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#### 1 Thermal-physical properties of nanoparticle-seeded nitrate molten salts

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#### 8 Abstract

Molten salts have been used extensively as energy storing materials, however, their 9 thermophysical properties, such as specific heat capacity and thermal conductivity 10 have limited their applications. In this study, potassium nitrate and sodium-11 potassium nitrate (NaNO<sub>3</sub>:KNO<sub>3</sub> with 60:40 molar ratio) are used as the base salts 12 with different types of nanoparticles, which are iron oxide (Fe<sub>2</sub>O<sub>3</sub>), titanium dioxide 13 (TiO<sub>2</sub>) and copper oxide (CuO) over a wide range of temperatures up to 773 K. Laser 14 flash analysis is used to measure thermal diffusivity and dynamic scanning 15 calorimeter for specific heat (latent heat and melting temperature) of the molten salts 16 and nanosalts. The addition of Fe<sub>2</sub>O<sub>3</sub> into sodium-potassium nitrate salt increases 17 thermal diffusivity up to 50%. Moreover, the highest increase in the latent heat 18 reaches 14.45% at 1 wt. % CuO-binary nitrate salt. In addition, the total thermal 19 energy storage of nanosalt increases up to 6% including both of sensible and latent 20 heat. The formation of the interface layer between nanoparticles and salts could be 21 the reason behind this enhancement in sensible and latent heats. The morphology of 22 nanosalt measured by scanning electron microscopy showed a heterogeneous 23 dispersion of nanoparticles, including agglomerated areas that could be sometimes 24 responsible for the degradation of the performance. 25

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- 27

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

#### 31 **1. Introduction**

32

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, 40 most of the concentrated solar thermal power plants have been integrated with 41 42 sensible storage tanks, i.e., one hot tank and one cold tank to store the energy up to 663 K. Considering that the melting temperature of solar salt (NaNO<sub>3</sub>: KNO<sub>3</sub> with 43 60:40 molar ratios) is 505 K and for potassium nitrate (KNO<sub>3</sub>) is around 607 K, any of 44 them is a good choice for sensible heat storage (Chieruzzi et al., 2013, Chieruzzi et 45 al., 2015). Another advantage of molten salt is its higher energy density due to its 46 change phase with an approximately constant temperature giving a higher latent 47 heat, e.g. the latent heat of KNO<sub>3</sub> is around 91.61 kJ/kg and solar salt is 110.01 48 kJ/kg (Chieruzzi et al., 2013, Chieruzzi et al., 2015a). The use of molten salt as a 49 phase change material (PCM) for solar thermal applications has been investigated 50 by many researchers such as (Feldhoff et al., 2012, Laing et al., 2009, Pfleger et al., 51 2015, Luo et al. 2017). However, their limited thermo-physical properties such as 52 thermal conductivity, k, (in the range from 0.1-0.6 W/m. K (Kong et al., 2014)) and 53 specific heat capacity (cp) have prevented its wide applications. 54

Nanoparticles have been recently proposed to solve the problem of low cp/k values 55 of the nitrate molten salt. Many work have shown that dispersing nanoparticles to a 56 base salt (here called nano-salt) at low concentrations could increase the cp value, 57 but the results are inconclusive. There are different types of nitrate molten salt 58 59 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 60 hybrid silica-alumina nanoparticles on single nitrate salt (KNO<sub>3</sub>) salt. On the other 61 hand, Lasfargues et al. (2015) studied the effect of dispersing CuO and TiO<sub>2</sub> 62 63 nanoparticles on a binary nitrate (solar salt) and showed that the maximum increase

in cp was 10.48 % at 713 K for 0.1 wt. % CuO-solar salt. Moreover, different types of 64 nanoparticles, with different concentrations and size have been dispersed into a 65 binary nitrate solar salt to improve the cp of nanosalt (Andreu-Cabedo et al., 2014, 66 Chieruzzi et al., 2013, Dudda and Shin, 2013, Lu and Huang, 2013, Riazi et al., 67 2016, Schuller et al., 2015, Luo et al., 2017). Others investigated the effect of 68 dispersing silica, multi-walled carbon nanotubes, hybrid silica-alumina, Mica, gold 69 and alumina nanoparticles into nitrate solar salt (Andreu-Cabedo et al., 2014, 70 Chieruzzi et al., 2013, Dudda and Shin, 2013, Jung and Banerjee, 2011, Lu and 71 Huang, 2013, Niu et al., 2014, Riazi et al., 2016, Schuller et al., 2015). Some of their 72 results showed a higher increase in cp of nanosalt, which was dependent on the 73 types, sizes, and concentrations of nanoparticles used. Others showed different 74 results. This increase or decrease in the literature for the cp values of the nanosalt 75 samples could be related to different sources of the materials used either molten salt 76 (with different purities and suppliers) or the nanoparticles (different sources of the 77 purchased companies or supplied by the researchers themselves). In addition, 78 different preparation protocols and measurement conditions could also be the 79 reasons. In order to explain the enhancement in cp of nanosalt samples, the 80 literature indicated that interfaces were formed between the molten salt and 81 nanoparticles (Riazi et al., 2016, Luo et al., 2017). Another explanation is the 82 increment in the thermal resistance due to the effect of nanoparticles, which own 83 higher surface areas. However, the simple mixing model, which relays on higher cp 84 85 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. 86

Furthermore, extensive studies have been conducted on the enhancement of 87 thermal conductivity by adding nanoparticles, and a term 'nanofluid' was coined 88 (Buongiorno et al., 2009, Chol, 1995). However, common liquids or base fluids 89 generally are used in energy systems such as water, mineral oils and 90 polyalphaolefins lubricant (PAO). Very limited work has been conducted on molten 91 salts. For instance, thermal conductivity (k) of binary nitrate salt with Al<sub>2</sub>O<sub>3</sub> 92 nanoparticles was measured using the laser flash analysis (LFA), which showed that 93 adding nanoparticle decreased k in a temperature range between 338 K- 427 K 94 (Schuller et al., 2012). Additionally, Myers et al. (2016) measured the thermal 95 conductivity of the solid phase for three different types of nitrate molten salts (i.e., 96

potassium nitrate, sodium nitrate, and the potassium-sodium nitrate eutectic (54 97 weight percent potassium nitrate) with copper oxide (CuO) nanoparticles. Their 98 results showed an increment in thermal conductivity of the nanosalt, due to the 99 formation of nanostructures between the nanoparticles and the molten salt. On the 100 other hand. Shin (2011) studied the thermal conductivity when dispersing silica 101 nanoparticles (1 wt.%) in carbonate salt of lithium: potassium carbonate salt (Li<sub>2</sub>CO<sub>3</sub>: 102 K<sub>2</sub>CO<sub>3</sub> with 62:38 by molar ratio) up to 573 K. The results showed an enhancement 103 in k by 37%-47%, and it was believed that smaller size of nanoparticles increment 104 105 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 106 predict the enhancement correctly. 107

It shall be noted that both cp 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 773 K by taking into consideration of both solid phase and liquid phase.

In this work, we investigate experimentally the thermal-physical properties (k, cp) of 115 nanosalts to reveal the performance of nanoparticles. Different concentrations (0.5 116 wt. %, 1 wt. % and 1.5 wt. %) of  $Fe_2O_3$ , CuO and TiO<sub>2</sub> on single salt (KNO<sub>3</sub>) and 117 binary solar salt are studied. The thermal conductivity is determined by a laser flash 118 analysis device; the thermal diffusivity data, including both solid and liquid phases, 119 are measured up to 773 K. The cp, melting temperature, and heat of fusion are 120 measured by a dynamic scanning calorimeter (DSC) device. In addition, material 121 characterization is also reported by the scanning microscopy (SEM) and the DLS of 122 the nanoparticles size. 123

124

#### 125 2. Experiments

#### 126 **2.1 Material**

127 The base material used for this study is nitrate molten salt. Sodium nitrate (NaNO<sub>3</sub>) 128 was purchased from (FISHER, Loughborough, UK) with 98% purity and potassium

nitrate (KNO<sub>3</sub>) 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<sub>2</sub>O<sub>3</sub>) nanoparticles (20–40 nm particle size) purchased from (iolitec-USA company). The commercial titanium dioxide (TiO<sub>2</sub>) 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. Briefly, 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 423 K until the water was fully evaporated from the samples.

140

#### 141 2.2 Measurement

#### 142 i) Differential scanning calorimetry (DSC)

143 Specific heat capacity tests were performed on a Mettler Toledo DSC (Differential scanning calorimetry, DSC1, Mettler Toledo, Leicester, UK) for single salt, binary 144 salt, nanoparticles (Fe<sub>2</sub>O<sub>3</sub>, CuO, and TiO<sub>2</sub>) and nanosalt (with different 145 concentrations of nanoparticles, e.g. 0.5 wt. %, 1 wt. % and 1.5 wt. %), as well as the 146 latent heat, and T<sub>melting</sub> of molten salt and nanosalt. The sample was placed in the 147 crucible made of platinum, sample's weight was in the range of 30 mg to 35 mg 148 excluding the weight of the crucible in order to have enough materials to fill the pan 149 but not too much to cause the overflow issue during the measurements. The sample 150 was measured by an Ultra-microbalance Mettler Toledo balance (UMX2 Ultra-151 microbalance, Mettler Toledo, Leicester, UK) with an uncertainty of 0.1 µg. Sapphire 152 was used as a standard material with known specific heat capacity values in the 153 range of temperatures of the experiments. The heating method used was modelled 154 at a rate of 423 K for 10 min, ramped from 423 K to 723 K at a rate of 10 K/min, then 155 maintained isothermally for 10 min at 723 K and finally cooled down from 723 K to 156 423 K at -40 K/min. It shall be noted that the maximum temperature in case of KNO<sub>3</sub> 157 base material is less than 673 K. The standard error of the DSC device used for this 158 experiments is less than 2.29% and each sample tested for three times and they 159

show a repeatable and coincide results. The uncertainty of DSC measurements ofdifferent samples is shown in Tables (11-12).

162

#### 163 ii) Laser flash analysis (LFA)

Laser flash analysis (laser flash analysis LFA, model LFA 427, Netzsch Company, Selb, Germany) 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=cpxρxa (1)

180 where k is thermal conductivity W/(m. K), cp is specific heat capacity J/(g. K) 181 (measured in the DSC device),  $\rho$  is density in g/m<sup>3</sup> and a, is thermal diffusivity m<sup>2</sup>/s. 182 According to Janz et al. (1972), the density of binary nitrate solar salt can be 183 calculated as a function of temperature depending on the Equation (2).

184 
$$\rho = 2064.31 \cdot (4.76248 \times 10^{-4} \times T^2) \cdot (3.36495 \times 10^{-7} \times T^2)$$
 (2)

The range of temperatures in Equation (2) is from ambient temperature (298 K) up to773 K.

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

188 
$$\rho_{\text{nanosalt}} = (\phi_{\text{np}} \times \rho_{\text{np}}) + ((1-\phi_{\text{np}}) \times \rho_{\text{salt}})$$
(3)

where  $\varphi_{np}$  is concentration of nanoparticles,  $\rho_{nanosalt}$ ,  $\rho_{np}$  and  $\rho_{salt}$  are the density of 189 nanosalt, nanoparticles and solar salt, respectively. Additionally, the density of solar 190 salt is calculated from Equation (2) in the range of temperature from ambient 191 temperature (298 K) up to 773 K. The density of nanoparticles is assumed as a 192 constant value taken from the MSDS of the material. For instance, density of CuO 193 nanoparticles equals 6320 kg/m<sup>3</sup> and density of Fe<sub>2</sub>O<sub>3</sub> nanoparticles as 5240 kg/m<sup>3</sup>. 194 Therefore the density of nanosalt in Equation (3) is dependent on the same range of 195 temperatures in Equation (2). Additionally, the uncertainty of LFA diffusivity 196 measurements and calculated thermal conductivities of different samples are 197 considered. Each sample is investigated three times, a repeatable results are found 198 with a standard error less than 2.6% of thermal diffusivity measurements using the 199 LFA instrument. Additionally, Figure (17) below shows the plot of thermal 200 conductivity k vs temperatures, with the error bars of all the experiments data for 201 different materials (solar salt and nanosalt). Moreover, Tables (13-14) illustrated the 202 error of different tests for thermal diffusivity and thermal conductivity, respectively. 203 The errors of thermal conductivity are the accumulated errors from the cp and 204 thermal diffusivity measurements therefore they are higher than others (errors of cp 205 and thermal diffusivity). However, the error are within acceptable values with the 206 207 maximum value of 0.0496.

208

#### 209 iii) Scanning electron microscopy

Morphology of the samples is performed by a scanning electron microscopy (scanning electron microscopy, SEM, model Hitachi SU8230, Hitachi company, Berkshire, UK) 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.

215

#### 216 iv) Dynamic light scattering

Dynamic light scattering DLS (dynamic light scattering DLS, Malvern Zetasizer ZS, Malvern Zetasizer, Malvern, UK) 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). The maximum error analysis obtained was 3.4%.

226

#### 227 3. Results and discussions

#### 228 **3.1 Specific heat capacity (cp)**

The cp 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<sub>3</sub>:40 KNO<sub>3</sub>)) 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 233 of nanosalt. For solid phase results, 1.5 wt. % samples have larger increments in cp 234 235 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 cp value than 0.5 wt. % 236 or 1.5 wt.%. The slight difference might be due to the fact that different types of 237 nanoparticles could behave differently with solar salt as well the differences in the 238 preparation procedure between ours and the work of Chieruzzi et al. (2013). 239 Chieruzzi et al. (2013) used an ultrasonic bath for 100 minutes and evaporated the 240 water at 473 K, while in ours, a probe sonicator was used with 423 K to evaporate 241 the water. The results of single salt, KNO<sub>3</sub>, are highly depending on the type of 242 nanoparticles used, which is similar to what concluded by Chieruzzi et al. (2015a). 243
- Figure (3) shows the dispersion of nanoparticles in KNO<sub>3</sub> or binary salt increases the 244 specific heat capacity of nanosalt at high temperature. However, this increase 245 depends on the type of the base material, concentrations and type of nanoparticles. 246 Mostly, TiO<sub>2</sub>-nanosalt shows a decrease in the cp of nano-binary salt, as shown in 247 Table (3). In contrast, Lasfargues et al. (2015) indicated a positive effect of TiO<sub>2</sub>-248 nanosalt and CuO-nanosalt. This difference could be due to different preparation 249 methods. For single salt case, Table (4) demonstrates that in most cases, cp 250 increases with the concentrations of nanoparticles. According to Chieruzzi et al. 251

252 (2015a), 1 wt.% of silica-KNO<sub>3</sub> salt has higher cp than KNO<sub>3</sub> while 1 wt.% of 253 alumina-KNO<sub>3</sub> salt has lower cp than KNO<sub>3</sub>. This is in similar to the results we got for 254 1 wt. % nano-KNO<sub>3</sub> however, Chieruzzi et al. (2015a) did not study the effect of 255 another concentration (0.5 wt.%). The increment of cp of nanosalt in solid phase is 256 slightly higher than that of liquid phase especially for the case of solar salt as the 257 base material, which is in agreement to Chieruzzi et al. (2017).

From Tables (1-4), Fe<sub>2</sub>O<sub>3</sub> nanoparticles seem to be a good option to increase the cp of the solid/liquid phase of the base material (either binary solar salt or single KNO<sub>3</sub> salt) followed by CuO nanoparticles. TiO<sub>2</sub> nanoparticle gives a very small enhancement in cp of nanosalt or in most of the cases it decreases the cp value.

There are some models used to predict the improvement in the cp 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)

266

$$cp_{,nf} = \frac{\rho_{np} \, \phi_{vnp} \, cp_{,np} + \rho_{salt} \, \phi_{vsalt} \, cp_{,salt}}{\rho_{np} \, \phi_{vnp} + \rho_{salt} \, \phi_{vsalt}} \tag{4}$$

Where  $cp_{,nf}$ ,  $cp_{,np}$  and  $cp_{,salt}$  represent cp of nanosalt, nanoparticle, and salt.  $\emptyset v_{np}$  and  $\emptyset vsalt$  are the volume fraction of nanoparticles and salt, respectively.  $\rho_{np}$  and  $\rho_{salt}$  are the density of nanoparticle and salt, respectively.

The range of temperatures in Equation (4) depends on the tested material (nitrate salt), as shown below

- In case of binary solar salt (and nano-solar salt)
- 273 Solid phase (423 K < Temperature < Tonset)
- 274 Liquid phase (523 K < Temperature < 723 K)
- In case of KNO<sub>3</sub> salt (nano-KNO<sub>3</sub>)
- 276 Solid phase (473 K < Temperature < Tonset)
- Liquid phase (623 < Temperature < 668 K)

However, this model would not show any enhancement in cp unlike the most of the experimental results. This discrepancy is due to the lower value of cp of nanoparticles comparing to the salt. For instance, cp of  $Fe_2O_3$  nanoparticle is smaller than that of a molten salt. Even the fact that cp of nanoparticles is larger, e.g. cp of

Fe<sub>2</sub>O<sub>3</sub> around (0.9 J/g. K), which is slightly higher than its bulk material (0.84 J/g. K) 282 in the range of (423 K - 723 K) as indicated by Snow et al. (2010). For more 283 emphasis, we measured the cp of all nanoparticles used for the current experiments. 284 In this experiments, cp of  $Fe_2O_3$  equals to (0.9 J/g. K), cp of CuO equals to (0.59 J/g. 285 K) and cp of TiO<sub>2</sub> is (1.06 J/g. K). Furthermore, Zhou and Wang (2003) referred that 286 cp of bulk CuO was (0.54 J/ g. K). While the cp of CuO nanoparticles measured in 287 the current experiment equals to (0.59 J/g. K) which is slightly higher than cp of its 288 bulk material. However, cp values of Fe<sub>2</sub>O<sub>3</sub> / CuO/ TiO<sub>2</sub> nanoparticles are still lower 289 290 than that of a molten salt. This indicates that the increases in cp are not due to the nanoparticle effect. Therefore, the classical model cannot predict the enhancement 291 in cp of nanosalt where the cp of molten salt is larger than that of the nanoparticles 292 used in the respective work. Therefore, this model needs to expand and include the 293 other factors such as the interfacial area formed at the surface of the nanoparticle 294 and the molten salt or other forces between nanoparticles and so on. 295

Moreover, higher surface area owned by nanoparticles causes an increase in the 296 thermal resistance between nanoparticles and the molecules of the molten salt, 297 resulting in a rise in the interfacial interaction between them, which could increase 298 the cp of a nanosalt. Additionally, during the preparation of the nanosalt sample and 299 due to the sonication and evaporation stages, molten salt molecules could form a 300 compressed layer on the surface of nanoparticles. These interfacial layers could 301 have different properties to the base material alone. Furthermore, these layers could 302 higher c<sub>p</sub>, which may lead to increase the cp of nanosalt according to the Equation 303 (5) 304

305 
$$cp_{nf} = \frac{\rho_{np} \, \emptyset v_{np} \, cp_{np} + \rho_c \, \emptyset v_c \, cp_c + \rho_{salt} \, \emptyset v_{salt} \, cp_{salt}}{\rho_{np} \, \emptyset v_{np} + \rho_c \, \emptyset v_c + \rho_{salt} \, \emptyset v_{salt}}$$
(5)

In addition, the mass fraction of these layers depends on size and concentrations of nanoparticles. It is assumed that the cp of an interfacial layer has a significant effect on the overall cp of nanosalt when there is no agglomeration of nanoparticles. For instance, an assumed value of cp=6.2 J/ (g. K) (of the interfacial layer) would predict

the experimental well. Other possible reasons that could have the higher effect on 313 the cp of the nanosalt are the sedimentation of nanoparticles, the Van der Waals 314 force, and surface charge between the nanoparticles, as well the attractive force 315 among the nanoparticles. These forces would help the agglomerations of these 316 nanoparticles, which impact badly on their dispersion in the nanosalt samples. 317 Therefore, there is a need to find a proper surfactant that could work efficiently at this 318 high temperature condition, which could help to solve the dispersion and stability 319 issue of nanoparticles in the nanosalt samples. Furthermore, cp vs temperature with 320 321 the error bars of all the experiments data are plotted for different materials (solar salt and nanosalt or KNO<sub>3</sub> and nano-KNO<sub>3</sub>) for both solid phase and liquid phase in 322 Figures (13-16). 323

324

#### 325 **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 CuOsingle 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 331 due to the rearrangement of nanoparticles in the nanosalt sample. Therefore, 332 nanosalt needs higher heat to melt this interfacial layers, which maybe one of the 333 reasons for increasing latent heat. Additionally, clusters of nanoparticles could lead 334 to an increase in the latent heat as suggested by Chieruzzi et al. (2015a) and 335 Lasfargues et al. (2015). More heat is needed to melt these agglomerations. 336 However, this increasing or decreasing of latent heat of different nanosalts depends 337 on the places of the presence of nanoparticles in the nanosalt sample. One example 338 of the current experiments is the increases in latent heat due to the addition of 1 wt. 339 % CuO nanoparticles into the binary salt. From SEM result Figure (5), it is clearly 340 shown the agglomerations of 1 wt. % CuO-nanosalt and this sample have a higher 341 value of latent heat as the clustering required more heat to melt, resulting in an 342 increment in latent heat. Additionally, as shown in Figure (6) of the samples tested 343 by SEM results, there is a presence of the agglomerations and clustering of the 344

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 348 nanoparticles in samples. T<sub>melting</sub> is decreased with an addition of nanoparticles in all 349 cases. In particular, the T<sub>melting</sub> of binary salt is decreased by 5 K in cases of all 350 nanosalt samples, i.e T<sub>melting</sub> of binary salt is 503 K while T<sub>melting</sub> of all the nanosalt is 351 between 498 K and 499 K. Furthermore, similar behaviour is observed in the case of 352 KNO<sub>3</sub> base material with a decrement in T<sub>melting</sub> of KNO<sub>3</sub>-nanosalt samples by 1 K. 353 This is similar to the results from Gimenez-Gavarrell et al. (2015), Chieruzzi et al. 354 (2013), Lasfargues et al. (2015) and Chieruzzi et al. (2015a). According to 355 Lasfargues et al. (2015), T<sub>melting</sub> decrease in nanosalt relies on the method of heat 356 transfer over nanosalt sample and the size of clustering of theses nanoparticles. 357 Moreover, nanoparticles in the sample could work as nucleation agents, which bring 358 the phase change earlier in comparison with the base salt, (Gimenez-Gavarrell et al., 359 2015). Although this decrement in melting temperature is low, it still considers an 360 advantage because it means the phase change starts earlier. As a result, melting 361 time will reduce which improves the heat transfer in the storage system with the 362 support of enhanced conduction by nanoparticles. 363

Furthermore, the base material in case of binary salt does not reach the eutectic 364 point as the melting temperature happened in a range of temperature not in a single 365 point. Because of this, the mixture binary salt behaves as a non-pure mixture 366 showing that it needs more heat to be melted or freezing completely. According to 367 Kramer and Wilson (1980), the addition of 60% molar ratio of NaNO<sub>3</sub> would result in 368 a melting temperature of the binary salt in a temperature range 494 K >  $T_{melting}$  > 514 369 K. On the other hand, KNO<sub>3</sub> with a composition of 100% have one value for the 370 T<sub>melting</sub> 608 K as it is a pure single material (Kramer and Wilson, 1980), Figure (7). 371 However, KNO<sub>3</sub> material used in this experiment was 98% pure. From the DSC 372 measurements, T<sub>melting</sub> of KNO<sub>3</sub> was in a range caused by its non-purity. The purity of 373 the material has an impact that influence the behaviour of the salt and nanosalt 374 375 properties.

#### 377 **3.3 Total thermal energy storage (TES)**

TES is the total amount of energy of the storage system by considering both sensible 378 and latent heats. TES of the nanosalt samples is different from the TES of molten 379 salt alone. There is an increase or decrease in the TES as shown in Tables (5 and 380 6). From Table (5), 1 wt. % of Fe<sub>2</sub>O<sub>3</sub> binary salt and 0.5 wt. % of CuO binary salt 381 represent the maximum increment in TES this is due to accumulated increment of 382 energy. For instance, 1 wt.% of Fe<sub>2</sub>O<sub>3</sub> binary salt own a higher increase in latent heat 383 than other concentrations alongside with the advantages of sensible increment in 384 both solid and liquid phases. Although, 1 wt.% of CuO binary salt gave the maximum 385 increases in latent heat, it owns less increment in the sensible heat in comparison to 386 the 0.5 wt.%. Therefore, 0.5 wt. % of CuO binary salt gave a higher TES than that of 387 1 wt. % of CuO-binary salt. 388

It seems to be 0.5 wt. % in single salt (KNO<sub>3</sub>) shows higher increases with 5.26% for 0.5 wt. %  $Fe_2O_{3-}$  KNO<sub>3</sub> 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

$$q_{storage} = q_{sensible} + q_{latent} \tag{6}$$

394

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

395 
$$q_{storage} = \left[\int_{T_{ambient}}^{T_{melt}} cp * dT + \int_{T_{liquid}}^{T_{max.}} cp * dT\right] + q_{latent}$$
(8)

The range of temperatures in Equation (8) depend on the tested material (nitrate salt), as shown below

In case of binary solar salt (and nano-solar salt)

$$T_{ambient} = 423 \text{ K}, T_{max.} = 723 \text{ K},$$

- In case of KNO<sub>3</sub> salt (nano-KNO<sub>3</sub>)
- 401  $T_{ambient} = 473 \text{ K}, T_{max.} = 668 \text{ K}.$

In order to increase the storage capacity of the molten salt, an improvement in the thermophysical 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 406 of the storage system, which indicated a higher level of the solar thermal power plant 407 efficiency. According to Feldhoff et al. (2012), 9 hour is the storage time inside a two 408 tank (hot and cold sensible tanks) in the solar thermal plant. The working 409 temperature in the cold and hot tanks are 565 K and 659 K respectively. Dispersing 410 nanoparticles into the base material will improve the cp of the base material. 14% is 411 the efficiency of TES using molten salt alone, (Feldhoff et al., 2012), while with 412 nanosalt as a storage medium this efficiency will increases. For instance, at T= 659 413 K, sensible heat of solar salt is 220.744 J/kg. However, this sensible heat (220.744 414 J/kg) can be increased when dispersing 1.5 wt. % of CuO in solar salt to 233.044 415 J/kg. As a result, the sensible heat of the nano-binary salt increased by 5.6% in 416 comparison to solar salt only, which mean increasing the efficiency of the TES 417 system. Furthermore, at T=659 K, the value of cp of nanosalt (KNO<sub>3</sub>+ 1 wt. % Fe<sub>2</sub>O<sub>3</sub>) 418 equals to (1.253 J/kg. K) while cp of molten salt (KNO<sub>3</sub>) = 1.1615 J/kg. K. Therefore 419 the sensible heat increased by 7.88% with the presence of nanoparticles. This 420 indicates the big impact of nanoparticles on the efficiency of the storage system. 421

422

#### 423 **3.4 Thermal conductivity**

On the other hand, thermal conductivity (k) of binary solar salt, Fe<sub>2</sub>O<sub>3</sub>-nanosalt, and 424 CuO-nanosalt were tested. The current results demonstrate that nanoparticles have 425 a significant effect on the thermal conductivity of nanosalts both at low and high 426 temperatures. Increasing concentration of CuO, from 0.5 wt. % to 1.5 wt. %, has a 427 negative effect on thermal conductivity of nanosalt. In contrast, Fe<sub>2</sub>O<sub>3</sub> nanoparticles 428 always increase k of nanosalt except for the case 1 wt. % Fe<sub>2</sub>O<sub>3</sub>-nanosalt. It is 429 concluded that small concentrations of nanoparticles are preferred for increasing k of 430 431 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<sub>2</sub>O<sub>3</sub>) seems to be more 438 conductive material than CuO-nanosalt ones as shown in Figure (8). This show the 439 effect of nanoparticles types on the nanosalt samples. Moreover, the higher surface 440 area of nanoparticles could be one of the reasons that causes an increases in 441 thermal conductivity for the nanosalt samples. In addition, Fe<sub>2</sub>O<sub>3</sub> nanoparticles have 442 less particle size means higher surface area than CuO nanoparticles and this could 443 be one of the reasons behind the high improvements in Fe<sub>2</sub>O<sub>3</sub>-nanosalt than CuO-444 nanosalt samples (Yoo et al., 2007). According to Hwang et al. (2006), k of nanofluid 445 446 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 447 conductivity than a thermal conductivity of molten salt. The improvements in k of 448 nanosalt are largely affected by particles loading, the temperature range of the test, 449 nanoparticles size and stability of the sample. The results of thermal conductivity are 450 listed in Table (7). 451

Additionally, both nanoparticles (CuO or Fe<sub>2</sub>O<sub>3</sub>) 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<sub>2</sub>O<sub>3</sub>-nanosalt give better enhancement than 1 wt. % Fe<sub>2</sub>O<sub>3</sub>-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 459 nanoparticle (Mintsa et al., 2009). However, Figure (9) does show a certain 460 discrepancy as the results for 0.5 wt. % nanosalt is slightly above others 461 concentrations. According to (Saidur et al., 2011), conductivity increases with 462 463 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 464 surface charge of molten salt could play an important role on the result of k-Temp 465 result. Furthermore, Assael et al. (2005) mentioned that increases concentrations 466 467 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. 468 469 Although we tested Fe<sub>2</sub>O<sub>3</sub>-nanosalt and CuO-nanosalt, which are different from the 470 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 475 Hamilton-Crosser model as shown in Table (9). According to Hamilton-Crosser 476 model, the predicted value of k is not matching the measurement values. There are 477 some reasons that could cause this difference. One of these reasons is the 478 assumption of the sample in theoretical part compared to the actual behaviour of 479 sample during the experiments, as the equation assumed the same size of 480 nanoparticles are dispersed homogeneously along the sample, whereas in the 481 experiment, it is very difficult to achieve due to the applomeration and sedimentation 482 effects of nanoparticles in the nanosalt sample. This could be due to the effects of 483 different forces such as Van der Waals and gravity forces as both could lead to 484 sedimentation or agglomerations of nanoparticles. Therefore, the calculated values 485 cannot predict the enhancement in k unless consideration is given to all the affected 486 factors. 487

Furthermore, the heat transfer will be improved in case of nanosalt due to the 488 advantages of both cp, thermal conductivity. Due to the effect of natural convection 489 during the phase change any increase in specific heat capacity or thermal 490 conductivity will causes an increase in the heat transfer rate according to Equation 491 (9). From heat transfer correlation equation, Nusselt number (Nu) is related to 492 Rayleigh number (Ra) with some correlations constants, e.g. (Nu=C  $Ra^n$ ) as C and n 493 are constant depending on the case. In addition, any increases in the Nu will causes 494 495 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. 496 Therefore, any increases in Nu will give a higher heat transfer. 497

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

499

498

#### 500 **3.5 Comparison with other results**

501 In order to check the accuracy of our results data and to see how much the data we 502 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 503 been compared with other experiments literature data. The average value of cp of 504 the KNO<sub>3</sub> salt in Chieruzzi et al. (2015b) was reported to be (1.118 J/g. K) and in the 505 current work is (1.19 J/g. K) in the liquid phase. The average value of cp of the 506 binary solar salt (NaNO<sub>3</sub>:KNO<sub>3</sub> with 60:40 molar ratio) for the liquid phase equals to 507 1.315 J/g. K in the range 523 K -768 K (Jung and Banerjee, 2011) and cp has a 508 value equals to 1.38 J/g. K in the range 523 K-723 K by the work of (Xie et al., 509 2016). In the current work, cp of the binary solar salt for the liquid phase equals to 510 1.37 J/ (g. K) in the range 523 K -723 K. 511

In order to compare the latent heat values of the current study, first of all, KNO<sub>3</sub> salt 512 has 91.61 J/g and T<sub>onset</sub> is 608.7 K according to Chieruzzi et al. (2015b), in similarity, 513 the current study  $KNO_3$  salt has a value equals to 93.89 J/g with  $T_{onset}$  is 605.47 K. 514 Secondly, in the current study, the latent heat of solar salt equals to 107.03 J/g with 515 Tonset is 492.11 K likely to 110.01 J/g and Tonset is 492.88 K by (Chieruzzi et al., 516 2013). The standard error of the DSC device used for this work is less than 2.29% 517 and each sample is tested for three times, which show a repeatable and consistent 518 results. However, the small different in the results between the literature and the 519 current work are more related to the precision of the device used and the thermal 520 cycle of the test along with the samples used (each salt purchased from different 521 522 sources in literature papers and the current work) and the types of crucible used in DSC device may cause this little differences. 523

Additionally, the thermal conductivity of nitrate salt has been reported by (Serrano-López et al., 2013). At a range of temperature 523 K- 673 K, 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 cp (based on our experiments), the
thermal conductivity has been calculated, which is approximately matching with the
reported values.

536

#### 537 **4. Conclusion**

The specific heat capacity, T<sub>melting</sub>, latent heat and thermal conductivity of nitrate 538 molten salt were studied using differential scanning calorimetry and laser-flash 539 analysis, respectively. Different types of nanoparticles (0.5 wt. %, 1 wt. % and 1.5 wt. 540 %) were dispersed in single salt (KNO<sub>3</sub>) and binary salt (NaNO<sub>3</sub>:KNO<sub>3</sub> with 60:40 541 542 molar ratio) to achieve good properties. Using Fe<sub>2</sub>O<sub>3</sub> nanoparticles, we got a higher improvement of cp up to 11% and thermal conductivity up to 60%. In particular, the 543 544 latent heat was increased up to 15% with 1 wt. % CuO-binary salt. The storage energy was improved up to 6% with Fe<sub>2</sub>O<sub>3</sub> nanoparticles in comparison to solar salt 545 only, which mean an increase of the efficiency of the TES system. Moreover, an 546 increase in the sensible energy of nano-KNO<sub>3</sub> by 7.88% was observed. 547

In summary, the use of nanosalt to store thermal energy is a potentially promising technique due to the improved thermal conductivity and heat capacity values, which could not only increase the energy storage density but also accelerate the charging/discharging process.

552

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555

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REAM















Figure 13 Solid phase of cp of different types and concentrations of nanoparticles dispersed into nitrate salt (binary solar salt) represented with error bars.



Figure 14 Solid phase of cp of different types and concentrations of nanoparticles dispersed into nitrate salt (KNO<sub>3</sub>) represented with error bars.

- 825
- 826
- 827
- 828



Figure 15 liquid phase of cp of different types and concentrations of nanoparticles
 dispersed into nitrate salt (binary solar salt) represented with error bars.









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Figure 17 Thermal conductivity with error bars of solar salt and nanosalt samples

#### 841 Tables

#### 842

### Table 1 Solid phase of cp (in range 423 K-488 K) of different types and concentrations of nanoparticles dispersed inside solar salt (NaNO<sub>3</sub>:KNO<sub>3</sub> by 60:40 molar ratios).

Run	Solar salt		$+ \mathbf{F}\mathbf{e}_2\mathbf{O}_3$			+ CuO			+ TiO <sub>2</sub>	
	-	0.5	1	1.5	0.5	1 wt.%	1.5	0.5	1 wt.%	1.5
		wt.%	wt.%	wt.%	wt.%		wt.%	wt.%		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
%	-	9.8%	9.1 %	10.5%	7%	6.3%	7.7%	-5.6%	1.6%	1.4%
Increase										

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#### 846

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### Table 2 Solid phase of cp (in range 473 K-588 K) of different types and concentrationsof nanoparticles dispersed into KNO3 salt.

Run	KNO3 salt	+ <b>Fe</b>	+ <b>Fe</b> <sub>2</sub> <b>O</b> <sub>3</sub>		+ CuO		ГіO <sub>2</sub>	
	-	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	
%	-	6.68%	3.9%	7.05%	-3.25%	-9.09%	-2.97%	
Increase								

848

849

### Table 3 Liquid phase of cp (in range 523 K-723 K) of different types and concentrations of nanoparticles dispersed inside solar salt (NaNO<sub>3</sub>:KNO<sub>3</sub> by 60:40 molar ratios).

-         0.5 wt.%         1 wt.%         1.5 wt.%         0.5 wt.%         1 wt.%         1.5 wt.%         0.5 wt.%         1 wt.%         1.5 wt.%         1.5 wt.%         1 wt.%         1.5 wt.%         1 wt.%         1.5 wt.%         1.5 wt.%         1.5 wt.%         1 wt.%         1.5 wt.%         1.5 wt.%	Run	Solar salt		$+ Fe_2O_3$			+ CuO			$+ \operatorname{TiO}_2$		
wt.%         wt.%         wt.%         wt.%         wt.%         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		-	0.5	1 wt.%	1.5	0.5	1 wt.%	1.5	0.5	1 wt.%	1.5	
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			wt.%		wt.%	wt.%		wt.%	wt.%		wt.%	
Run 2         1.37         1.363         1.46         1.39         1.37         1.34         1.34         1.3         1.35         1.32	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	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	Average	1.37	1.394	1.4	1.383	1.377	1.343	1.38	1.25	1.34	1.17	
<b>%</b> - 1.75% 2.19% 0.95% 0.51% -1.97% 0.73% -8.76% -2.19% -14.6%	%	-	1.75%	2.19%	0.95%	0.51%	-1.97%	0.73%	-8.76%	-2.19%	-14.6%	
Increase	Increase											

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## Table 4 Liquid phase of cp (in range 623 K-668 K) of different types and concentrations of nanoparticles dispersed into KNO<sub>3</sub> salt

Run	KNO3 salt	+ <b>F</b>	e <sub>2</sub> O <sub>3</sub>	+ C	uO	+ TiO <sub>2</sub>		
	-	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
%	-	5.9%	7.56%	-0.25%	1.261%	2.69%	-1.93%
Increase							

#### Table 5 latent heat, onset temperature and total thermal energy storage capacity of different types and concentrations of nanoparticles dispersed in solar salt (NaNO<sub>3</sub>:KNO<sub>3</sub> by 60:40 molar ratios).

Material	Latent heat (k.I/kg)	Onset temperature	T <sub>onset</sub> differences	Total TES capacity	% TES
	(10,119)	(K)	(K)	(kJ/kg)	
Pure salt	107.03	492.11	-	466.83	-
Salt + 0.5 wt. % Fe <sub>2</sub> O <sub>3</sub>	109.27	489.22	2.89	482.27	3.31%
Salt + 1 wt. % Fe <sub>2</sub> O <sub>3</sub>	119.09	492	0.11	492.69	5.54%
Salt + 1.5 wt % Fe <sub>2</sub> O <sub>3</sub>	115.25	489.66	2.45	486.65	4.25%
Salt + 0.5 wt % CuO	118.08	489.01	3.1	485.28	3.95%
Salt + 1 wt % CuO	122.5	491.21	0.9	482.3	3.31%
Salt + 1.5 wt % CuO	110.32	490.05	2.06	478.72	2.55%
Salt + 0.5 wt % TiO <sub>2</sub>	95.41	489.33	2.78	426.41	-8.66%
Salt + 1 wt % TiO <sub>2</sub>	100.37	488.88	3.23	455.55	-2.42%
Salt + 1.5 wt % TiO <sub>2</sub>	89.65	486.31	5.8	410.65	-12.03%

Table 6 latent heat, onset temperature and total thermal energy storage capacity of different types and concentrations of nanoparticles dispersed inside KNO3 salt.

Material	Latent heat (kJ/kg)	Onset temperature (K)	T <sub>onset</sub> differences (K)	Total TES capacity (kJ/kg)	% TES
KNO <sub>3</sub> salt	93.89	605.47	0	331.47	-
KNO3 salt + 0.5 wt. % Fe2O3	96.41	605.12	0.35	348.91	5.26%
<b>KNO</b> <sub>3</sub> salt + 1 wt. % $Fe_2O_3$	94.08	598.53	6.94	345.28	4.17%
KNO3 salt + 0.5 wt % CuO	95.14	605.3	0.17	340.78	2.81%
KNO <sub>3</sub> salt + 1 wt % CuO	94.42	603.78	1.69	329.65	-0.55%
KNO <sub>3</sub> salt+ 0.5 wt % TiO <sub>2</sub>	91.02	600.56	4.91	321.02	-3.15%
KNO <sub>3</sub> salt+ 1 wt % TiO <sub>2</sub>	92.9	598.55	6.92	324.66	-2.05%

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

Т, К	Molten salt	Molten salt+ 0.5 wt.% Fe <sub>2</sub> O <sub>3</sub>	Molten salt+ 1 wt.% Fe <sub>2</sub> O <sub>3</sub>	Molten salt+ 1.5 wt.% Fe <sub>2</sub> O <sub>3</sub>	Molten salt+ 0.5 wt.% CuO	Molten salt+ 1 wt.% CuO	Molten salt+ 1.5 wt.% CuO
298	0.79	1.02	0.828	0.665	0.906	0.42	0.198
373	0.687	0.823	0.55	0.78	0.705	0.5	0.27
473	0.359	0.524	0.35	0.515	0.536	0.358	0.32
523	0.589	0.83	0.566	0.7	0.701	0.545	0.39
573	0.558	0.87	0.583	0.69	0.713	0.52	0.439
673	0.649	0.927	0.632	0.774	0.87	0.525	0.543
723	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, K	Molten salt+ 0.5 wt.% Fe <sub>2</sub> O <sub>3</sub>	Molten salt+ 1 wt.% Fe <sub>2</sub> O <sub>3</sub>	Molten salt+ 1.5 wt.% Fe <sub>2</sub> O <sub>3</sub>	Molten salt+ 0.5 wt.% CuO	Molten salt+ 1 wt.% CuO	Molten salt+ 1.5 wt.% CuO
298	29.1	4.81	-15.8	14.68	-46.84	-74.94
373	19.8	-19.94	13.54	2.62	-27.22	-60.7
473	45.96	-2.51	43.45	49.3	-0.28	-10.86
523	40.92	-3.9	18.85	19.02	-7.47	-33.79
573	55.91	4.48	23.66	27.78	-6.81	-21.33
673	42.84	-2.62	19.26	34.05	-19.11	-16.33
723	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, K	Molten salt+ 0.5 wt.% Fe <sub>2</sub> O <sub>3</sub>	Molten salt+ 1 wt.% Fe <sub>2</sub> O <sub>3</sub>	Molten salt+ 1.5 wt.% Fe <sub>2</sub> O <sub>3</sub>	Molten salt+ 0.5 wt.% CuO	Molten salt+ 1 wt.% CuO	Molten salt+ 1.5 wt.% CuO
	298	0.8	0.81	0.821	0.802	0.814	0.826
	373	0.696	0.705	0.714	0.697	0.708	0.718
	473	0.364	0.369	0.374	0.364	0.37	0.375

#### **Table 10 Nomenclature**

Symbol	Definition	Symbol	Definition
Fe <sub>2</sub> O <sub>3</sub>	Iron oxide nanoparticles	DSC	Differential scanning calorimetry
TiO <sub>2</sub>	Titanium dioxide	mg	Milligram
CuO	Copper oxide nanoparticles	min	Minute
NaNO <sub>3</sub>	Sodium nitrate salt	LFA	Laser flash analysis
KNO <sub>3</sub>	Potassium nitrate salt	m <sup>3</sup>	Cubic meter
K	Kelvin	ρ	Density, g/m <sup>3</sup>
KJ	Kilo Joule	a	Thermal diffusivity m <sup>2</sup> /s
kg	kilogram	Т	Temperature, K
ср	Specific heat capacity, (J/g. K)	$oldsymbol{arphi}_{np}$	Nanoparticle concentration, wt.%
k	Thermal conductivity, W/(m. K)	$ ho_{np}$	Nanoparticles density, g/ m <sup>3</sup>
PAO	polyalphaolefins lubricant.	$\rho_{salt}$	Salt density, g/ m <sup>3</sup>
Al <sub>2</sub> O <sub>3</sub>	Alumina nanoparticles	$\rho_c$	Compressed layer density, g/ m <sup>3</sup>
LFA	laser flash analysis	$ ho_{nanosalt}$	Nanosalt density, g/ m <sup>3</sup>
wt. %	Weight percent concentration	cp <sub>np</sub>	Specific heat capacity of nanoparticles, J/(g. K)
Li <sub>2</sub> CO <sub>3</sub>	lithium carbonate salt	cp <sub>salt</sub>	Specific heat capacity of salt, J/(g. K)
K <sub>2</sub> CO <sub>3</sub>	potassium carbonate salt	cp <sub>nf</sub>	Specific heat capacity of nanosalt, J/(g. K)
SEM	scanning electron microscopy	cp <sub>c</sub>	Specific heat capacity of compressed layer, J/(g. K)
DLS	Dynamic light scattering	Øv <sub>salt</sub>	Volume fraction of salt
nm	Nanometre	Øv <sub>np</sub>	Volume fraction of nanoparticles
ml	Millilitre	Øv <sub>c</sub>	Volume fraction of compressed layer
T <sub>melting</sub>	Melting temperature, K	TES	Total thermal energy
Ĵ			storage
<b>q</b> <sub>storage</sub>	Storage energy, J/kg	q <sub>sensible</sub>	Sensible energy, J/kg
q <sub>latent</sub>	Latent energy, J/kg	$\mathbf{q}_{sensible}$ in solid phase	Sensible energy of solid phase, J/kg
T <sub>ambent</sub>	Ambient temperature, K	$\mathbf{q}_{sensible}$ in liquid phase	Sensible energy of liquid phase, J/kg
T <sub>melt</sub>	Melting temperature, K	Nu	Nusselt number
T <sub>liquid</sub>	Liquid phase temperature, K	Ra	Rayleigh number
T <sub>max.</sub>	Maximum temperature, K	С	Constant
h	Heat transfer coefficient, W/(m <sup>2</sup> . K)	n	Constant parameter
Lc	characteristic length, m	β	Expansion coefficient, K <sup>-1</sup>
g	Gravity, m/sec <sup>2</sup>	μ	Viscosity, Pa.s
ΔΤ	Temperature difference, K	Tonset	Onset temperature, K

### Table 11 of error from DSC device for the cp measurements of solar salt and nano-solar salt

	Solar salt	+0.5 wt.% Fe <sub>2</sub> O <sub>3</sub>	+1 wt.% Fe <sub>2</sub> O <sub>3</sub>	+1.5 wt.% Fe <sub>2</sub> O <sub>3</sub>	+0.5 wt.% CuO	+1 wt.% CuO	+1.5 wt.% CuO	+0.5 wt.% TiO <sub>2</sub>	+1 wt.% TiO <sub>2</sub>	+1.5 wt.% TiO <sub>2</sub>
Solid phase	0.015	0.0202	0.0227	0.0229	0.0227	0.0228	0.0221	0.0173	0.0167	0.0212
Liquid phase	0.011	0.0086	0.0059	0.0089	0.0081	0.0122	0.0118	0.0024	0.0053	0.0181

### Table 12 of error from DSC device for the cp measurements of KNO<sub>3</sub> and nano-KNO<sub>3</sub> salt

	KNO3	+0.5 wt.% Fe <sub>2</sub> O <sub>3</sub>	+1 wt.% Fe <sub>2</sub> O <sub>3</sub>	+0.5 wt.% CuO	+1 wt.% CuO	+0.5 wt.% TiO <sub>2</sub>	+1 wt.% TiO <sub>2</sub>
Solid phase	0.0007	0.0029	0.0062	0.0049	0.006	0.0061	0.0059
Liquid phase	0.0056	0.0073	0.0092	0.0046	0.0094	0.0057	0.007

## Table 13 of error from LFA device for the diffusivity measurements of solar salt and nanosalts samples.

Solar salt	+0.5 wt.%	+1 wt.%	+1.5 wt.%	+0.5 wt.%	+1 wt.%	+1.5 wt.%
	Fe <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CuO	CuO	CuO
0.0223	0.0266	0.0181	0.0206	0.0217	0.0128	0.0145

#### 

Table 14 of error for the calculated	l thermal	conductivity	of solar	salt and	nanosalts
	sample	es.			

Solar salt	+0.5 wt.%	+1 wt.%	+1.5 wt.%	+0.5 wt.%	+1 wt.%	+1.5 wt.%
	Fe <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CuO	CuO	CuO
0.0485	0.0486	0.0453	0.0423	0.0496	0.0266	0.0429