %

Figure 3.3 Variation of Specific Heat capacity - Pure Eutectic and 30nm nanofluid against Temperature

The enhancement attained when 30nm nanoparticles added to the pure sample were found to be about 19 %.

3.1.4. 60nm SiO$_2$ Nanoparticles with base salt

Table 3.4 Comparison of Pure hitec xl v/s 60nm Nanofluid

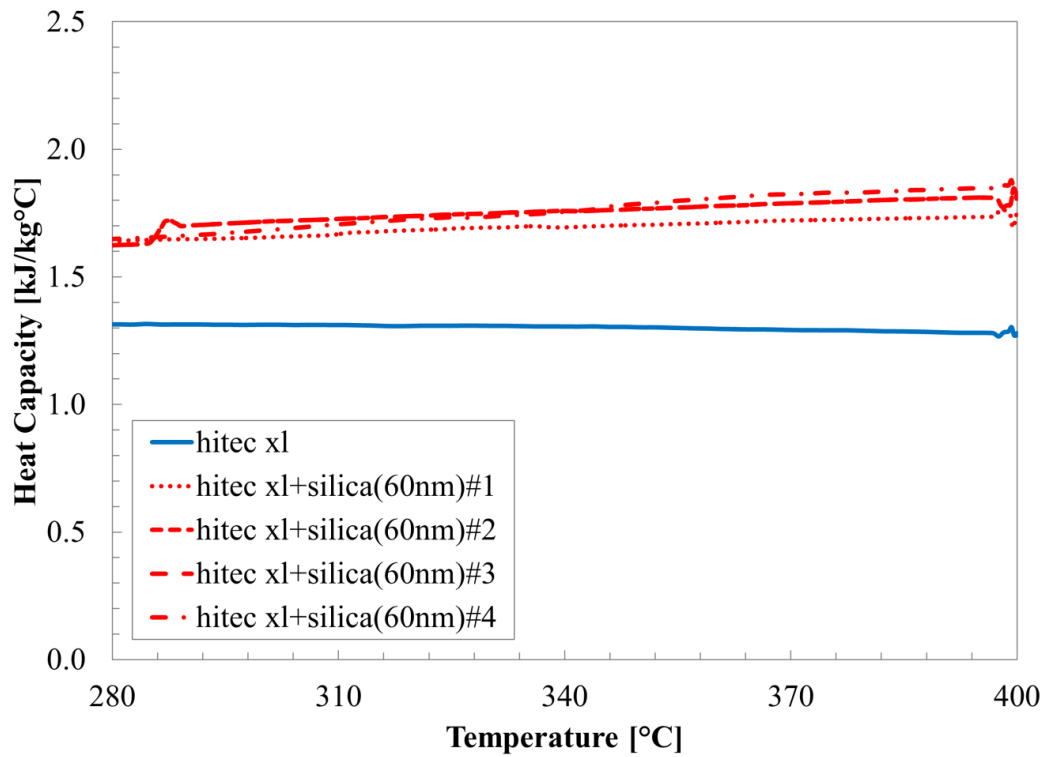| Heat Capacity (kJ/kg°C)	Pure	Nanofluid
Repeat # 1	1.31	1.72
Repeat # 2	1.31	1.65
Repeat # 3	1.31	1.65
Repeat # 4	1.30	1.79
Average	1.31	1.70
Enhancement	-	30 %
Measurement Uncertainty	0.4 %	3.4 %

Figure 3.4 Variation of Specific Heat capacity - Pure Eutectic and 60nm nanofluid against

Temperature

The enhancement observed from the 60nm samples is found to be 30 %. The results show that there is enhancement after doping of nanoparticles to the base salt. 10nm sized sample yield the maximum enhancement followed by 60nm, 5nm and then 30nm. The variation in specific heat capacity with respect to the different sized nanomaterials is listed in listed in Figure 5.5.
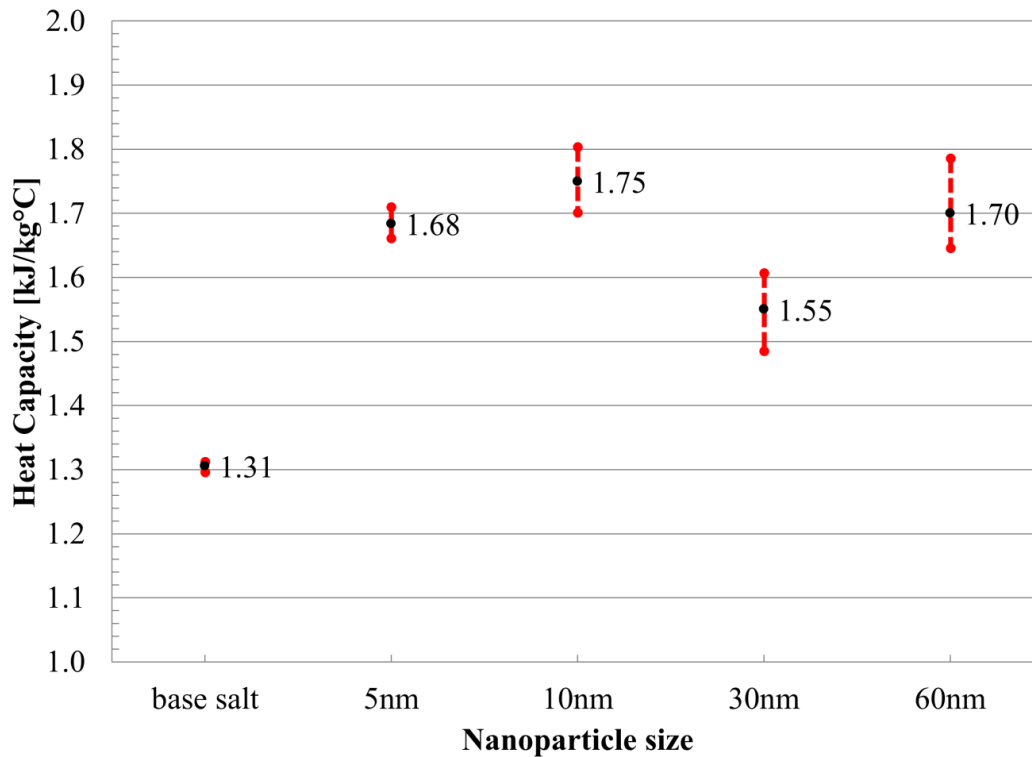
Figure 3.5 Variation of Specific Heat capacities - Pure Eutectic and 60nm nanofluid against

Temperature

3.2 Material Characterization results

The images from the scanning electron microscope compare the physical changes in the molecules between the pure hitec xl and the nanoparticle doped nanofluids. The variation in characteristics is hugely dependent on their molecular changes which are reflected on the images obtained. The results are discussed with varying magnifications, density of the current, applied voltage, aperture size and beam strength.

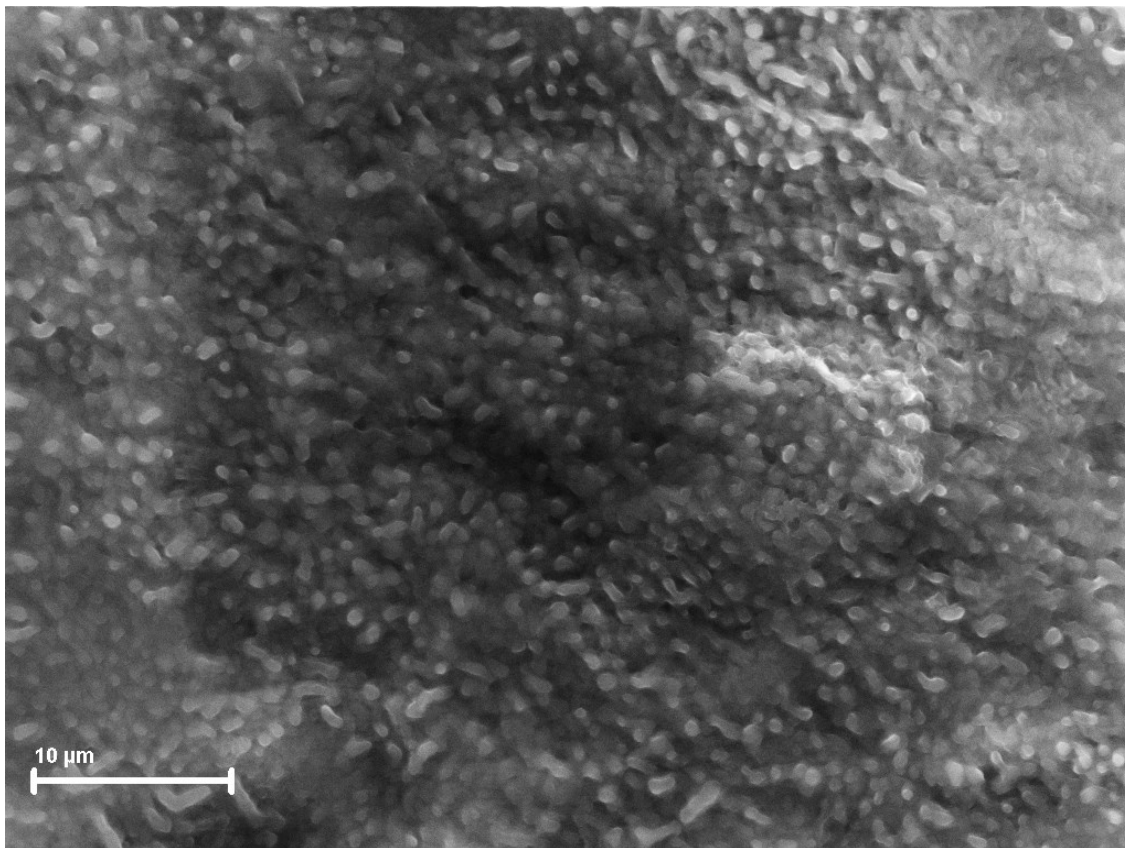*3.2.1. Pure hitec xl image at 2000X*

Figure 3.6 SEM image of pure hitec xl without nanoparticles showing no unique structures

The pure sample after undergoing scanning electron microscopy shows no distinct structures. The image acquired at a magnification of 2000X shows no unique structure but just the conventional molten salt structure of the ternary salt composition.

3.2.2. 5nm SiO$_2$ added with Pure hitec xl image at 2000X

Figure 3.7 SEM image of hitec xl with 5nm nanomaterials showing bright spots

The sample shows an enhanced specific heat capacity of about 28% compared to the pure hitec xl.

3.2.3. 10nm SiO$_2$ added with Pure hitec xl image at 2000X

Figure 3.8 SEM image of hitec xl with 10nm nanomaterials showing large bright spots and

uniform distribution

The sample shows highest enhancement in specific heat capacity of about 34% compared to the pure hitec xl.

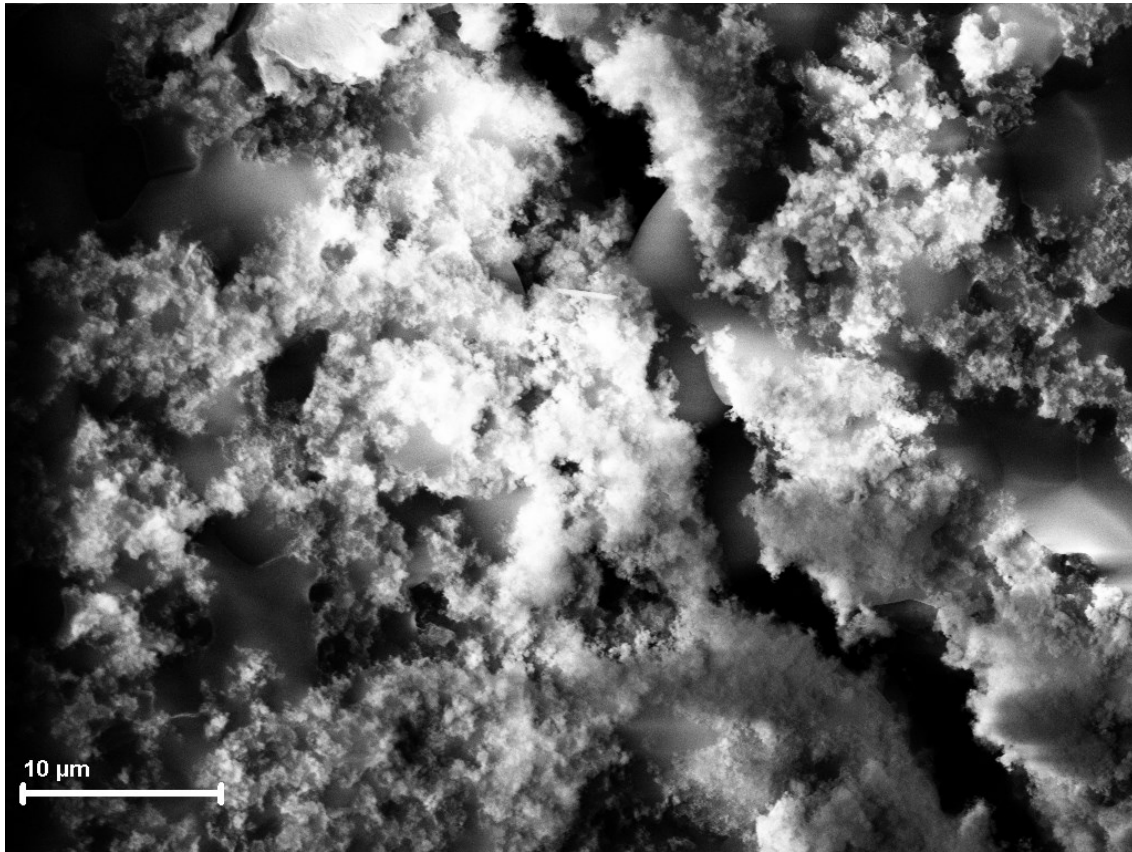*3.2.4. 30nm SiO$_2$ added with Pure hitec xl image at 2000X*

Figure 3.9 SEM image of hitec xl with 30nm nanomaterials showing less bright spots

The sample shows an enhancement in specific heat capacity of about 19% compared to the pure hitec xl.

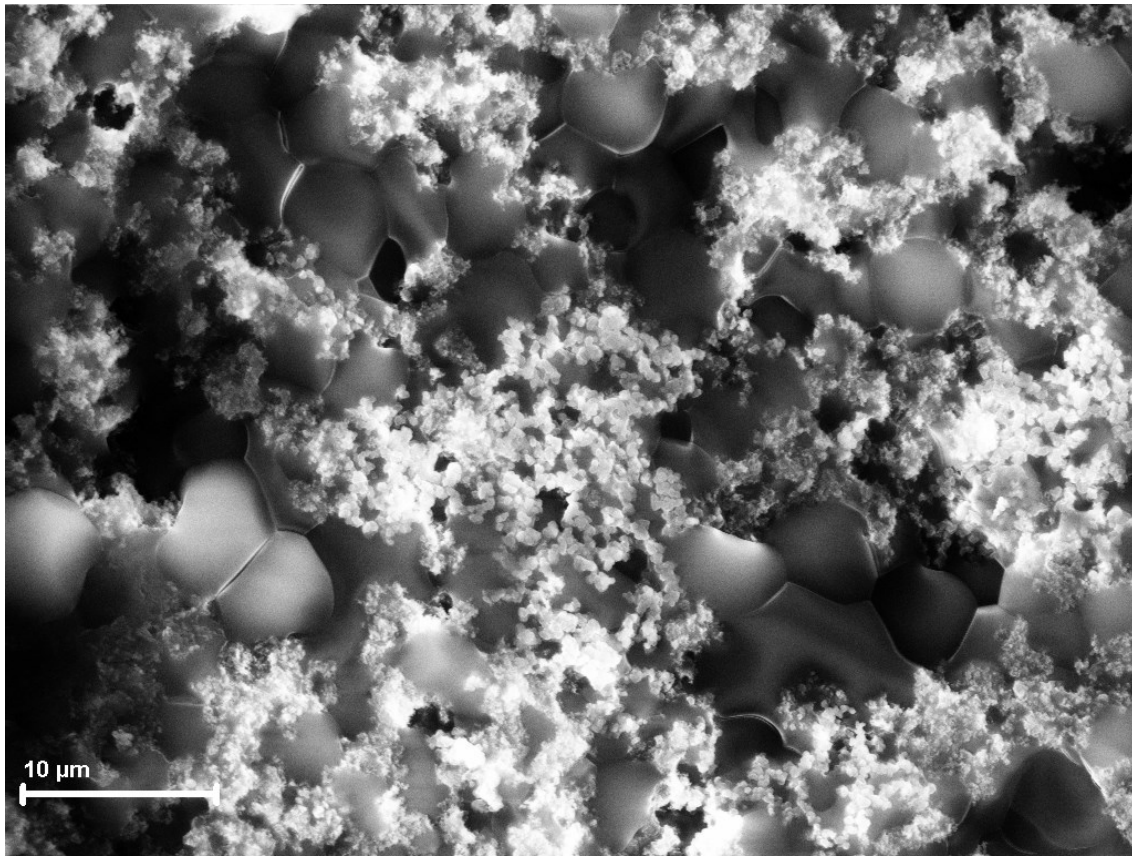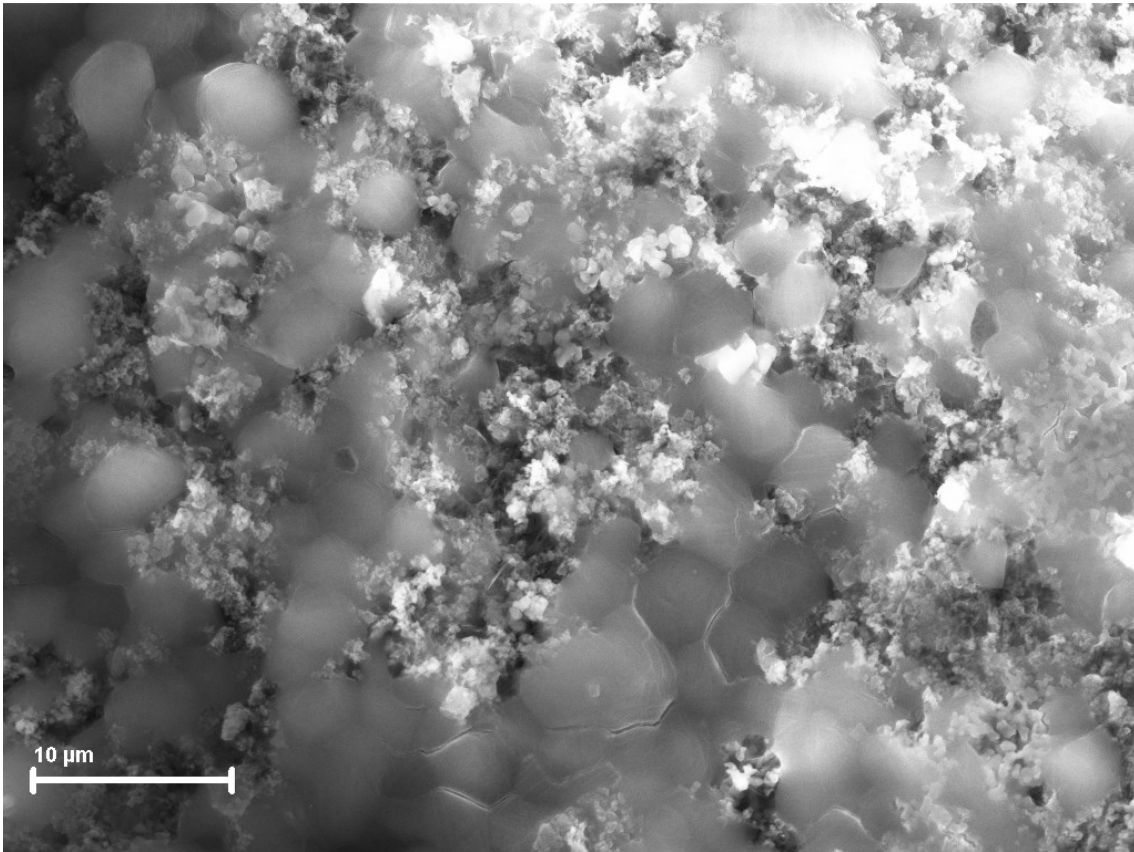*3.2.5. 60nm SiO$_2$ added with Pure hitec xl image at 2000X*
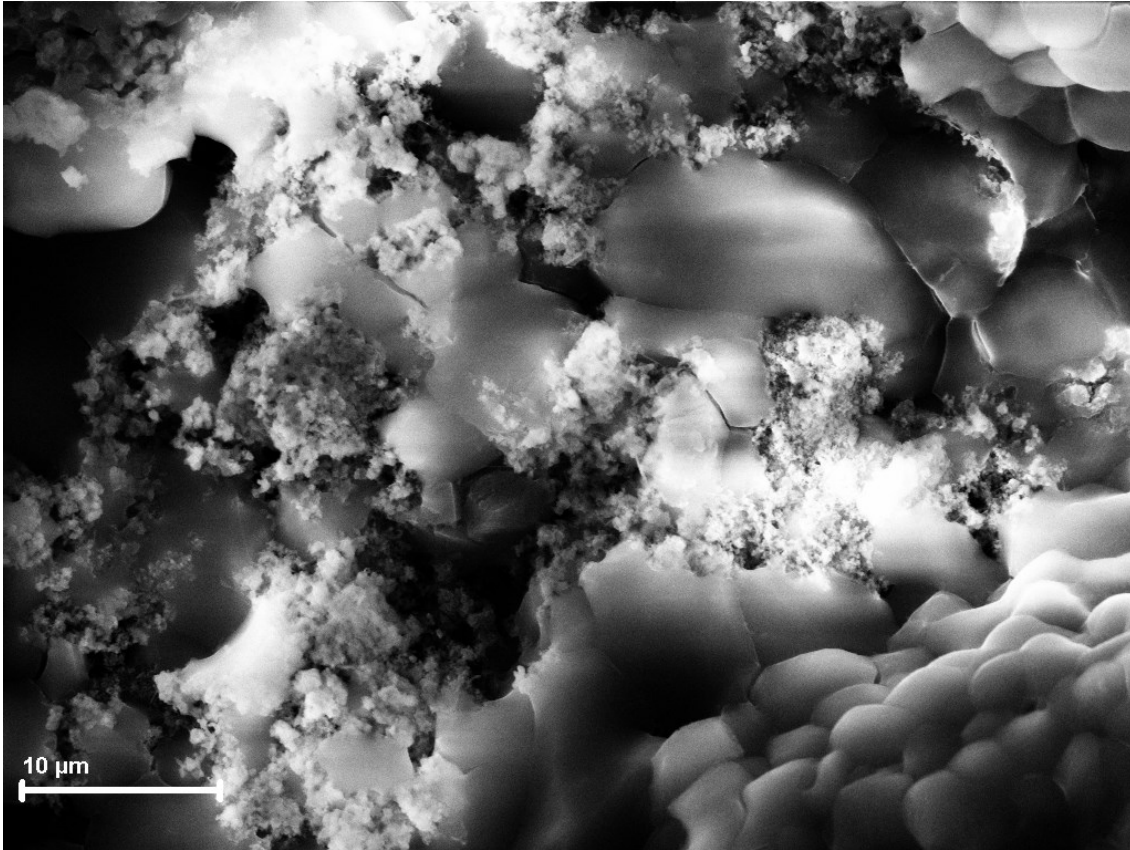
Figure 3.10 SEM image of hitec xl with 60nm nanomaterials showing uniformly distributed bright spots

The sample shows an enhanced specific heat capacity of about 30% compared to the pure hitec xl.

3.2.6. High Resolution image showing nanostructure

Figure 3.11 High resolution SEM image of nanostructures

Small thread like and web shaped structures are shown brighter than the bulk salt eutectic. The structures have large specific area compared to the eutectic material. The diameter varies from 10nm ~ 100nm. Also there is no significant trend or effect of nanoparticle size on the enhancement in specific heat capacity. This proves that nanoparticles of various sizes or the nanoparticles themselves may not be responsible behind the specific heat capacity enhancements.

Shin and Banerjee [17, 18], proposed the formation of nanostructure by nanoparticle dispersions in a salt mixture may be responsible for the enhanced specific heat capacity. Figure 3.6 to 3.11 show scanning electron microscope images for pure hitec xl, nanomaterials with various nanoparticle sizes (5 nm, 10 nm, 30 nm, and 60 nm), and a high-resolution image of distinct nanostructures observed in nanomaterials. Each image was taken with a gun voltage of 30kV, extractor voltage of 4.5kV and an aperture size of 30μm. Figure 3.6 shows the pure hitec xl (i.e., without addition of any nanoparticles to ternary nitrate salt eutectic). Figure 3.7 to 3.10 shows the SEM image of the hitec xl doped with 5 nm, 10 nm, 30 nm, and 60 nm nanoparticles. Distinct nanometer sized structures ("nanostructure") were formed and spread out all over the samples. Enhanced specific heat capacity of about 19 ~ 34 % was observed in the nanomaterials and the nanostructure can be one of the reasons for the large enhancement in the specific heat capacity. A high resolution image as shown in Figure 3.11 shows distinct nanostructures. These thread-like structures were found to be not nanoparticles but different formations of the salt eutectic.

According to the recent report about nanostructure formations in nanoparticle / salt mixture system [19], dispersion of oxide nanoparticles in a salt mixture forms hydroxide (OH-) ions on the surface of the nanoparticle which interacts with surrounding salt ions. Each ion in a salt mixture Na+, K+, and Ca2+ will differently interact with OH- on the nanoparticle surface and thus each salt of the mixture will be separated and crystallized through which the nanostructure is formed. This phenomenon will locally separate salt mixture near nanoparticles and induce the nanostructures to develop further away from nanoparticles. According to the literature [20, 21], nanoparticles tend to have high specific heat capacity due to their large specific surface area. Due to the large surface area per volume, the number of exterior atoms to interior atoms will be dramatically increased in the nanoparticles compared with the bulk material.

The surface photons contribute on the specific heat capacity which dominates the heat capacity mechanism of nanoparticles. Hence the nanoparticles have higher specific heat capacity than the bulk. The high heat capacity of the nanoparticles was theoretically proved by Wang et al. [20] and the enhancement in specific heat capacity of Al_2O_3 nanoparticles measured with the bulk was experimentally measured as 25 % by Wang et al. [21]. The specific surface area of these nanostructures is very large and thus the contribution of surface energy by the structure may not be neglected on a macro-scale. They dominate the heat capacity mechanism which results in overall improvement of specific heat [22].

CHAPTER 4

CONCLUSION AND FUTURE WORK

In this study, we investigated the enhancement in specific heat capacity of ternary nitrate salt eutectic consisting of KNO_3, $NaNO_3$ and $Ca(NO_3)_2$ (30:49:21 by weight) by doping SiO_2 nanoparticles (1% by weight). A modulated differential scanning calorimeter was used to measure the specific heat capacity. SiO_2 nanoparticles of 5nm, 10nm, 30nm and 60nm were investigated. The enhancements recorded with respect to the various nanoparticle sizes were between 19% to 34% in the liquid phase and the most suitable size of nanomaterial to be selected for maximum enhancement is found to be 10nm which yields 34% enhancement with hitec xl base salt. The measurement uncertainty was less than 3 %. A scanning electron microscope was used to perform the material characterization analysis. The results from SEM observed thread like or web shaped nanometer sized structures with diameter of each thread ranging between ~10-100 nm. These structures were found to be fairly spread out all over the sample. Formation of these web-like nanostructures seems to be responsible for the enhancement in heat capacity. Due to the presence of web shaped structures the specific surface area of nanomaterial was dramatically increased. Contribution of surface energy on specific heat capacity from the web-like nanostructures may be primarily responsible for the enhancement in specific heat capacity [23].

The use of ternary nitrate salt (hitec xl) dispersed with silica nanoparticles has several benefits as a HTF in CSP. Due to the low freezing point of the ternary nitrate salt the potential risk of HTF being crystallized at low temperatures can be greatly reduced. Thus expensive freeze protection methods like auxiliary heater or extra insulation are not required. The enhancement in specific heat capacity can greatly reduce the amount of HTF used in TES. The

cost of electricity produced from the CSP can hence be significantly reduced. According to the recent costing analysis [24], enhancement in specific heat capacity of HTF about 19 % to 34 % can reduce the cost of electricity more than 12 %.The future work here is to investigate the thermal stability, flow characteristics like Viscosity and other dispersion techniques for practical use in the CSP.

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BIOGRAPHICAL INFORMATION

Ramaprasath Devaradjane was born in 1988 in Chennai, India. He pursued his schooling in Chennai and graduated from Sri Sairam Engineering College, Anna University in 2010 where he did his Bachelor of Engineering in Mechanical Engineering. He was then employed as a Graduate Engineer in TUV India (Member of TUV Nord, Germany) in the Automotive homologation and Product Certification division. Later in 2013 he completed his Master of Science in Mechanical Engineering from the University of Texas at Arlington.

Born as the eldest child to Devaradjanes, Ramaprasath's father Dr. G. Devaradjane is a Professor by profession and is currently the Head of the department of Automobile Engineering at Anna University; mother Dr. D. Vijayalakshmi is also a Professor in the field of Education and is currently working at Balavihar teacher training college. Ramaprasath's younger brother Ramprakash Devaradjane is currently pursuing his BE in Computer Science Engineering, MIT, Anna University.