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Effect of Al_2O_3 Dispersion on Enthalpy and Thermal Stability of Ternary Nitrate Eutectic Salt

Yathin Krishna[1,5], R. Saidur[2,3], M. Faizal[1*], Navid Aslfattahi [4], K.C. Ng[1], A. Arifutzzaman[2] and Shashikantha Karinka[6]

[1]*Taylors University, School of Engineering, Jalan Taylors, 47500 Subang Jaya, Selangor, Malaysia.*

[2]*Research Centre for Nano-Materials and Energy Technology (RCNMET), School of Science and Technology, Sunway University, No. 5, Jalan Universiti, Bandar Sunway, Petaling Jaya 47500, Selangor Darul Ehsan, Malaysia.*

[3]*Department of Engineering, Lancaster University, LA1 4YW, United Kingdom.*

[4]*Department of Mechanical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia.*

[5]*PA College of Engineering, Nadupadav, Mangalore, Karnataka, India 574153.*

[6]*NMAM Institute of Technology, Nitte, Karkala Taluk, Udupi District, Karnataka, India 574110.*

ABSTRACT

The system efficiency of concentrated solar power (CSP) was determined by using the working temperature of heat transfer fluid (HTF). Initially, organic HTFs were used for this purpose, which had a maximum operating temperature of 400 °C. However, it exhibits poor thermal storage property. The use of inorganic salts which are stable at high temperature (500~600 °C) can significantly increase the system efficiency. These salts can be used as energy storage materials as well. In this paper, nanocomposite comprising of ternary nitrate eutectic molten salt having pre-defined mass dispersed with Al_2O_3 nanoparticles of 0.1, 0.3, 0.5, and 1 wt.% was tested. The enthalpy and melting point measurements were performed using differential scanning calorimetry (DSC). Thermogravimetric analysis (TGA) was conducted to study the thermal stability of the eutectic salt and mass loss measurement at a temperature higher than 600 ^{0}C. The homogeneity and microstructure of synthesized molten salt were examined using scanning electron microscopy (SEM) imaging. The results showed that the melting point of eutectic salt was reduced by 23% with the addition of 1 wt.% of Al_2O_3 nanoparticles. By increasing the doping of Al_2O_3, the enthalpy of the mixture increased, indicating that the eutectic mixture could be used for thermal energy storage. SEM imaging analysis revealed the uniform dispersion of Al_2O_3 nanoparticles in the pure eutectic mixture. Based on the DSC and TGA results, both enthalpy and thermal stability of the molten salt have increased by the addition of Al_2O_3 nanoparticle, making it a potential candidate salt for CSP applications.

Keywords: Molten Salts, Thermal Energy Storage, Heat Transfer Fluid, Concentrated Solar Power.

1. INTRODUCTION

Due to its rapid economic growth, global energy consumption grew by 2.3% in 2018, which is twice the average growth rate since 2010. Although renewable energy sources proliferated in the past decade, it is not enough to meet the energy demands by the rapidly growing economy of the world. Fossil fuels being the major contributor for greenhouse gasses, of which coal alone is responsible for 0.3 ^{0}C of the 1 ^{0}C rise in the surface temperature of the planet [1]. Many

*Corresponding Author: *MohdFaizal.Fauzan@taylors.edu.my*

countries have implemented renewable energy sources like wind, solar, geothermal, ocean thermal, and biomass as the alternative to fossil fuels due to their advantages of being a sustainable and clean form of energy. Solar thermal energy is one of the cleanest forms of renewable energy sources. Solar thermal energy can become dispatchable if there is an integration of thermal energy storage (TES) to the present available CSP systems around the world [2].

CSP systems produce electricity by converting heat from concentrated solar radiation, reflected on to an absorber tube in which HTF is flowing. The HTF exchanges heat, to produce steam and finally electricity. The heat produced is also used for TES for utilising it during non-sunlight hours. In the CSP system, by increasing the working temperature of HTF, the cycle efficiency can be enhanced. It is found that molten salt can remain stable at a temperature of as high as 560 ^{0}C [3]. Thus, the research on adding nanoparticles into molten salts to enhance its thermophysical properties has drawn a greater number of researchers. Aslfattahi *et al.* investigated the effect on the thermophysical property of solar salt and by adding 5wt.% of MgO nanoparticles and found 7% enhancement in enthalpy compared to pure solar salt [4]. TES is classified into sensible heat, latent heat, and thermochemical storage systems. In sensible heat storage, the energy is stored or released by increasing or decreasing the temperature of the storage medium in a solid or liquid state [2]. Aslfattahi *et al.* doped MgO to solar salt and they found a decrease in melting point and enthalpy by 7% and 12.4% respectively [5]. Guerraiche *et al.* investigated the performance of the solar collector with water and solar salt as PCM and found that the daily thermal efficiency of the collector enhanced by 6.56 % compared to water as HTF for a day [6].

CSP plants require a large amount of HTF and TES materials. Therefore, it is essential to minimise the cost of these materials while improving their thermal storage and heat transfer properties. Selection of materials for TES and heat transfer is crucial, and many researchers have studied the preparation and characterisation of the HTF utilised in a solar thermal power plant [7]. Solar two Heliostat system used Solar salt ($NaNO_3$-KNO_3: 60-40 wt.%). Zhao *et al.* investigated the thermophysical properties of $NaNO_3$ and $Ca(NO_3)$ mixtures with different molar ratios. They found that the samples had the best thermal storage property when the molar ratio is 3:7 [8]. Roget *et al.* investigated a binary and ternary, molten salt $LiNO_3$-$NaNO_3$, and $LiNO_3$-KNO_3-$NaNO_3$ respectively and measured their cycle stability, enthalpy, and corrosion properties [9]. Initially, most of the power plants used synthetic oil as HTF but, because of their high price and low thermal stability at high temperature (>400^{0}C), recent power plants use inorganic molten salts.

The state-of-the-art molten salts like Solar salt, Hitec, and Hitec XL have been commercially used as TES in parabolic and power tower systems [10, 11]. Doping nanoparticles (less than 100nm) to HTF in volume concentration lower than 10% emerged as promising material utilised for heat transfer and storage[12]. Moreover, many researchers have shown that the addition of NPs into molten salt have enhanced their thermal capacity and thermal conductivity. To fulfil the necessity of HTF being used as both HTF and TES material Shin and Banerjee utilised inorganic molten salt (Li_2CO_3-K_2CO_3 62:38mol) as base fluid and doped silica Nanoparticles (NPs) into it. They suggested that cost might get cut off by 50% because of high operating temperature (high thermodynamic efficiency) attained by the combination of salt and NPs and hence less amount of storage material for the same thermal energy storage.

The major challenge faced with molten salt is its high freezing point, which leads to complications in the solar fields related to freezing protection. The synthetic oil which is currently used freezes at 15 ^{0}C, whereas ternary and binary molten salts freeze at 120 ^{0}C to 220 ^{0}C [13]. Whereas, very few articles have been published investigating inorganic phase change materials operating at high temperatures. Nitrate salts are given more importance because of their wide range of operating temperatures. Chen *et al.* investigated ($Ca(NO_3)_2$: $NaNO_3$: KNO_3 32:24:44 wt.%) and found that adding $Ca(NO_3)_2$ for solar salt the melting temperature is reduced to 80 ^{0}C and has better thermal storage performance. The composite salt decomposed at 750 ^{0}C. [14]. However, the article does not report the effect on thermophysical properties by the addition of NPs in it. According to the literature survey, very few articles are available, which discussed the thermal stability of molten salt based nanofluids.

This paper uses ($Ca(NO_3)_2$: $NaNO_3$: KNO_3 32:24:44, wt.%) as base molten salt and investigates its enthalpy, melting point and thermal stability by doping 0.1, 0.3, 0.5, and 1 wt.% of Al_2O_3 at high temperature (~800 ^{0}C). SEM images of the samples were examined to investigate the morphology of the eutectic composite mixture and dispersion of nanoparticles in the base molten salt.

2. MATERIALS AND METHODOLOGY

Samples of Molten salt were prepared and Al_2O_3 nanoparticles are doped to the solution of molten salt and water. The mixture is sonicated and dried in hotplate for evaporation of water. The resulted nano-enhanced molten salt is tested for enhancement in enthalpy using differential scanning calorimetry. A scanning electron microscope is utilised to justify the enhancement in enthalpy of the eutectic mixture, due to the addition of Al_2O_3 nanoparticles. The experimental setup is presented in Figure 1.

Calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$) and Potassium nitrate(KNO_3) were procured from Fisher Scientific chemicals company, and Sodium nitrate is obtained from R&M chemicals Co. Aluminium oxide (Al_2O_3) nanoparticles procurement is through US Research Nanomaterials Inc. The average particle size of Al_2O_3 is confirmed with the manufacturer to be 30nm. The method of preparation of molten salt is discussed as follows: To obtain 10g of molten salt-based nanofluid, 3.2168g of $Ca(NO_3)_2$ was measured using microbalance (Shimadzu, TX323L, UNIBLOC) and added to Borosilicate beaker (250ml), then 50g of ultrapure deionised (DI) water (Direct-Q UV, MERCK) was poured into the beaker. Beaker consisting of $Ca(NO_3)_2$ and DI water are stirred on a hotplate (RCT BASIC, IKA) at 700rpm at 50 ^{0}C to assure the uniform dissolving of sodium nitrate in DI water. The increase in Brownian motion in the solution will increase the solubility of the salt. After that, 2.3976 g of sodium nitrate ($NaNO_3$), was added to the beaker followed by stirring for 15min at 700 RPM. This was followed by the addition of 4.3756 g of potassium nitrate (KNO_3) and further stirring for 15min at 700 RPM, and hot plate temperature was maintained 50 ^{0}C. When all the salts are homogeneously dissolved in water 10mg of Al_2O_3 (0.1 wt.%) is added to the glass beaker, and the same method of stirring is repeated. Synthesised molten salt-based Aluminium oxide was sonicated for 90min using an ultrasonic probe sonicator (FS 1200N) with set on time of 7sec and set off time of 3 sec maintaining the power of sonicator at 55%. When there was a uniform distribution of solvents, the beaker is placed on a hotplate at 130 ^{0}C for 2 hours with stirring at 200rpm to evaporate water from the sample.

The beaker was partially covered with porous aluminium foil to avoid air bubble formation in the solution. Finally, the mixture was placed in a dry oven at 200 ^{0}C for 12 h to remove chemically bonded water molecules. The same protocol is used to synthesise pure molten salt, 0.3, 0.5, 1 wt.% of molten salt with Al_2O_3 nanoparticles. Since the $Ca(NO_3)_2$ present sample ~~is~~ absorbed more moisture, the sample was kept for 18 h in a vacuum oven at 100 millibar pressure and 150 ^{0}C before placing samples in aluminium crucibles for measurements of properties. Melting point and enthalpy of the sample was measured using differential scanning calorimetry (DSC-1000/C LINSEIS GERMANY). To obtain reliability in measurements, consistent methods of testing and characterisation was followed for all samples, which is essential while preparing molten salts based nanofluids. The heating rate for all samples was fixed ~~to~~ at10 ^{0}C/min from 30 ^{0}C to 550 ^{0}C. HDSC value is fixed at 25μV to obtain higher resolution, and the mass value was considered as 15mg for every measurement of samples. Thermal stability of the samples is performed using thermogravimetric analysis (TGA 4000, PerkinElmer) from 30 ^{0}C up to 800 ^{0}C. The heating rate of TGA was fixed at 10 ^{0}C/min under nitrogen gas (flow rate of 20 ml/min is maintained) to accomplish thermal stability evaluation and mass loss assessment. Alumina crucibles are used as pans for placing the samples in the weighing balance of TGA.

Dispersion and homogeneity of the eutectic salt with Al_2O_3 nanoparticles was checked using scanning electron microscopy (SEM) (VEGA3, TESCAN). Before SEM imaging, the molten salts are dried in a vacuum oven for one hour and then mounted on SEM to get samples free from moisture and to avoid chunk formation. Platinum ion coating was applied to the sample for SEM imaging in a fixed current of 3mA and 300 seconds using digital ion coater (COXEM Co, SPT-20).

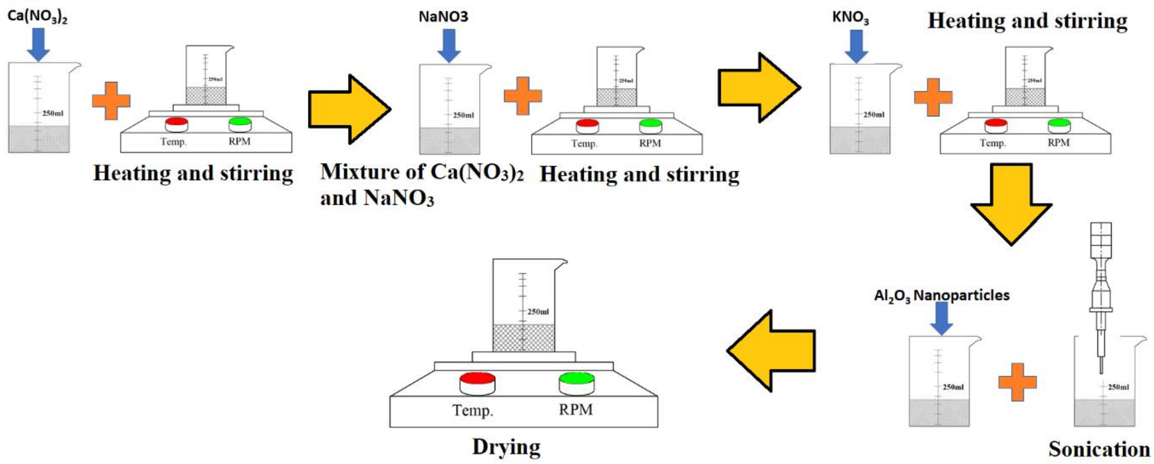


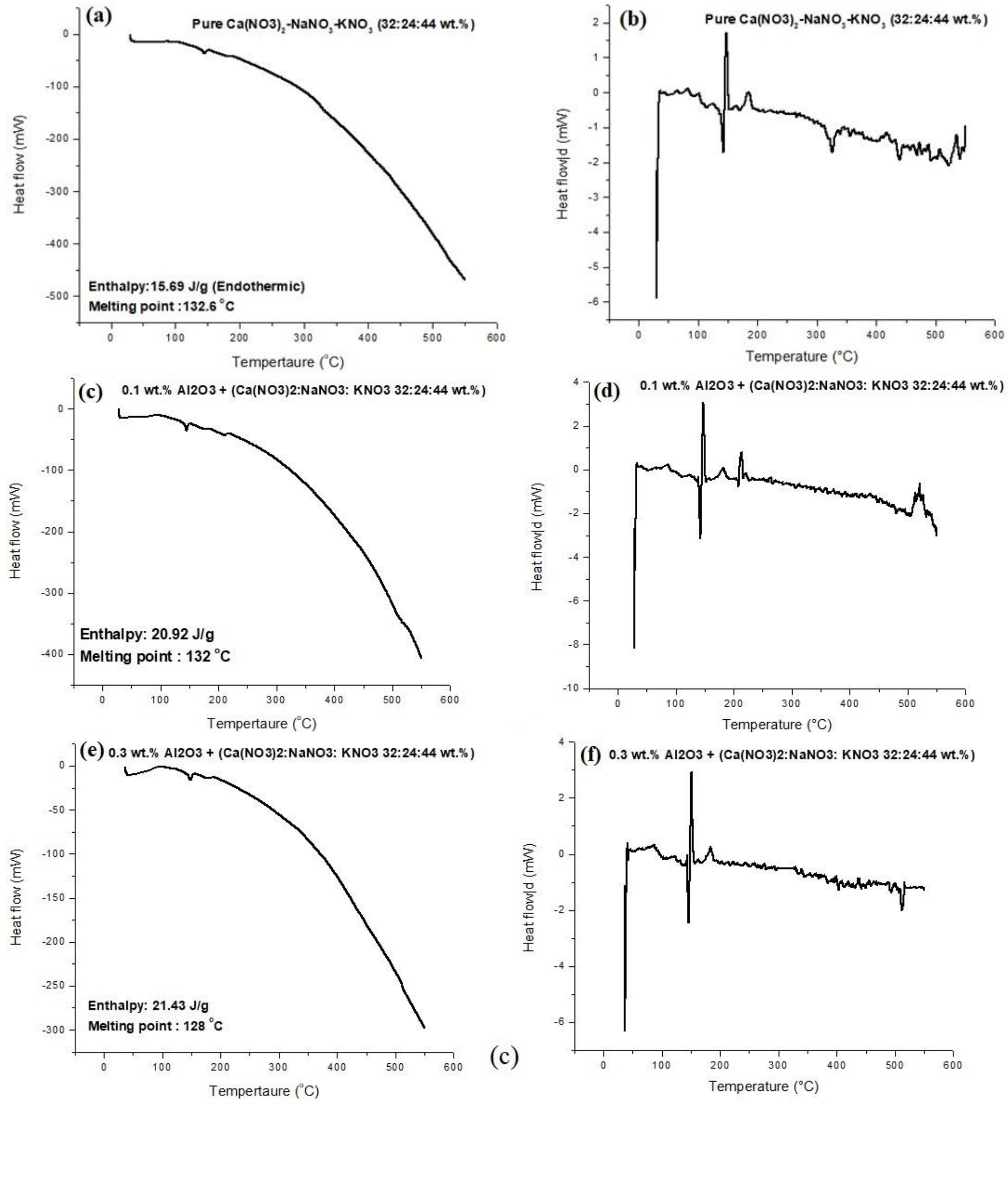
Figure 1. Schematic representation of the experimental setup.

3. RESULTS AND DISCUSSION

Enthalpy, melting point, and stability at high temperature are important parameters for molten salts to be used as heat transfer and thermal energy storage materials. Experimental results of enthalpy values and melting point values for pure eutectic salt and molten salt doped with nanoparticles obtained from DSC measurements, along with their derivative curves, are presented in Figure 2. Heating curves show a very narrow endothermic signal. The mixture exhibits glass-like behaviour in this region. Because of the glass-like nature of calcium nitrate present in the mixture, the heat of fusion is difficult to measure, the value of 15.69 J/g is obtained for pure eutectic mixture reflecting the glassy nature of $Ca(NO_3)_2$ present in the mixture, which is similar to the value obtained in the work of Iverson *et al.* from Sandia national laboratories containing calcium-based nitrate salt [15].

The experimental results show that enthalpy of fusion increased with increase in Al_2O_3 nanoparticles weight ratios. This may be due to the higher molecular density of the Al_2O_3 and its large surface area which lead to more significant intermolecular attraction in the ternary molten salt/Al_2O_3 composite, which resulted in improved latent heat storage capacity [16]. The measured value of the melting point for pure eutectic is found to be 132 ^{0}C, and the melting point got reduced by 0.5, 3.5, 5.7 and 23% with the addition of 0.1, 0.3, 0.5, and 1 wt.% of Al_2O_3 respectively to the pure eutectic. This may be due to the interaction of nanoparticles with molten salt making the ionic bonding of molten salt weaker, hence reducing its melting point. The derivative curves (Figure 2 (b, d, f, h, j)) were utilised to define unambiguously the key signal characteristics, such as minimum, maximum, as well as end and start points of thermal events, with uncertainties directly related to the actual noise of each signal.

The derivative curve of examined molten salt proves the melting point at 132.6 °C (point of reaction), as well as the melting-mediated crystallisation, starts at 139.2 C°. The post-transition (maximum peak) of the derivative curve was revealed at 148.8 °C. The acquired meting-mediated crystallisation temperatures for concentrations of 0.1 wt.%, 0.3 wt.%, 0.5 wt.%, and 1 wt.% were 142.1 ^{0}C, 143.1 ^{0}C, 137.7 ^{0}C, and 130.2 °C, respectively. The achieved sharp peaks prove that the accuracy of the reaction occurred ~~in~~ at melting point, including the transition of the crystallinity. It was clear that the minor signal noise observed from the derivative curves, ~~which~~ prove the accurate resolution of the utilised DSC (0.03 mW). Figure 3 shows the enthalpy and melting point temperature values with increase in a weight concentration of Al_2O_3. In this study, it is proved that by increasing the wt.% of Al_2O_3 nanoparticles in $Ca(NO_3)_2$: $NaNO_3$: KNO_3, the melting point of the mixture can be reduced.



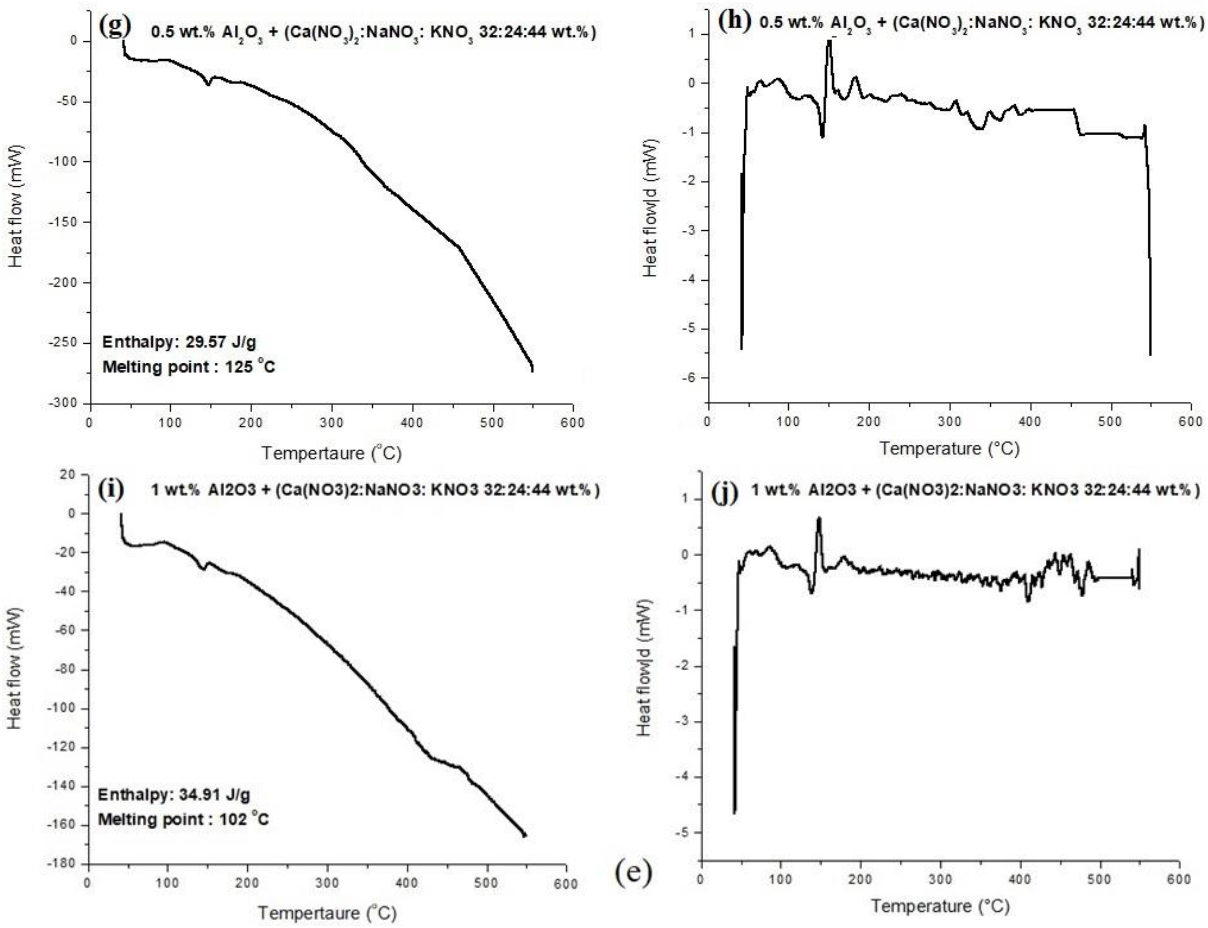


Figure 2. DSC (a), (c), (e), (g), (i) and derivative curve (b), (d), (f), (h), (j) of pure eutectic (a,b) , 0.1 wt.% Al_2O_3 (c,d), 0.3 wt.% Al2O3(e,f), 0.5 wt.% Al2O3 (i,j).

Thermal stability was investigated by thermogravimetric analysis (TGA), and the results are presented in Figure 4. The obtained data reveals that the degradation of the pure eutectic mixture starts at the temperature of 712.21 ^{0}C. In the figure, it is found that the sample decomposes completely at 718.45 ^{0}C, 726.48 ^{0}C, 730.26 ^{0}C, and 735.59 ^{0}C for 0.1 wt.%, 0.3 wt.%, 0.5 wt.%, and 1 wt.% doping of Al_2O_3 nanoparticles respectively. There was no decomposition found below 600 ^{0}C; this shows that the mixture is stable below 600 ^{0}C. The first decomposition took place between 650 ^{0}C and 736 ^{0}C for pure eutectic mixtures and eutectic salt doped with Al_2O_3 nanoparticles. It is also found from the experimental results that the stability of the mixture increases with increase in wt.% of Al_2O_3 nanoparticles, which are represented in Figure 4. The physical changes in the molecular structure are determined by the scanning electron microscope; the results are discussed in Figure 5 with magnifications between 474 to 5.02Kx and varying electron beam voltage, beam strength, and aperture size. There are no unique structures followed by pure samples but, due to the presence of $Ca(NO_3)_2$ which is tetrahydrate, the sample resulted in chunk formation, which is shown in Figure 5(a).

Most of the literature on molten salt-based nanofluids found chain-like or fractal-like structure (Shin, Tiznobaik, & Banerjee, 2014) in comparison with the pure eutectic mixture. The chain-like structure in Figure 5(e) is similar to the structure of conventional nanofluids, but it can be seen as more significant in number in the figure. This implies that base fluids may form the chain-like structure when doped with nanoparticles. The chain-like structure in Figure 5(c) and 5(d) are brighter than the base eutectic salt. This indicates that separated ionic compounds from the mixture later formed chain-like nanostructure. This can be explained by the phenomenon in which separated ionic compound integration with oxide nanoparticle of Al_2O_3.

When an oxide nanoparticle is doped into the molten salt containing three different ionic compounds, they may get attracted differently to a nanoparticle creating concentration gradient within the eutectic mixture towards the nanoparticles. This is because of the difference in electrostatic interaction between the ions of molten salt and the larger nanoparticle surface. When molten salts get separated, they crystallize and form a solid structure. Since the phenomenon occurs at the nanoscale, they start to crystallise on a nanoparticle surface growing away from the surface a forming chain-like structure. From the morphology study of the salt, the chain-like structures (SEM images) increased due to the presence of Al_2O_3 nanoparticles resulting in the reduction in the melting point and enhancing the thermal storage capacity of the salt.

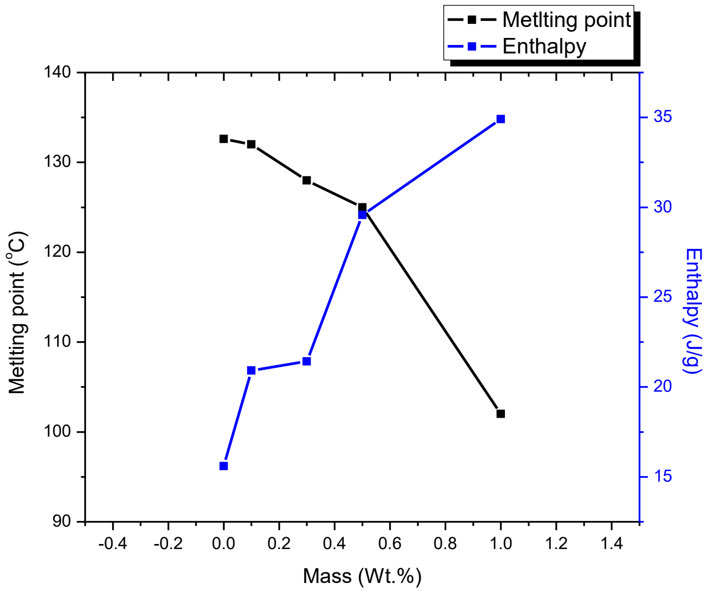


Figure 3. Enthalpy increase and decrease in melting point due to the increase in wt.% of Al_2O_3 nanoparticles.

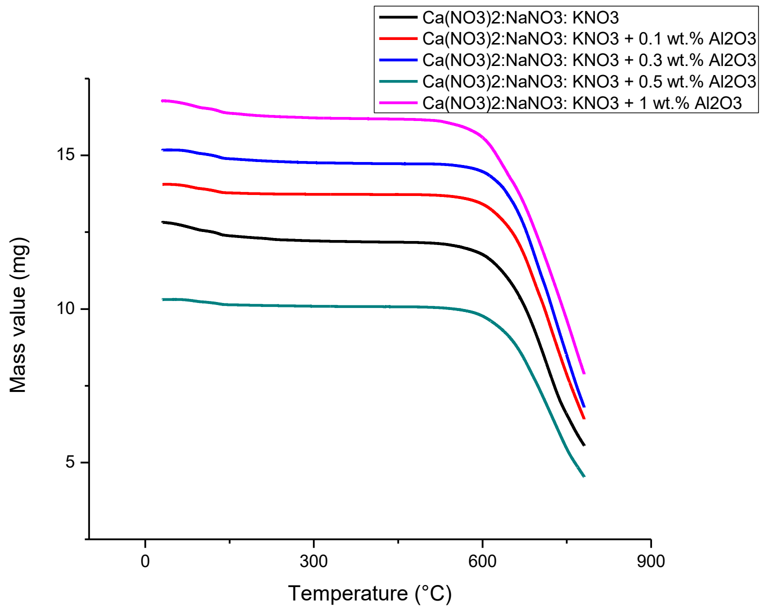


Figure 4. TGA curves for Pure eutectic and nanoparticles doped eutectic salt.

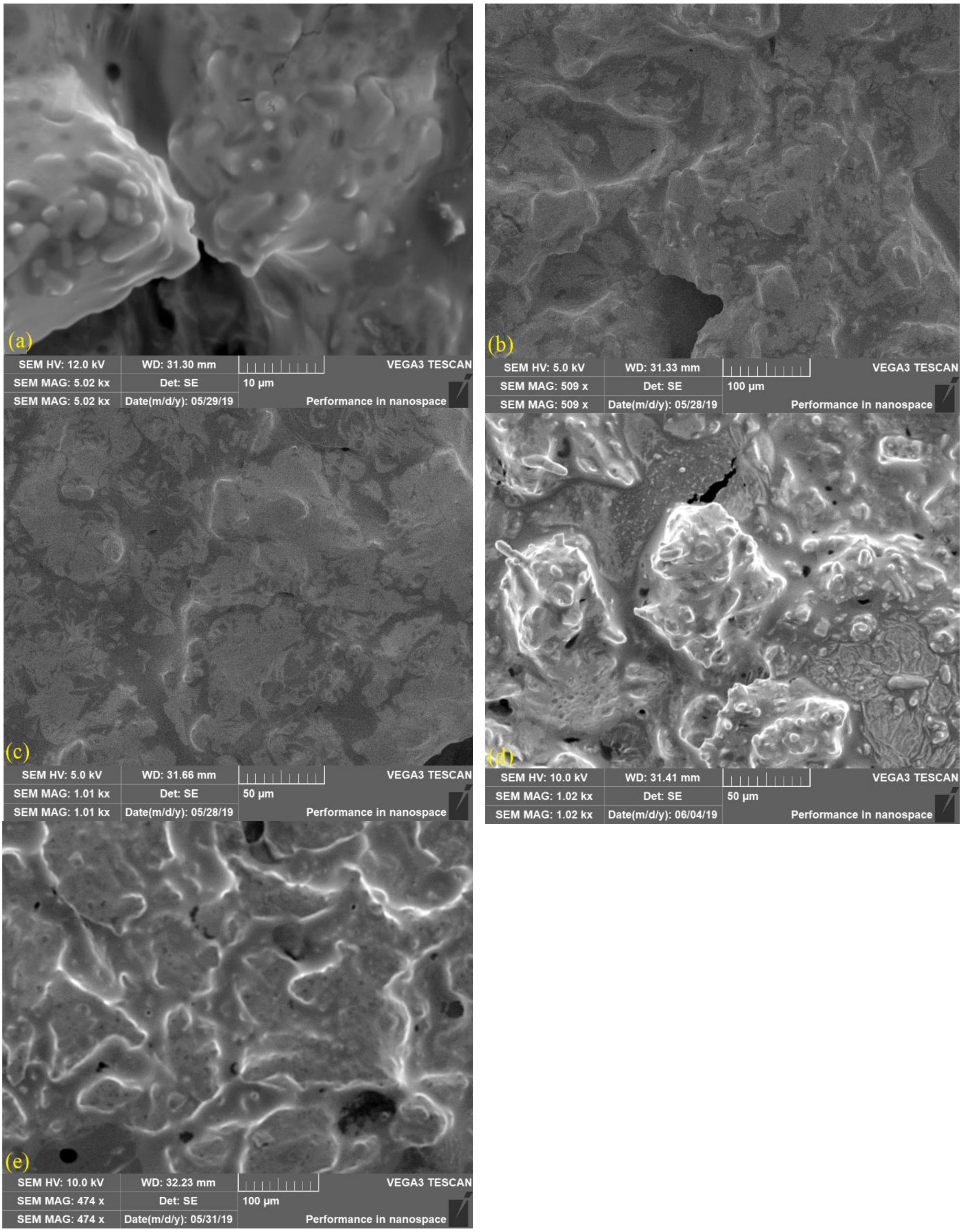


Figure 5. SEM (Scanning electron microscope images for (a) pure eutectic ternary salt, (b) eutectic salt +0.1 wt.% Al_2O_3, (c) eutectic salt +0.3 wt.% Al_2O_3, (d) eutectic salt +0.5 wt.% Al_2O_3, (e) eutectic salt +1 wt.% Al_2O_3.

4. CONCLUSION

In this study, investigation on enhancement in enthalpy, stability, and reduction in the melting point of ternary nitrate salt eutectic $Ca(NO_3)_2$-$NaNO_3$-KNO_3 (32:24:44 by weight) by doping Al_2O_3 nanoparticles (0.1, 0.3,0.5 and 1% by weight) is conducted. DSC method is used to measure the enthalpy and melting point of the composite salt. The experimental methods showed that the enthalpy of fusion increased by 122.5% by doping 1 wt.% of Al_2O_3 nanoparticles when compared to pure eutectic salt. This may be due to the increase in intermolecular forces between eutectic salt and Al_2O_3 nanoparticle. The reduction in melting point is found with the increase in nanoparticle concentration. A decrease in the melting point by 23% is found by doping 1wt.% of Al_2O_3 nanoparticles. This may be the result of a weak force of attraction between the ionic bonds of eutectic salts due to the doping of nanoparticles. TGA is used to determine the mass loss and stability at temperature >600 ^{0}C. It is found that the ternary nitrate molten salt is stable in the range of 650 ^{0}C and 750 ^{0}C. Due to the addition of nanoparticles with increasing wt.% the stability of the ternary eutectic salt increased. With 1wt.% alumina nanoparticles maximum stability of 735.59 ^{0}C is obtained. SEM imaging was used to obtain the material characterization analysis in which, the chain-like structures were observed with the increase in the concentration of Al_2O_3 nanoparticles showed good dispersion of the nanoparticles. The use of ternary nitrate salt having low melting point temperature serve potential benefits as HTF in concentrated solar power plants. Due to the lower melting point of these salts, expenses on freeze protection can be drastically reduced by improving the thermal efficiency of the plant. The enhancement in the enthalpy by loading the eutectic base mixture with Al_2O_3 nanoparticles could significantly reduce the cost of TES media in concentrated solar power plant, and therefore reducing the Levelized Cost of electricity produced by the concentrated solar power system. The future work is to investigate the specific heat, viscosity, and thermal conductivity for practical use in solar thermal systems.

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