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Corresponding Author: Professor Dongsheng Wen,

Corresponding Author's Institution: University of leeds

First Author: Afrah Awad

Order of Authors: Afrah Awad; Helena Navarro; Yulong Ding; Dongsheng Wen

Highlights

- Three types of nanoparticle were dispersed into two different types of solar salts.
- Nanosalts show enhanced thermal diffusivity/conductivity, sensible heat and latent heat.
- 0.5 wt. % Fe_2O_3-nanosalt increased thermal diffusivity of solar salt up to 50%.
- 14.5 % enhancement of the latent heat of solar salt was found for KNO_3.
- 5.3 % enhancement of the total storage capacity was found at 155 ºC<T<435 ºC.

Thermal-physical properties of nanoparticle-seeded nitrate molten salts

Afrah Awad[1], Helena Navarro[2], Yulong Ding[2], Dongsheng Wen[3,1*]

[1]School of Chemical and Process Engineering, University of Leeds, UK

[2]School of Chemical Engineering, University of Birmingham, Birmingham, UK

[3]School of Aeronautic Science and Engineering, Beihang University, China

Email: d.wen@leeds.ac.uk

Abstract

Molten salts have been used extensively as energy storing materials, however, their thermophysical properties, such as specific heat capacity and thermal conductivity have limited their applications. In this study, potassium nitrate and sodium–potassium nitrate ($NaNO_3$:KNO_3 with 60:40 molar ratio) are used as the base salts with different types of nanoparticles, which are iron oxide (Fe_2O_3), titanium dioxide (TiO_2) and copper oxide (CuO) over a wide range of temperatures up to 500 ^{0}C. Laser flash analysis is used to measure thermal diffusivity and dynamic scanning calorimeter for specific heat (latent heat and melting temperature) of the molten salts and nanosalts. The addition of Fe_2O_3 into sodium–potassium nitrate salt increases thermal diffusivity up to 50%. Moreover, the highest increase in the latent heat reaches 14.45% at 1 wt. % CuO-binary nitrate salt. In addition, the total thermal energy storage of nanosalt increases up to 6% including both of sensible and latent heat. The formation of the interface layer between nanoparticles and salts could be the reason behind this enhancement in sensible and latent heats. The surface area of the nanosalt measured by scanning electron microscopy showed a heterogeneous dispersion of nanoparticles in the nanosalt samples, including agglomerated areas that could be sometimes responsible for the degradation of the sensible or latent heats.

Keywords: nanofluid, nitrate salt, specific heat capacity, latent heat, thermal energy storage, thermal diffusivity.

1. Introduction

Solar energy is a promising renewable energy source for our energy future, (Thirugnanasambandam et al., 2010), but can be only used during the daylight. An integration with a storage system must be done to ensure the reliability and availability of the system. Solar energy can be stored in three different forms as sensible heat, latent heat or in thermochemical form. Thermochemical reactions could provide higher energy storage density but it needs very complex systems to control these reactions.

Molten salt is generally used to store energy in sensible/latent forms. For example, most of the concentrated solar thermal power plants have been integrated with sensible storage tanks, i.e., one hot tank and one cold tank to store the energy up to 390 ˚C. Considering that the melting temperature of solar salt ($NaNO_3$: KNO_3 with 60:40 molar ratios) is 232 ˚C and for potassium nitrate (KNO_3) is around 334 ˚C, any of them is a good choice for sensible heat storage (Chieruzzi et al., 2013, Chieruzzi et al., 2015). Another advantage of molten salt is its higher energy density due to its change phase with an approximately constant temperature giving a higher latent heat, e.g. the latent heat of KNO_3 is around 91.61 KJ/kg and solar salt is 110.01 KJ/kg (Chieruzzi et al., 2013, Chieruzzi et al., 2015a). The use of molten salt as a phase change material (PCM) for solar thermal applications has been investigated by many researchers such as (Feldhoff et al., 2012, Laing et al., 2009, Pfleger et al., 2015, Luo et al. 2017). However, their limited thermo-physical properties such as thermal conductivity, k, (in the range from 0.1-0.6 W/m.˚K (Kong et al., 2014)) and specific heat capacity (cp) have prevented its wide applications.

Nanoparticles have been recently proposed to solve the problem of low cp/k values of the nitrate molten salt. Many work have shown that dispersing nanoparticles to a base salt (here called nano-salt) at low concentrations could increase the cp value, but the results are inconclusive. There are different types of nitrate molten salt studied, including single nitrate salt, binary or ternary nitrate salt, which are briefly reviewed below. Chieruzzi et al. (2015b) studied the effect of silica, alumina and hybrid silica-alumina nanoparticles on single nitrate salt (KNO_3) salt. On the other hand, Lasfargues et al. (2015) studied the effect of dispersing CuO and TiO_2 nanoparticles on a binary nitrate (solar salt) and showed that the maximum increase

in cp was 10.48% at 440 ^{0}C for 0.1 wt. % CuO-solar salt. Moreover, different types of nanoparticles, with different concentrations and size have been dispersed into a binary nitrate solar salt to improve the cp of nanosalt (Andreu-Cabedo et al., 2014, Chieruzzi et al., 2013, Dudda and Shin, 2013, Lu and Huang, 2013, Riazi et al., 2016, Schuller et al., 2015, Luo et al., 2017). Others investigated the effect of dispersing silica, multi-walled carbon nanotubes, hybrid silica-alumina, Mica, gold and alumina nanoparticles into nitrate solar salt (Andreu-Cabedo et al., 2014, Chieruzzi et al., 2013, Dudda and Shin, 2013, Jung and Banerjee, 2011, Lu and Huang, 2013, Niu et al., 2014, Riazi et al., 2016, Schuller et al., 2015). Some of their results showed a higher increase in cp of nanosalt, which was dependent on the types, sizes, and concentrations of nanoparticles used. Others showed different results. This increase or decrease in the literature for the cp values of the nanosalt samples could be related to different sources of the materials used either molten salt (with different purities and suppliers) or the nanoparticles (different sources of the purchased companies or supplied by the researchers themselves). In addition, different preparation protocols and measurement conditions could also be the reasons. In order to explain the enhancement in cp of nanosalt samples, the literature indicated that interfaces were formed between the molten salt and nanoparticles (Riazi et al., 2016, Luo et al., 2017). Another explanation is the increment in the thermal resistance due to the effect of nanoparticles, which own higher surface areas. However, the simple mixing model, which relays on higher cp of nanoparticles itself in most of the cases, is not applicable to the nanosalt case as the cp of the nanoparticle is still less than cp of the molten salt.

Furthermore, extensive studies have been conducted on the enhancement of thermal conductivity by adding nanoparticles, and a term ‘nanofluid’ was coined (Buongiorno et al., 2009, Chol, 1995), However, the base-fluids tested were water, mineral oils and polyalphaolefins lubricant (PAO). Only very limited work has been conducted on molten salts. For instance, thermal conductivity (k) of binary nitrate salt with Al_2O_3 nanoparticles was measured using the laser flash analysis (LFA), which showed that adding nanoparticle decreased k in a temperature range between 65^0 C- 145^0 C (Schuller et al., 2012). Additionally, Myers et al. (2016) measured the thermal conductivity of the solid phase for three different types of nitrate molten salts (i.e., potassium nitrate, sodium nitrate, and the potassium–sodium nitrate eutectic

(54 weight percent potassium nitrate) with copper oxide (CuO) nanoparticles. Their results showed an increment in thermal conductivity of the nanosalt, due to the formation of nanostructures between the nanoparticles and the molten salt. On the other hand, Shin (2011) studied the thermal conductivity when dispersing silica nanoparticles (1 wt.%) in carbonate salt of lithium: potassium carbonate salt (Li_2CO_3: K_2CO_3 with 62:38 by molar ratio) up to 300 ^{0}C. The results showed an enhancement in k by 37%-47%, and it was believed that smaller size of nanoparticles increment the interfacial thermal resistances resulted in a k decrease. They also indicated that none of the two models, The Hamilton_Crosser and Maxwell_Garnett models could predict the enhancement correctly.

It shall be noted that both c_p and k, or thermal diffusivities, values are needed to assess the performance of a molten salt, including the storage capacity and charging/discharging behaviour. However, none of the work reported so far have reported these properties in one study. From the k side, none of the previous studies shows the effect of different nanoparticles on thermal conductivity over a wide range of temperatures up to 500 ^{0}C by taking into consideration of both solid phase and liquid phases.

In this work, we investigate experimentally the thermal-physical properties (k, c_p) of nanosalts to reveal the performance of nanoparticles. Different concentrations (0.5 wt. %, 1 wt. % and 1.5 wt. %) of Fe_2O_3, CuO and TiO_2 on single salt (KNO_3) and binary solar salt are studied. The thermal conductivity is determined by a laser flash analysis device; the thermal diffusivity data, including both solid and liquid phases, are measured up to 500 ^{0}C. The cp, melting temperature, and heat of fusion are measured by a dynamic scanning calorimeter (DSC) device. In addition, material characterization is also reported by the scanning microscopy (SEM) and the DLS of the nanoparticles size.

2. Experiments

2.1Material

The base material used for this study is nitrate molten salt. Sodium nitrate ($NaNO_3$) was purchased from (FISHER, Loughborough, UK) with 98% purity and potassium

nitrate (KNO_3) from (SIGA-ALDRICH, Suffolk, UK) with 98% purity. The additive materials were copper oxide (CuO) nanoparticles (<50 nm particle size) purchased from Sigma-Aldrich Company, and iron oxide (Fe_2O_3) nanoparticles (20–40 nm particle size) purchased from (iolitec-USA company). The commercial titanium dioxide (TiO_2) nanoparticles purchased from nanostructured & amorphous materials Inc., with purity of 99.8% and an average diameter of 50 nm.

The samples were prepared by the two-step method. Birefly, the nanoparticles were firstly mixed with molten salt and distilled water (30 ml), followed by a sonication process to ensure a good dispersion of nanoparticles within the sample. Then evaporation of water from the sample was conducted on a hot plate at a temperature around 150 ^{0}C until the water was fully evaporated from the samples.

2.2 Measurement

i) Differential scanning calorimetry (DSC)

Specific heat capacity tests were performed on a Mettler Toledo DSC (DSC1, Mettler Toledo, Leicester, UK) for single salt, binary salt, nanoparticles (Fe_2O_3, CuO, and TiO_2) and nanosalt (with different concentrations of nanoparticles, e.g. 0.5 wt. %, 1 wt. % and 1.5 wt. %), as well as the latent heat, and $T_{melting}$ of molten salt and nanosalt. The sample was placed in the crucible made of platinum, sample‘s weight was in the range of 30 mg to 35 mg excluding the weight of the crucible in order to have enough materials to fill the pan but not too much to cause the overflow issue during the measurements. The sample was measured by an Ultra-microbalance Mettler Toledo balance. Sapphire was used as a standard material with known specific heat capacity values in the range of temperatures of the experiments. The heating method used was modelled at a rate of 150 ˚C for 10 min, ramped from 150 ˚C to 450 ˚C at a rate of 10 ˚C/min, then maintained isothermally for 10 min at 450 ˚C and finally cooled down from 450 ˚C to 150 ˚C at -40 ˚C/min. It shall be noted that the maximum temperature in case of KNO_3 base material is less than 400 ^{0}C.

ii) Laser flash analysis (LFA)

Laser flash analysis (LFA) device was implemented to measure thermal diffusivity of the sample. In the LFA measurement, the diffusivity was determined by heating the front face of the sample by a laser with simultaneous record of the temperature profile on the rear face

Three layers model is used in a LFA measurement. The sample is the layer with unknown diffusivity and the other two layers represent the samples' holder and the crucible lid with known properties, as shown in Figure (1). The elegance of the method lies in the fact that the troublesome measurement of the absolute quantity of laser energy absorbed by the sample and of the resulting absolute temperature increase is replaced with a more accurate and direct measurement of time and relative temperature increase.

In order to calculate the thermal conductivity of the samples, the values of density and the specific heat capacity are needed, and k can be calculated as shown in the Equation (1).

$$k = c_p \times \rho \times a \qquad (1)$$

where k is thermal conductivity W/m. ^{0}K, c_p is specific heat capacity J/kg. ^{0}K (measured in the DSC device), ρ is density in kg/m^3 and a, is thermal diffusivity m^2/s. According to Janz et al. (1972), the density of binary nitrate solar salt can be calculated as a function of temperature depending on the Equation (2)

$$\rho = 2064.31 - (4.76248 \times 10^{-4} \times T^2) - (3.36495 \times 10^{-7} \times T^2) \qquad (2)$$

For nanosalt Equation (3) has been used by (Vajjha et al., 2009):

$$\rho_{nanosalt} = (\varphi_{np} \times \rho_{np}) + ((1-\varphi_{np}) \times \rho_{salt}) \qquad (3)$$

where φ_{np} is concentration of nanoparticles, $\rho_{nanosalt}$, ρ_{np} and ρ_{salt} are the density of nanosalt, nanoparticles and solar salt, respectively.

iii) Scanning electron microscopy

Morphology of the samples is performed by a scanning electron microscopy (Hitachi SU8230, SEM) device. SEM was used to show the surface morphology of molten

salt without and with nanoparticles. The samples were in powder form and their morphology before and after repeatable thermal cycles were studied.

iv) Dynamic light scattering

Dynamic light scattering (Malvern Zetasizer ZS, DLS) was used to measure the size of nanoparticles in this work. Nanoparticles were dispersed in distilled water and then measured in DLS where the intensity vs particles size was obtained. Three different samples of three different nanoparticles (Fe_2O_3, CuO, and TiO_2) used in this work mixed with distilled water and sonicate before testing in the DLS device. We did not used any type of surfactant to stabilise the nanofluid, and as nanoparticles might have suffered from agglomeration, leading to a large particle size, shown in Figure (12).

3. Results and discussions

3.1 Specific heat capacity (cp)

The c_p results showed that adding nanoparticles to any of the nitrate molten salt used in the experiments (either single salt (KNO_3) or binary salt (60 $NaNO_3$:40 KNO_3)) had either a positive or negative effect, depending on many factors such as concentration, size or type of the nanoparticles used.

Figures (2-3) indicate that nanoparticles significantly affect the specific heat capacity of nanosalt. For solid phase results, 1.5 wt. % samples have larger increments in c_p of nano-binary salt. In a similar study by using silica nanoparticles, Chieruzzi et al. (2013) who reported that 1 wt. % silica-nanosalt had higher c_p value than 0.5 wt. % or 1.5 wt.%. The slight difference might be due to the fact that different types of nanoparticles could behave differently with solar salt as well the differences in the preparation procedure between ours and the work of Chieruzzi et al. (2013). Chieruzzi et al. (2013) used a ultrasonic bath for 100 minutes and evaporated the water at 200 ^{0}C, while in ours, a probe sonicator was used with 150 ^{0}C to evaporate the water. The results of single salt, KNO_3, are highly depending on the type of nanoparticles used, which is similar to what concluded by Chieruzzi et al. (2015a).

Figure (3) shows the dispersion of nanoparticles in KNO_3 or binary salt increases the specific heat capacity of nanosalt at high temperature. However, this increase

depends on the type of the base material, concentrations and type of nanoparticles. Mostly, TiO_2-nanosalt shows a decrease in the c_p of nano-binary salt, as shown in Table (3). In contrast, Lasfargues et al. (2015) indicated a positive effect of TiO_2-nanosalt and CuO-nanosalt. This difference could be due to different preparation methods. For single salt case, Table (4) demonstrates that in most cases, c_p increases with the concentrations of nanoparticles. According to Chieruzzi et al. (2015a), 1 wt.% of silica-KNO_3 salt has higher c_p than KNO_3 while 1 wt.% of alumina-KNO_3 salt has lower cp than KNO_3. This is in similar to the results we got for 1 wt. % nano-KNO_3 however, Chieruzzi et al. (2015a) did not study the effect of another concentration (0.5 wt.%). The increment of c_p of nanosalt in solid phase is slightly higher than that of liquid phase especially for the case of solar salt as the base material, which is in agreement to Chieruzzi et al. (2017).

From Tables (1-4), Fe_2O_3 nanoparticles seem to be a good option to increase the c_p of the solid/liquid phase of the base material (either binary solar salt or single KNO_3 salt) followed by CuO nanoparticles. TiO_2 nanoparticle gives a very small enhancement in c_p of nanosalt or in most of the cases it decreases the c_p value.

There are some models used to predict the improvement in the c_p when nanoparticles are added and these models are mentioned by many researchers for example Seo and Shin (2014). The classical model of the effective specific heat can be given by Equation (4)

$$c_{p,nf} = \frac{\rho_{np}\,\emptyset_{np}\,c_{p,np} + \rho_f\,\emptyset_f\,c_{p,f}}{\rho_{np}\,\emptyset_{np} + \rho_f\,\emptyset_f} \qquad \textbf{(4)}$$

where $c_{p,\mathrm{nf}}$, $c_{p,np}$ and $c_{p,f}$ represent c_p of nanosalt, nanoparticle, and salt. $\emptyset_{np}$ and $\emptyset_f$ are the volume fraction of nanoparticles and salt. ρ_{np} and ρ_f are the density of nanoparticle and salt respectively. However, this model would not show any enhancement in c_p unlike the most of the experimental results. This discrepancy is due to the lower value of c_p of nanoparticles comparing to the salt. For instance, c_p of Fe_2O_3 nanoparticle is smaller than that of a molten salt. Even the fact that c_p of nanoparticles is larger, e.g. c_p of Fe_2O_3 around (0.9 J/g. ^{0}C), which is slightly higher than its bulk material (0.84 J/g. ^{0}C) in the range of (150 ^{0}C – 450 ^{0}C) as indicated by Snow et al. (2010). For more emphasis, we measured the c_p of all nanoparticles used for the current experiments. In this experiments, c_p of Fe_2O_3 equals to 0.9 J/g

C, c_p of CuO equals to 0.59 J/(g C) and cp of TiO_2 is 1.06 J/g C. Furthermore, Zhou and Wang (2003) referred that c_p of bulk CuO was 0.54 J/ (g. ^{0}C). While the cp of CuO nanoparticles measured in the current experiment equals to 0.59 J/ (g. ^{0}C) which is slightly higher than cp of its bulk material. However, c_p values of Fe_2O_3 / CuO/ TiO_2 nanoparticles are still lower than that of a molten salt. This indicates that the increases in c_p are not due to the nanoparticle effect. Therefore, the classical model cannot predict the enhancement in cp of nanosalt where the cp of molten salt is larger than that of the nanoparticles used in the respective work. Therefore, this model needs to expand and include the other factors such as the interfacial area formed at the surface of the nanoparticle and the molten salt or other forces between nanoparticles and so on.

Moreover, higher surface area owned by nanoparticles causes an increase in the thermal resistance between nanoparticles and the molecules of the molten salt, resulting in a rise in the interfacial interaction between them, which could increase the c_p of a nanosalt. Additionally, during the preparation of the nanosalt sample and due to the sonication and evaporation stages, molten salt molecules could form a compressed layer on the surface of nanoparticles. These interfacial layers could have different properties to the base material alone. Furthermore, these layers could higher c_p, which may lead to increase the c_p of nanosalt according to the Equation (5)

$$c_{p,nf} = \frac{\rho_{np}\,\emptyset_{np}\,c_{p,np} + \rho_c\,\emptyset_c\,c_{p,c} + \rho_f\,\emptyset_f\,c_{p,f}}{\rho_{np}\,\emptyset_{np} + \rho_c\,\emptyset_c + \rho_f\,\emptyset_f} \qquad (5)$$

where $c_{p,c}$, $\emptyset_c$ and ρ_c represent c_p, volume fraction, and density of compressed layer (interfacial layer), respectively.

In addition, the mass fraction of these layers depends on size and concentrations of nanoparticles. It is assumed that the c_p of an interfacial layer has a significant effect on the overall c_p of nanosalt when there is no agglomeration of nanoparticles. For instance, an assumed value of c_p=6.2 J/g.^{0}K (of the interfacial layer) would predict the experimental well. Other possible reasons that could have the higher effect on the c_p of the nanosalt are the sedimentation of nanoparticles, the Van der Waals force, and surface charge between the nanoparticles, as well the attractive force among the nanoparticles. These forces would help the agglomerations of these

nanoparticles, which impact badly on their dispersion in the nanosalt samples. Therefore, there is a need to find a proper surfactant that could work efficiently at this high temperature condition, which could help to solve the dispersion and stability issue of nanoparticles in the nanosalt samples.

2.2 Latent heat

Latent heat is extensively affected by dispersing nanoparticles into the molten salt. Particularly, 1 wt. % of Fe_2O_3 and CuO in binary salt, 0.5 wt. % of Fe_2O_3 and CuO-single salt, increases the latent heat. The maximum improvement was found within CuO-binary salt up to 15% and Fe_2O_3-single salt up to 3%. This increment in latent heat of nanosalt will result with more energy stored per unit volume.

An interface is formed during the preparation of nanosalt sample. This interface is due to the rearrangement of nanoparticles in the nanosalt sample. Therefore, nanosalt needs higher heat to melt this interfacial layers, which maybe one of the reasons for increasing latent heat. Additionally, clusters of nanoparticles could lead to an increase in the latent heat as suggested by Chieruzzi et al. (2015a) and Lasfargues et al. (2015). More heat is needed to melt these agglomerations. However, this increasing or decreasing of latent heat of different nanosalts depends on the places of the presence of nanoparticles in the nanosalt sample. One example of the current experiments is the increases in latent heat due to the addition of 1 wt. % CuO nanoparticles into the binary salt. From SEM result Figure (5), it is clearly shown the agglomerations of 1 wt. % CuO-nanosalt and this sample have a higher value of latent heat as the clustering required more heat to melt, resulting in an increment in latent heat. Additionally, as shown in Figure (6) of the samples tested by SEM results, there is a presence of the agglomerations and clustering of the nanoparticles in the nanosalt samples. These results are consistent with the observation from Chieruzzi et al. (2015a) and Lasfargues et al. (2015) for the enhancements of latent heat of nanosalt samples.

Likewise, the melting point of a nanosalt is highly affected by the addition of nanoparticles in samples. $T_{melting}$ is decreased with an addition of nanoparticles in all cases. In particular, the $T_{melting}$ of binary salt is decreased by 5 ^{0}C in cases of all nanosalt samples, i.e $T_{melting}$ of binary salt is 230 ^{0}C while $T_{melting}$ of all the nanosalt is

between (225 ^{0}C-226 ^{0}C). Furthermore, similar behaviour is observed in the case of KNO_3 base material with a decrement in $T_{melting}$ of KNO_3-nanosalt samples by 1 ^{0}C. This is similar to the results from Gimenez-Gavarrell et al. (2015), Chieruzzi et al. (2013), Lasfargues et al. (2015) and Chieruzzi et al. (2015a). According to Lasfargues et al. (2015), $T_{melting}$ decrease in nanosalt relies on the method of heat transfer over nanosalt sample and the size of clustering of theses nanoparticles. Moreover, nanoparticles in the sample could work as nucleation agents, which bring the phase change earlier in comparison with the base salt, (Gimenez-Gavarrell et al., 2015). Although this decrement in melting temperature is low, it still considers an advantage because it means the phase change starts earlier. As a result, melting time will reduce which improves the heat transfer in the storage system with the support of enhanced conduction by nanoparticles.

Furthermore, the base material in case of binary salt does not reach the eutectic point as the melting temperature happened in a range of temperature not in a single point. Because of this, the mixture binary salt behaves as a non-pure mixture showing that it needs more heat to be melted or freezing completely. According to Kramer and Wilson (1980), the addition of 60% molar ratio of $NaNO_3$ would result in a melting temperature of the binary salt in a temperature range 221 ˚C> T_{melt} > 241 ˚C. On the other hand, KNO_3 with a composition of 100% have one value for the T_{melt} 335 ˚C as it is a pure single material (Kramer and Wilson, 1980), Figure (7). However, KNO_3 material used in this experiment was 98% pure. From the DSC measurements, $T_{melting}$ of KNO_3 was in a range caused by its non-purity. The purity of the material has an impact that influence the behaviour of the salt and nanosalt properties.

3.3 Total thermal energy storage (TES)

TES is the total amount of energy of the storage system by considering both sensible and latent heats. TES of the nanosalt samples is different from the TES of molten salt alone. There is an increase or decrease in the TES as shown in Tables (5 and 6). From Table (5), 1 wt.% of Fe_2O_3-binary salt and 0.5 wt.% of CuO-binary salt represent the maximum increment in TES this is due to accumulated increment of energy. For instance, 1 wt.% of Fe_2O_3-binary salt own a higher increase in latent heat than other concentrations alongside with the advantages of sensible increment in

both solid and liquid phases. Although, 1 wt.% of CuO-binary salt gave the maximum increases in latent heat, it owns less increment in the sensible heat in comparison to the 0.5 wt.%. Therefore, 0.5 wt. % of CuO-binary salt gave a higher TES than that of 1 wt. % of CuO..

It seems to be 0.5 wt. % in single salt (KNO_3) shows higher increases with 5.26% for 0.5 wt. % Fe_2O_3- KNO_3 as shown in Table (6). TES represents by the summation of sensible heat (in the range of working temperatures of solid and liquid phases) and of latent heat as shown in the following equations

$$q_{storage} = q_{sensible} + q_{latent} \quad (6)$$

As $$q_{sensible} = q_{sensible\ in\ solid\ phase} + q_{sensible\ in\ liquid\ phase} \quad (7)$$

$$q_{storage} = [\int_{T_{ambent}}^{T_{melt}} cp * dT + \int_{T_{liquid}}^{T_{max.}} cp * dT] + q_{latent} \quad (8)$$

In order to increase the storage capacity of the molten salt, an improvement in the thermal properties of the molten salt is required. Therefore adding nanoparticles to the base material (molten salt) indicated an increase in the sensible/latent storage. Most of the cases, nanosalt will have a higher cp and higher latent heat than the base material (molten salt) and this leading to a higher efficiency of the storage system, which indicated a higher level of the solar thermal power plant efficiency. According to Feldhoff et al. (2012), 9 hour is the storage time inside a two tank (hot and cold sensible tanks) in the solar thermal plant. The working temperature in the cold and hot tanks are 292 ^{0}C and 386 ^{0}C respectively. Dispersing nanoparticles into the base material will improve the c_p of the base material. 14% is the efficiency of TES using molten salt alone, (Feldhoff et al., 2012), while with nanosalt as a storage medium this efficiency will increases. For instance, at T= 386 ^{0}C, sensible heat of solar salt is 220.744 J/kg. However, this sensible heat (220.744 J/kg) can be increased when dispersing 1.5 wt. % of CuO in solar salt to 233.044 J/kg. As a result, the sensible heat of the nano-binary salt increased by 5.6% in comparison to solar salt only, which mean increasing the efficiency of the TES system. Furthermore, at T=386 ^{0}C, the value of c_p of nanosalt (KNO_3+ 1 wt. % Fe_2O_3) equals to 1.253 J/kg. ^{0}C while c_p of molten salt (KNO_3) = 1.1615 J/kg. ^{0}C. Therefore the

sensible heat increased by 7.88% with the presence of nanoparticles. This indicates the big impact of nanoparticles on the efficiency of the storage system.

3.4 Thermal conductivity

On the other hand, thermal conductivity (k) of binary solar salt, Fe_2O_3-nanosalt, and CuO-nanosalt were tested. The current results demonstrate that nanoparticles have a significant effect on the thermal conductivity of nanosalts both at low and high temperatures. Increasing concentration of CuO, from 0.5 wt. % to 1.5 wt. %, has a negative effect on thermal conductivity of nanosalt. In contrast, Fe_2O_3 nanoparticles always increase k of nanosalt except for the case 1 wt. % Fe_2O_3-nanosalt. It is concluded that small concentrations of nanoparticles are preferred for increasing k of nanosalt samples.

The increase in temperature leads to an increase in Brownian motion of particles and this may lead to the enhancement observed in k. Additionally, these nanoparticles have higher k values in comparison with the base salt and therefore when the nanoparticle is mixed with base salt it would lead to a high k. However, this increment in k of nanosalt depends on the additive material properties, such as concentration and the type of nanoparticles. For instance, the sample prepared by the mixing of base salt and the additive material (Fe_2O_3) seems to be more conductive material than CuO-nanosalt ones as shown in Figure (8). This show the effect of nanoparticles types on the nanosalt samples. Moreover, the higher surface area of nanoparticles could be one of the reasons that causes an increases in thermal conductivity for the nanosalt samples. In addition, Fe_2O_3 nanoparticles have less particle size means higher surface area than CuO nanoparticles and this could be one of the reasons behind the high improvements in Fe_2O_3-nanosalt than CuO-nanosalt samples (Yoo et al., 2007). According to Hwang et al. (2006), k of nanofluid is affected by the conductivity of both base and additive materials, which could be the same case for the current results as both nanoparticles used here have higher conductivity than a thermal conductivity of molten salt. The improvements in k of nanosalt are largely affected by particles loading, the temperature range of the test, nanoparticles size and stability of the sample. The results of thermal conductivity are listed in Table (7).

Additionally, both nanoparticles (CuO or Fe_2O_3) almost show that the lowest concentration (0.5 wt. %) give more increment in thermal conductivity than higher concentrations (1 wt. % or 1.5 wt. %). Although, 1.5 wt. % Fe_2O_3-nanosalt give better enhancement than 1 wt. % Fe_2O_3-nanosalt case. As shown in Table (7), there is a maximum increment of nanosalt (in 0.5 wt. %) over the range of concentrations tested. Figure (9) shows the effect of weight fraction of nanoparticles on thermal conductivity.

In general, k of nanofluids increases with increasing the concentration of nanoparticle (Mintsa et al., 2009). However, Figure (9) does show a certain discrepancy as the results for 0.5 wt. % nanosalt is slightly above others concentrations. According to (Saidur et al., 2011), conductivity increases with particles loading. This has some differences with current work due to the effect of the base material. Molten salt behaves differently than water, in addition, the effect of the surface charge of molten salt could play an important role on the result of k-Temp result. Furthermore, Assael et al. (2005) mentioned that increases concentrations from 0.1 to 6 mass % give a decreasing in k by 0.3% to 5% in respective. This is in matching with the results we got as an increment in particle loading give a lower k. Although we tested Fe_2O_3-nanosalt and CuO-nanosalt, which are different from the material tested by Assael et al. (2005), their material was carbon nanotube-water based material. It indicates the big effect of the concentration on the improvement of k of nanosalt. More work needs to be considered in order to measure k of nanosalt over a wide range of concentrations to compare the effect of k with nanoparticles' loading in the nanosalt samples.

In order to calculate thermal conductivity theoretically, we would like to consider the Hamilton-Crosser model as shown in Table (9). According to Hamilton-Crosser model, the predicted value of k is not matching the measurement values. There are some reasons that could cause this difference. One of these reasons is the assumption of the sample in theoretical part compared to the actual behaviour of sample during the experiments, as the equation assumed the same size of nanoparticles are dispersed homogeneously along the sample, whereas in the experiment, it is very difficult to achieve due to the agglomeration and sedimentation effects of nanoparticles in the nanosalt sample. This could be due to the effects of different forces such as Van der Waals and gravity forces as both could lead to

sedimentation or agglomerations of nanoparticles. Therefore, the calculated values cannot predict the enhancement in k unless consideration is given to all the affected factors.

Furthermore, the heat transfer will be improved in case of nanosalt due to the advantages of both cp, thermal conductivity. Due to the effect of natural convection during the phase change any increase in specific heat capacity or thermal conductivity will causes an increase in the heat transfer rate according to Equation (9). From heat transfer correlation equation, Nusselt number (Nu) is related to Rayleigh number (Ra) with some correlations constants, e.g. (Nu=CRa^n) as C and n are constant depending on the case. In addition, any increases in the Nu will causes an increment in the heat transfer coefficient according to (h=Nu*k/L)) where h is heat transfer coefficient, L is the characteristic length and k is thermal conductivity. Therefore, any increases in Nu will give a higher heat transfer.

$$Ra = \frac{g\,\rho^2\,\beta\,\Delta T\,L_c}{\mu} * cp * k \qquad (9)$$

3.5 Comparison with other results

In order to check the accuracy of our results data and to see how much the data we got are reliable, a comparison was carried out with the literature data.

Specific heat capacity and latent heat of molten salt and nanosalt samples have been compared with other experiments literature data. The average value of c_p of the KNO_3 salt in Chieruzzi et al. (2015b) was reported to be (1.118 J/g. ^{0}C) and in the current work is (1.19 J/g. ^{0}C) in the liquid phase. The average value of c_p of the binary solar salt ($NaNO_3$:KNO_3 with 60:40 molar ratio) for the liquid phase equals to 1.315 J/g. ^{0}K in the range 250 ˚C -495 ˚C (Jung and Banerjee, 2011) and c_p has a value equals to 1.38 J/g. ˚K in the range 250 ˚C- 450 ˚C by the work of (Xie et al., 2016). In the current work, cp of the binary solar salt for the liquid phase equals to 1.37 J/g. K in the range 250 ˚C -450 ˚C.

In order to compare the latent heat values of the current study, first of all, KNO_3 salt has 91.61 J/g and T_{onset} is 335.7 ˚C according to Chieruzzi et al. (2015b), in similarity, the current study KNO_3 salt has a value equals to 93.89 J/g with T_{onset} is

332.47 ˚C. Secondly, in the current study, the latent heat of solar salt equals to 107.03 J/g with T_{onset} is 219.11 ˚C likely to 110.01 J/g and T_{onset} is 219.88 ˚C by (Chieruzzi et al., 2013). The standard error of the DSC device used for this experiments is around 1% and each sample tested for three times and they show a repeatable and coincide results. However, the small different in the results between the literature and the current work are more related to the precision of the device used and the thermal cycle of the test along with the samples used (each salt purchased from different sources in literature papers and the current work) and the types of crucible used in DSC device may cause this little differences.

Additionally, the thermal conductivity of nitrate salt has been reported by (Serrano-López et al., 2013). At a range of temperature 250 ^{0}C- 400 ^{0}C, the difference between current experiment values and the literature seems to be acceptable in term of different method used to the measurements as shown in Figure (11).

According to Serrano-López et al. (2013), none of the cited literature has mentioned laser-flash analysis as a measurement device for thermal conductivity of molten salts. The methods were used for the measurements are transient hot wire, coaxial cylinder, rough hard sphere, etc. In our experiment, laser-flash analysis have been used to measure thermal diffusivity of the samples and with the input of known values of density (based on the literature) and c_p (based on our experiments), the thermal conductivity has been calculated, which is approximately matching with the reported values.

4. Conclusion

The specific heat capacity, $T_{melting}$, latent heat and thermal conductivity of nitrate molten salt were studied using differential scanning calorimetry and laser-flash analysis, respectively. Different types of nanoparticles (0.5 wt. %, 1 wt. % and 1.5 wt. %) were dispersed in single salt (KNO_3) and binary salt ($NaNO_3$:KNO_3 with 60:40 molar ratio) to achieve good properties. Using Fe_2O_3 nanoparticles, we got a higher improvement of c_p up to 11% and thermal conductivity up to 60%. In particular, the latent heat was increased up to 15% with 1 wt. % CuO-binary salt. The storage energy was improved up to 6% with Fe_2O_3 nanoparticles in comparison to solar salt

only, which mean an increase of the efficiency of the TES system. Moreover, an increase in the sensible energy of nano-KNO_3 by 7.88% was observed.

In summary, the use of nanosalt to store thermal energy in term of charging/discharging processes will be very helpful due to their positive effects on both thermal conductivity and heat capacity.

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Tables and Figures

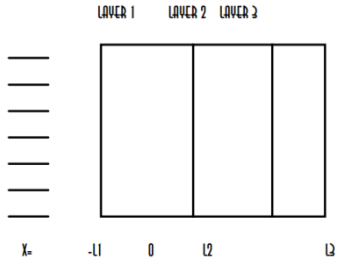


Figure 1 three layer model (NETZSCH, 2017)

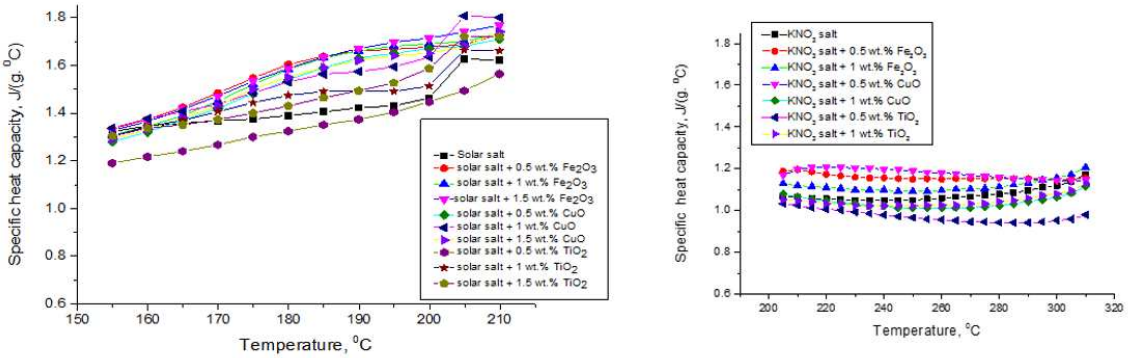


Figure 2 Solid phase of cp of different types and concentrations of nanoparticles dispersed into nitrate salt.

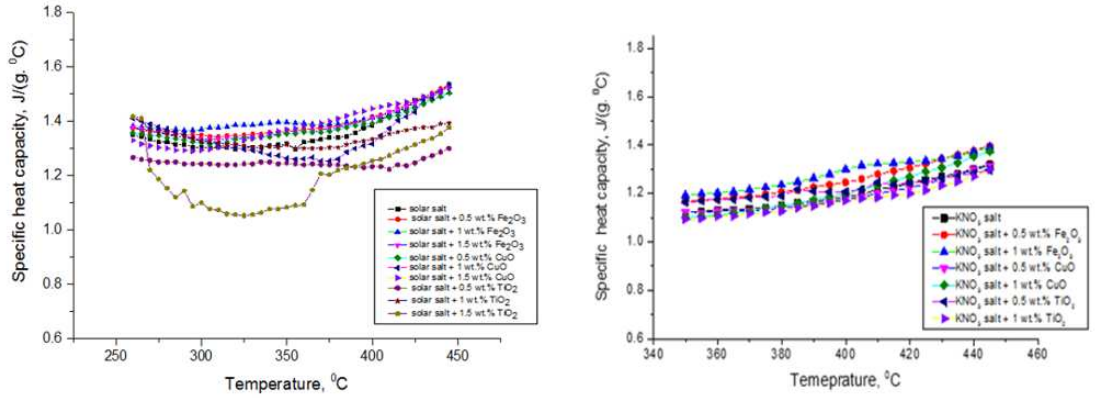
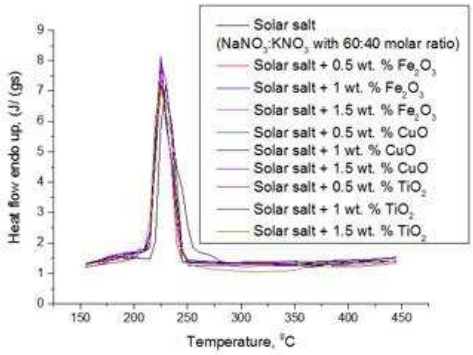
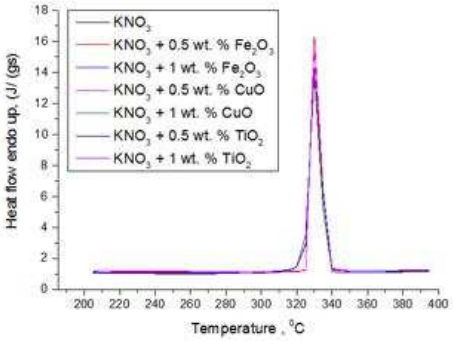


Figure 3 Specific heat capacity of liquid phase of different types and concentrations of nanoparticles dispersed in nitrate salt



Heat flow vs. temperature of binary salt and nanosalts



Heat flow vs. temperature of KNO3 and nanosalts

Figure 4 Heat flow vs. temperature of salt and nanosalts

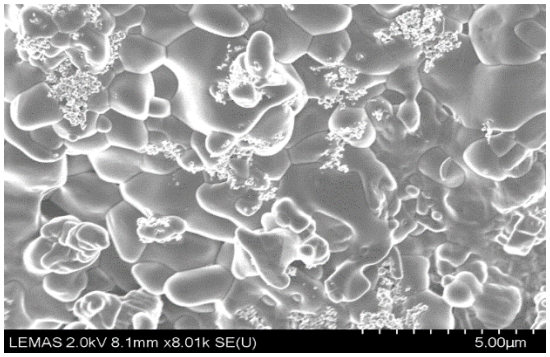
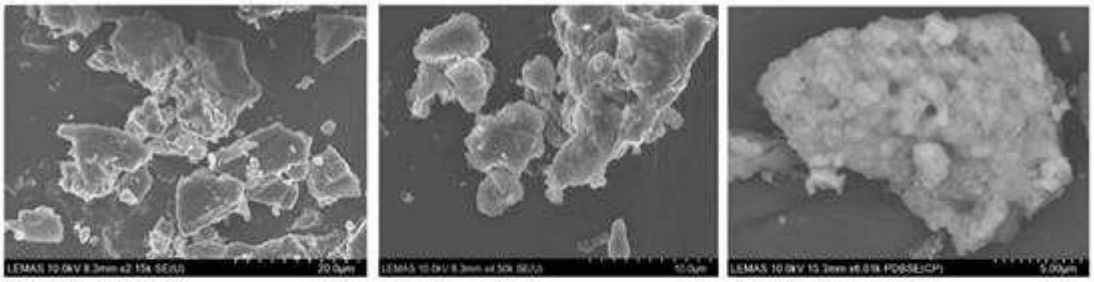
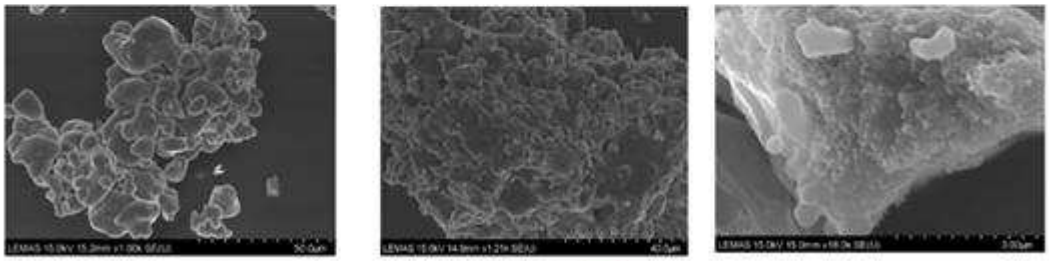


Figure 5 SEM test of 1 wt. % CuO dispersed in solar salt.



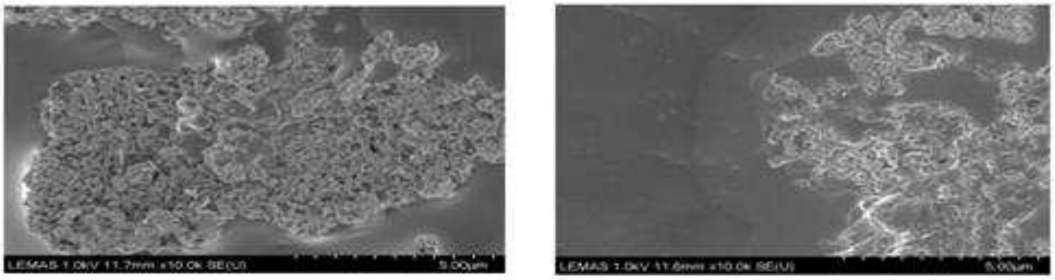
1 wt. % Fe_2O_3 dispersed in solar salt.



1 wt. % Fe_2O_3 dispersed in KNO_3 salt.

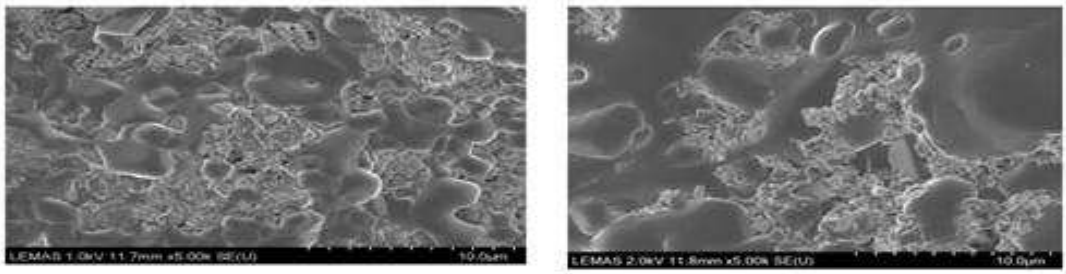
0.5 wt. % CuO dispersed in solar salt

0.5 wt. % CuO dispersed in KNO_3 salt.



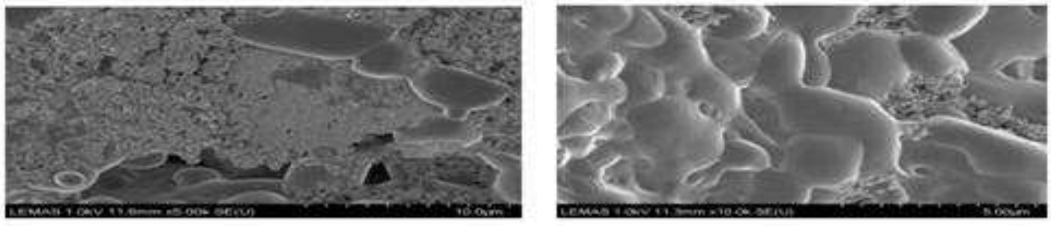
0.5 wt. % Fe_2O_3 dispersed in KNO_3 after melting/solidification cycles

0.5 wt. % TiO_2 dispersed in KNO_3 after melting/solidification cycles



0.5 wt. % CuO dispersed in solar salt after melting/solidification

0.5 wt. % Fe_2O_3 dispersed in solar salt after melting/solidification



1 wt. % Fe_2O_3 dispersed in solar salt after melting/solidification

1 wt. % TiO_2 dispersed in solar salt after melting/solidification

Figure 6 SEM shows nanoparticle agglomerations after the preparation

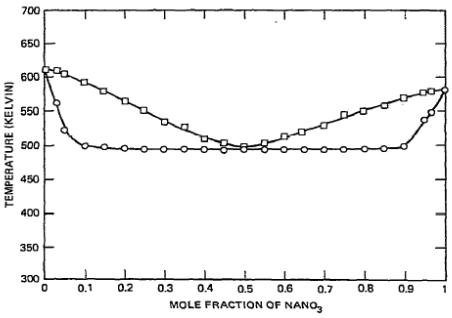


Figure 7 phase diagram of solar salt with different composition of $NaNO_3$ (Kramer and Wilson, 1980)

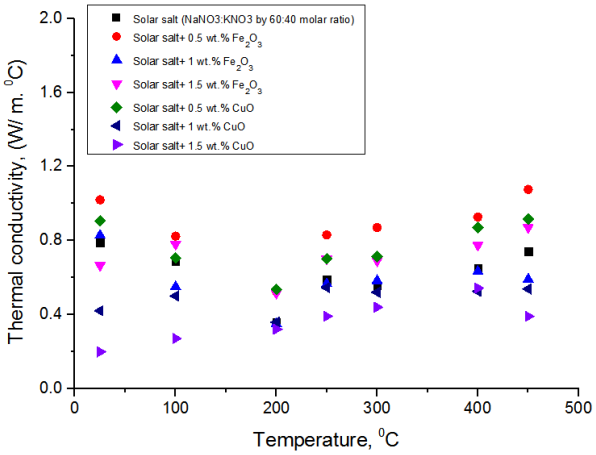


Figure 8 thermal conductivity vs. temperature of different samples.

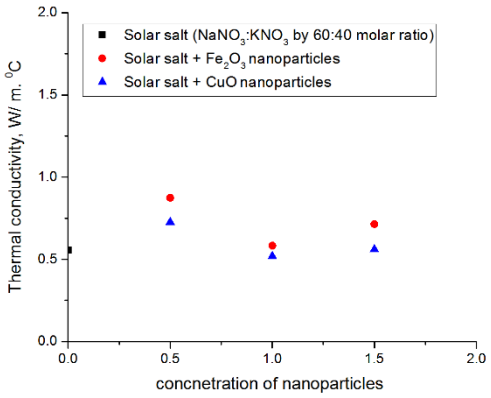


Figure 9 Thermal conductivity of nanosalt vs concentration of nanoparticles

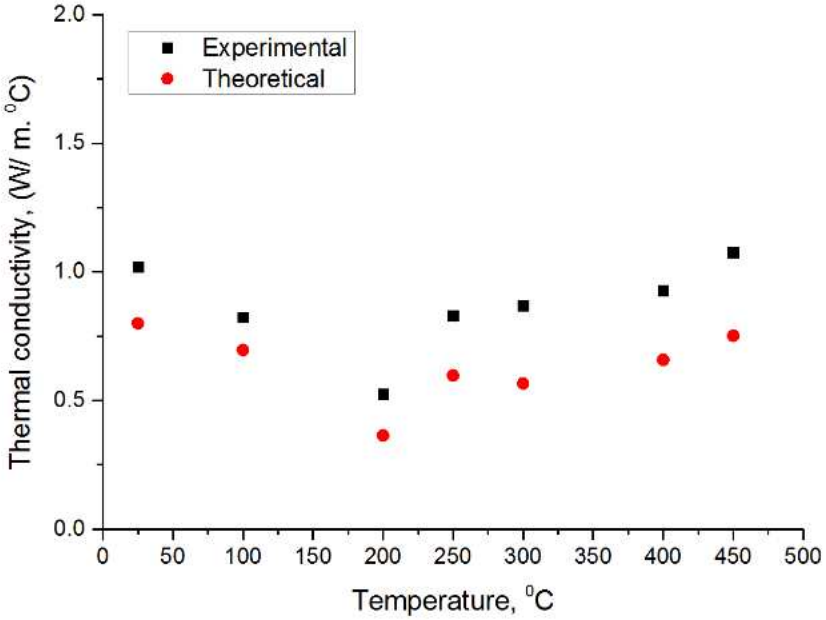


Figure 10 thermal conductivity vs temperature for 0.5 wt. % Fe_2O_3-nanosalt both experimental and calculated values

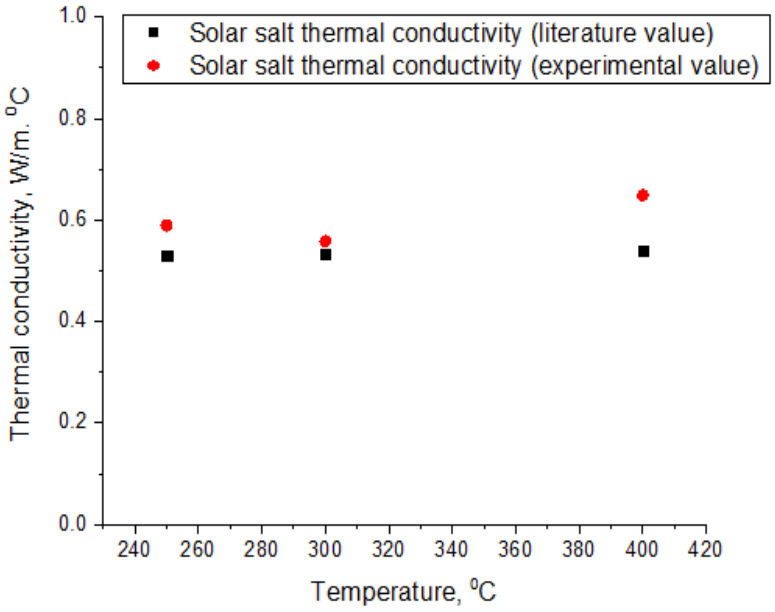
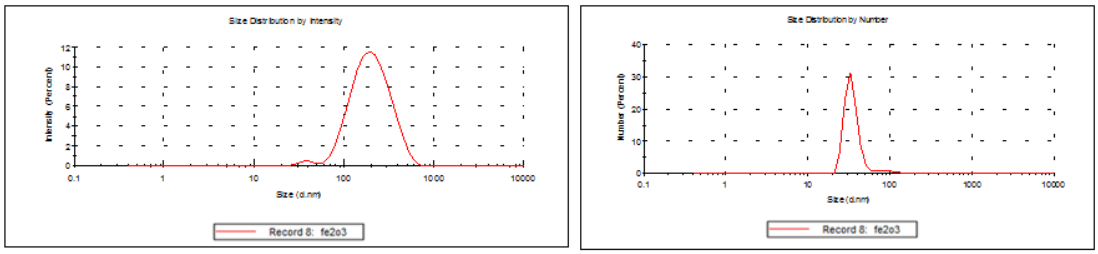
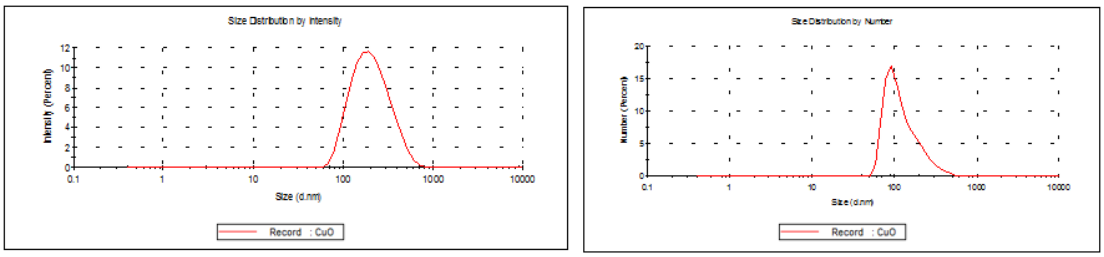


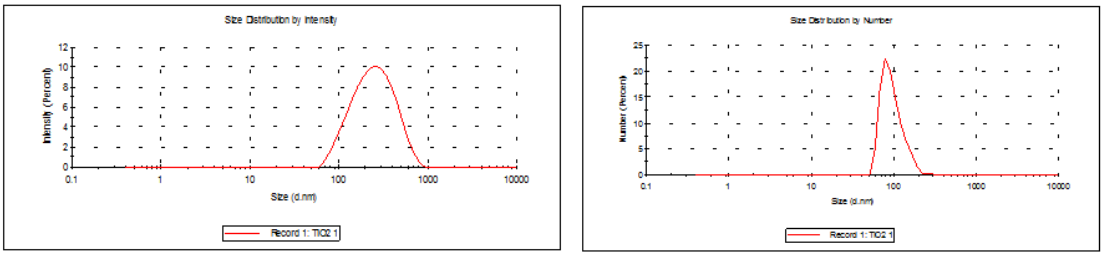
Figure 111 thermal conductivity of current experiment and in the literature (Serrano-López et al., 2013)



Fe_2O_3-nanofluid with average size of (175.5 nm)



CuO-nanofluid with average size of (182.5 nm)



TiO2-nanofluid with average size of (214 nm)

Figure 122 Size measurement in DLS device for different nanofluid samples.

Table 1 Solid phase of cp (in range 150 ^{0}C-215 ^{0}C) of different types and concentrations of nanoparticles dispersed inside solar salt ($NaNO_3$:KNO_3 by 60:40 molar ratios).

Run	Solar salt	+ Fe_2O_3			+ CuO			+ TiO_2		
	-	0.5 wt.%	1 wt.%	1.5 wt.%	0.5 wt.%	1 wt.%	1.5 wt.%	0.5 wt.%	1 wt.%	1.5 wt.%
Run 1	1.43	1.67	1.63	1.67	1.59	1.37	1.64	1.27	1.31	1.3
Run 2	1.44	1.49	1.54	1.53	1.48	1.63	1.49	1.41	1.52	1.53
Run 3	1.43	1.54	1.51	1.53	1.51	1.56	1.48	1.36	1.53	1.52
Average	1.43	1.57	1.56	1.58	1.53	1.52	1.54	1.35	1.453	1.45
% Increase	-	9.8%	9.1 %	10.5%	7%	6.3%	7.7%	-5.6%	1.6%	1.4%

Table 2 Solid phase of cp (in range 200 ^{0}C-315 ^{0}C) of different types and concentrations of nanoparticles dispersed into KNO_3 salt.

Run	KNO3 salt	+ Fe_2O_3		+ CuO		+ TiO_2	
	-	0.5 wt.%	1 wt.%	0.5 wt.%	1 wt.%	0.5 wt.%	1 wt.%
Run 1	1.09	1.17	1.12	1.16	1.06	0.78	1.06
Run 2	1.072	1.15	1.11	1.151	1.03	1.085	1.04
Run 3	1.073	1.13	1.13	1.150	1.04	1.065	1.039
Average	1.078	1.15	1.12	1.154	1.043	0.98	1.046
% Increase	-	6.68%	3.9%	7.05%	-3.25%	-9.09%	-2.97%

Table 3 Liquid phase of cp (in range 250 ^{0}C-450 ^{0}C) of different types and concentrations of nanoparticles dispersed inside solar salt ($NaNO_3$:KNO_3 by 60:40 molar ratios).

Run	Solar salt	+ Fe_2O_3			+ CuO			+ TiO_2		
	-	0.5 wt.%	1 wt.%	1.5 wt.%	0.5 wt.%	1 wt.%	1.5 wt.%	0.5 wt.%	1 wt.%	1.5 wt.%
Run 1	1.38	1.36	1.33	1.37	1.36	1.37	1.35	1.14	1.27	0.9
Run 2	1.37	1.363	1.46	1.39	1.37	1.34	1.34	1.3	1.35	1.32
Run 3	1.35	1.46	1.42	1.39	1.4	1.32	1.45	1.31	1.39	1.30
Average	1.37	1.394	1.4	1.383	1.377	1.343	1.38	1.25	1.34	1.17
% Increase	-	1.75%	2.19%	0.95%	0.51%	-1.97%	0.73%	-8.76%	-2.19%	-14.6%

Table 4 Liquid phase of cp (in range 350 ^{0}C-390 ^{0}C) of different types and concentrations of nanoparticles dispersed into KNO_3 salt

Run	KNO3 salt	+ Fe_2O_3		+ CuO		+ TiO_2	
	-	0.5 wt.%	1 wt.%	0.5 wt.%	1 wt.%	0.5 wt.%	1 wt.%
Run 1	1.18	1.22	1.28	1.21	1.18	1.14	1.171

Run 2	1.2	1.28	1.27	1.18	1.22	1.28	1.17
Run 3	1.2	1.27	1.28	1.17	1.216	1.245	1.16
Average	1.19	1.26	1.28	1.187	1.205	1.222	1.167
% Increase	-	5.9%	7.56%	-0.25%	1.261%	2.69%	-1.93%

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794 **Table 5 latent heat, onset temperature and total thermal energy storage capacity of**
795 **different types and concentrations of nanoparticles dispersed in solar salt**
796 **($NaNO_3$:KNO_3 by 60:40 molar ratios).**

Material	Latent heat (kJ/kg)	Onset temperature (°C)	T_{onset} differences	Total TES capacity (kJ/kg)	% TES
Pure salt	**107.03**	**219.11**	**-**	**466.83**	**-**
Salt + 0.5 wt. % Fe_2O_3	**109.27**	**216.22**	**2.89**	**482.27**	**3.31%**
Salt + 1 wt. % Fe_2O_3	**119.09**	**219**	**0.11**	**492.69**	**5.54%**
Salt + 1.5 wt % Fe_2O_3	**115.25**	**216.66**	**2.45**	**486.65**	**4.25%**
Salt + 0.5 wt % CuO	**118.08**	**216.01**	**3.1**	**485.28**	**3.95%**
Salt + 1 wt % CuO	**122.5**	**218.21**	**0.9**	**482.3**	**3.31%**
Salt + 1.5 wt % CuO	**110.32**	**217.05**	**2.06**	**478.72**	**2.55%**
Salt + 0.5 wt % TiO_2	**95.41**	**216.33**	**2.78**	**426.41**	**-8.66%**
Salt + 1 wt % TiO_2	**100.37**	**215.88**	**3.23**	**455.55**	**-2.42%**
Salt + 1.5 wt % TiO_2	**89.65**	**213.31**	**5.8**	**410.65**	**-12.03%**

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799 **Table 6 latent heat, onset temperature and total thermal energy storage capacity of**
800 **different types and concentrations of nanoparticles dispersed inside KNO_3 salt.**

Material	Latent heat (kJ/kg)	Onset temperature (°C)	T_{onset} differences	Total TES capacity (kJ/kg)	% TES
KNO_3 salt	**93.89**	**332.47**	**0**	**331.47**	**-**
KNO_3 salt + 0.5 wt. % Fe_2O_3	**96.41**	**332.12**	**0.35**	**348.91**	**5.26%**
KNO_3 salt + 1 wt. % Fe_2O_3	**94.08**	**325.53**	**6.94**	**345.28**	**4.17%**
KNO_3 salt + 0.5 wt % CuO	**95.14**	**332.3**	**0.17**	**340.78**	**2.81%**
KNO_3 salt + 1 wt % CuO	**94.42**	**330.78**	**1.69**	**329.65**	**-0.55%**
KNO_3 salt+ 0.5 wt % TiO_2	**91.02**	**327.56**	**4.91**	**321.02**	**-3.15%**
KNO_3 salt+ 1 wt % TiO_2	**92.9**	**325.55**	**6.92**	**324.66**	**-2.05%**

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Table 7 thermal conductivity (k, W/m. C) of different types and concentrations of nanosalt

T, ^{0}C	Molten salt	Molten salt+ 0.5 wt.% Fe_2O_3	Molten salt+ 1 wt.% Fe_2O_3	Molten salt+ 1.5 wt.% Fe_2O_3	Molten salt+ 0.5 wt.% CuO	Molten salt+ 1 wt.% CuO	Molten salt+ 1.5 wt.% CuO
25	0.79	1.02	0.828	0.665	0.906	0.42	0.198
100	0.687	0.823	0.55	0.78	0.705	0.5	0.27
200	0.359	0.524	0.35	0.515	0.536	0.358	0.32
250	0.589	0.83	0.566	0.7	0.701	0.545	0.39
300	0.558	0.87	0.583	0.69	0.713	0.52	0.439
400	0.649	0.927	0.632	0.774	0.87	0.525	0.543
450	0.742	1.076	0.59	0.87	0.915	0.538	0.39

Table 8 Enhancement in thermal conductivity of different types and concentrations of nanosalt

T, ^{0}C	Molten salt+ 0.5 wt.% Fe_2O_3	Molten salt+ 1 wt.% Fe_2O_3	Molten salt+ 1.5 wt.% Fe_2O_3	Molten salt+ 0.5 wt.% CuO	Molten salt+ 1 wt.% CuO	Molten salt+ 1.5 wt.% CuO
25	29.1	4.81	-15.8	14.68	-46.84	-74.94
100	19.8	-19.94	13.54	2.62	-27.22	-60.7
200	45.96	-2.51	43.45	49.3	-0.28	-10.86
250	40.92	-3.9	18.85	19.02	-7.47	-33.79
300	55.91	4.48	23.66	27.78	-6.81	-21.33
400	42.84	-2.62	19.26	34.05	-19.11	-16.33
450	45.01	-20.49	17.25	23.32	-27.49	-47.44

Table 9 theoretical calculations of thermal conductivity for different types and concentrations of nanosalt

T, ^{0}C	Molten salt+ 0.5 wt.% Fe_2O_3	Molten salt+ 1 wt.% Fe_2O_3	Molten salt+ 1.5 wt.% Fe_2O_3	Molten salt+ 0.5 wt.% CuO	Molten salt+ 1 wt.% CuO	Molten salt+ 1.5 wt.% CuO
25	0.8	0.81	0.821	0.802	0.814	0.826
100	0.696	0.705	0.714	0.697	0.708	0.718
200	0.364	0.369	0.374	0.364	0.37	0.375
250	0.597	0.605	0.613	0.598	0.607	0.616
300	0.566	0.573	0.581	0.566	0.575	0.583
400	0.658	0.666	0.675	0.659	0.669	0.679
450	0.752	0.761	0.771	0.753	0.764	0.776