Experimental Assessment of a Novel Eutectic Binary Molten Salt-based Hexagonal Boron Nitride nanocomposite as a Promising PCM with Enhanced Specific Heat Capacity

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ABSTRACT

In this study, novel nanocomposites containing the pre-defined mass ratio of binary molten salt (NaNO3-KNO3: 60-40 wt.%) dispersed with hexagonal boron nitride (hBN) nanoparticles with nominal size of 70 nm, were prepared through one-phase preparation method. Four different types of samples including pure binary molten salt and binary molten salt-based hBN nanocomposites with loading concentrations of 0.5, 1 and 1.5 wt.% were prepared. The proposed amount of sodium nitrate and potassium nitrate was added to certain amount of DI water, comprising with 0.5, 1 and 1.5 wt.% concentration of hBN nanoparticles. Scanning electronic microscopy (SEM) was conducted to evaluate the uniformity of the synthesized binary molten salt-based hBN nanocomposites. The SEM images revealed uniform dispersion of hexagonal boron nitride nanoparticles and fractal-like structures were observed clearly. Specific heat capacity \( c_p \) and melting temperature measurements were performed using a differential scanning calorimetry (DSC). The experimental achieved data for melting temperature proved that hexagonal boron nitride nanoparticles do not affect the melting temperature of the synthesized nanocomposites. The experimentally achieved data for the average \( c_p \) values of the binary molten salt in solid and liquid phases were 1.14 and 1.13 J/g K, respectively. While, the average \( c_p \) values for the binary molten salt-based hBN nanocomposite with the highest loading concentration of nanoparticles (1.5 wt.%) in solid and liquid phases were 2 and 3.17 J/g K, respectively. The measured average \( c_p \) value in the liquid phase for binary molten salt-based hBN nanocomposite with the highest loading concentration (1.5 wt.%) of nanoparticles revealed enhancement of \( \sim 180\% \) in comparison with pure binary molten salt. Thermal stability measurements expressed enhancement of thermal stability in binary molten salt induced with hBN nanoparticles. Binary molten salt-based hBN nanocomposite with loading concentration of 1.5 wt.% represented \( \sim 16\% \) enhancement in thermal stability over the binary molten salt.

Keywords: Molten salt; hBN; TES; Specific heat capacity; PCM

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1. Introduction

Over the past decades the world energy demand (fossil-based energy) has increased excessively due to the development of the globe economy and enhancement of 60% is anticipated in the energy demand by 2030 [1]. Renewable energy sources are promising replacements for petroleum resources. The significance of solar energy as a noticeable clean source of renewable energy is elucidated [2]. Solar energy is considered as eco-friendly abundant source of energy with expectation of supplying the 70% of the world energy demand by 2100 [3]. Capturing the solar radiation energy by using solar thermal systems depends on the efficient conversion of the thermal energy from sun. Accessibility to broad range of operation temperatures in solar thermal systems can be achieved by improvement of the efficient light-to-heat conversion process in high temperatures (above 300 °C).
In solar thermal systems, thermal energy storage (TES) medium and heat transfer fluids (HTFs), play dominant role, since the thermal storage and transporting the thermal energy occurs through these critical components. Improvement in the efficiency of the solar thermal systems can be obtained by using nanofluids as promising HTFs as effective medium to absorb the solar radiation consequently [4]. Conventional HTFs such as water and industrial oils with addition of nanoparticles as practical nanofluids have been studied extensively in terms of thermal storage and thermal conductivity [5]. However, the conventional HTFs are not applicable for several industrial processes and concentrated solar thermal systems that require the application of the fluids at higher temperatures due to the limitation in operation temperatures. Lower thermal stability up to 400 °C is another drawback of conventional nanofluids. These issues have attracted scientists to study new class of nanofluids to overcome the operation temperature limitations with improved efficiency in TES [6]. The enhancement of the theoretical thermodynamic efficiency (The Carnot efficiency) can be obtained from 50 to 65% by increasing the operation temperature from 300-400 °C to 560 °C [7]. Molten salts are capable candidates to be considered as working fluids at high temperatures (up to 600 °C) [8, 9]. High temperature stability of the molten salts can significantly improve the thermodynamic efficiency of the systems that utilize these TES materials as working fluid, especially in concentrated solar power (CSP) system the cost of the generated electricity will be reduced drastically [7]. Molten salts are naturally abundant and environmentally safe with lower price compared with conventional TES materials. However, poor thermophysical properties of the molten salts, particularly specific heat capacity ($c_p$ is less than 2 kJ/kg °C) is important challenge in terms of using molten salts as TES materials [8, 10]. Nanoparticles dispersion can enhance the specific heat capacity of the nanofluids when they are doped into a fluid mixture. Nelson et al. [11] reported 50% enhancement in the specific heat capacity of the polyalpapholefin (PAO)-based graphite nanofluids with loading concentration of 0.6 wt.%. In a research work conducted by Shin and Banerjee [12], they revealed 15% and 26% enhancement in the specific heat capacity of molten salt-based silica nanofluids with loading concentration of 1 wt.% of silica nanoparticles. Bridge et al. [13] represented enhancement of 30% in the specific heat capacity of the ionic liquid mixture-based Al$_2$O$_3$ nanofluids with loading concentration of less than 2.5 wt.%. Chieruzzi et al. [14] investigated the effects of different types of nanoparticles including Al$_2$O$_3$ and hybrid SiO$_2$-Al$_2$O$_3$ on the specific heat capacity of a binary molten salt (NaNO$_3$-KNO$_3$ 60:40 wt.%) in the loading concentrations of 0.5, 1 and 1.5 wt.%. They reported enhancement of 15 to 57% in the specific heat capacity (solid phase) and enhancement of 1 to 22% in the specific heat capacity (liquid phase). Dudda et al. [15] evaluated the effects of the nanoparticles on the specific heat capacity of a binary nitrate salt eutectic. They prepared binary molten salt-based SiO$_2$ nanoparticles in the loading concentration of 1 wt.% and with variety of the nanoparticles size consisting of 5, 10, 30 and 60 nm. They reported enhancements of 8, 12, 19 and 27% in the specific heat capacity for the nanoparticle sizes of 5, 10, 30 and 60 nm, respectively. Enhancement of 13% in specific heat capacity of a ternary nitrate salt doped with SiO$_2$ nanoparticles (loading concentration of 1 wt.%) was reported by Seo et al. [16]. Influence of the MWCNT and Au nanoparticles on the specific heat capacity of the binary molten salt was investigated by Liu et al. [17] extensively. They proved that application of MWCNT and Au nanoparticles to the binary molten salts can remarkably increase the specific heat capacity by a factor approaching 100%. However, In a research study conducted by Chierruzi et al. [18], they reported reduction of 16.4% in $c_p$ value for solar salt induced with 0.5 wt.% of SiO$_2$ nanoparticles in solid phase as well as 19.3% decrease in $c_p$ value in liquid phase. They proved the reduction of 14.4% and 15.6% in $c_p$ value for solar salt mixture with TiO$_2$ nanoparticles in the solid and liquid phases, respectively.

Hexagonal boron nitride (hBN) has attracted great attention of the scientists due to the high thermal conductivity, a large band gap (almost 5.9 eV) and low density with promising performance.
for the applications in thermal interface materials (TIMs) [19, 20]. Fang et al. [21] utilized hexagonal boron nitride as a filler in paraffin-based composite phase change materials. They proved that the inclusion of 10 wt.% hBN in the composite will cause enhancement in thermal conductivity by up to 60% and decrease in latent heat of fusion by less than 12%. Su et al. [22] introduced hexagonal boron nitride nanoparticles to the eutectic mixture of n-octadecane (ODE) and stearic acid (SA) as phase change materials to investigate the thermal properties of the composite PCM (CPCM). They reported that the thermal conductivity of the eutectic SA-ODE composite PCM with loading concentration of 10 wt.% of the hBN nanoparticles increased, whereas their latent heat of fusion decreased slightly.

The present study, investigates the effects of the hexagonal boron nitride nanoparticles in thermophysical properties of binary nitrate base molten salt. A conventional binary molten salt (NaNO₃-KNO₃: 60-40 wt.%) is utilized as a base fluid and the suspended nanoparticles are hBN nanoparticles in three different loading concentrations of 0.5, 1 and 1.5 wt.%. Investigation of the thermo-physical properties, including specific heat capacity (cₓ) and thermal durability of the eutectic binary molten salt-based hBN nanocomposite as PCMs is the first study to the best of authors’ knowledge. Well-dispersed binary molten salt-based hBN nanocomposite was synthesized in one-phase preparation method. The specific heat capacity (cₓ) and melting temperature of alkali binary molten salt with/without nanoparticles were measured using DSC. Measured specific heat capacity (cₓ) of the synthesized binary molten salt was compared with literature to verify the accuracy. The nanostructures of the synthesized binary molten salt with/without NPs were observed using SEM images.

2. Methodology
2.1 Materials

Potassium nitrate (KNO₃) with molar mass of 101.1 g/mol was procured from Merck company. Sodium nitrate (NaNO₃) with molar mass of 84.99 g/mol was supplied by R&M Chemicals company. Hexagonal boron nitride (hBN) nano powder with average particle size of 70 nm and purity of 99% procurement was through Lower Friction company.

2.2 Preparation of eutectic alkali binary molten salt-based hBN nanocomposites

Purity and the average particle size (70 nm) of the hexagonal boron nitride (hBN) was confirmed with the supplier [23]. The method of synthesizing the eutectic alkali binary molten salt is similar to that adopted by Shin and Banerjee [12] consisting of some modifications in the method. Initially, 6 g of sodium nitrate (NaNO₃) was measured by using microbalance (TX323L, UNIBLOC) and added to a glass beaker (of 100 ml volume). Then 50 ml of deionized (DI) water was added to the beaker, followed by stirring the solution on the hot plate (RCT BASIC, IKA) at 600 rpm. The temperature of hot plate was maintained at 50 °C to assure the uniform dissolving of the sodium nitrate in DI water. Afterward, 4 g of potassium nitrate (KNO₃) was added to the beaker, followed by stirring for 15 minutes at 600 rpm. Finally, the resultant solution was sonicated by using probe sonicator (FS-1200N) for 60 minutes with on/off time of 7/3 seconds and power of 70%. Synthesizing the binary molten salt-based hBN nanocomposite with different loading concentrations of nanoparticles consisting of 0.5, 1 and 1.5 wt.% was followed by adopting same protocol (one-phase preparation) for all samples to assure the uniform synthesis method. For synthesizing binary molten salt-based hBN nanocomposite with loading concentration of 0.5 wt.% of nanoparticles, 570 mg of NaNO₃ and 380 mg of KNO₃ were added to the beaker followed by addition of 50 mg of hBN. Then, 50 ml of DI water was added to the beaker, followed by stirring the solution on the hot plate at 600 rpm for 1 h in the
maintained temperature of 50 °C. Probe sonication was conducted for 60 minutes with on/off time of 7/3 seconds and power of 70%. Same method was conducted for preparation of binary molten salt-based hBN nanocomposite with loading concentrations of 1 and 1.5 wt.%. The utilized amount of NaNO₃ and KNO₃ for the synthesis of binary molten salt-based hBN nanocomposite with loading concentration of 1 wt.% was 540 and 360 mg respectively including the addition of 100 mg of hBN nanoparticles. Addition of 150 mg of hBN nanoparticles was considered for the binary molten salt-based hBN nanocomposite with loading concentration of 1.5 wt.%. The utilized amount of NaNO₃ and KNO₃ for the preparation of the mixture with loading concentration of 1.5 wt.% was 510 and 340 mg, respectively.

2.3 Characterization method

2.3.1 Morphology and elemental analysis of the binary molten salt-based hBN nanocomposites

Morphology and homogeneity of the synthesized alkali binary molten salt-based hBN phase change materials were checked through scanning electronic microscopy (VEGA3, TESCAN) and energy-dispersive x-ray spectroscopy (EDX, OXFORD INSTRUMENT). Digital Ion coater (COXEM Co, SPT-20) was utilized for Pt coating of the samples in the fixed current of 3 mA for 300 seconds for the purpose of SEM imaging.

2.3.2 Specific heat capacity (c_p) and melting temperature measurements

In this study, the specific heat capacity (c_p) and melting temperature measurements of the pure binary molten salt and alkali binary molten salt-based hBN nanocomposites are performed using a differential scanning calorimetry (DSC). DSC-8000 (Perkin Elmer, USA) is a double-furnace, power compensation DSC with greater sensitivity and accuracy instrument. The colorimetric and temperature accuracy of the above-mentioned DSC is considered as <±0.2% and ±0.05 °C, respectively. The measurements are conducted using aluminum crucibles of 40 µl. The temperature range for measurements is between 25-500 °C with the heating rate of 10 °C/min. The c_p values and melting temperature analysis was through Pyris software.

2.3.3 Thermal durability characterization

Thermogravimetric analysis (TGA) of the pure binary molten salt and alkali binary molten salt-based hBN nanocomposites are conducted using Perkin Elmer TGA 4000. A 180 µl alumina crucible (with temp. ~1750 °C) under an ultra-high pure nitrogen gas flow of 19.8 ml/min with the gas pressure of 2.6 bar is selected to examine the samples. The utilized heating rate is 10 °C/min for raising the temperature from 30 to 850 °C. About 12 mg of the synthesized samples is used for the decomposition temperature measurement. The obtained data is analyzed using Pyris Software.

3. Results

3.1 Morphological characterization of alkali binary molten salt-based hBN nanocomposites

Scanning electronic microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDX) were performed to evaluate the homogeneity and dispersion of nanoparticles in the synthesized alkali binary molten salt-based hBN nanocomposites and elemental analysis, respectively. The flat surface area of the nitrate materials and existence of some holes in the surface area can be observed form
Uniform structure of the synthesized binary molten salt and smooth corners can be observed from figure 1. b, which is in agreement with the morphology analysis performed by Huang et al. [24] for the same binary molten salt mixture. EDX spectroscopy analysis for the binary molten salt represented the existence of ~15.7, ~7.7, ~19.7 and ~57 weight% of sodium, potassium, nitrogen and oxygen, respectively. Atomic% value for sodium, potassium, nitrogen and oxygen was found ~11.7, ~3.3, ~24 and ~61, respectively. Energy-dispersive spectroscopy analysis for synthesized alkali binary molten salt-based hBN nanocomposite in three different loading concentrations of nanoparticles indicated good dispersion of nanoparticles in the matrix of molten salt. Figure 1. (c, d) show SEM images of synthesized binary molten salt-based hBN nanocomposites with loading concentration of 0.5 wt.% of nanoparticles. Chain-like structures due to the presence of hBN nanoparticles are evident in the achieved images. EDX results for nanocomposites with loading concentration of 0.5 wt.%, indicated the values of ~12.3, ~9.6, ~19.5, ~53.1 and ~5.3 weight% for sodium, potassium, nitrogen, oxygen and boron, respectively. The achieved weight% values of the components is in good agreement with the pre-defined mass fraction of utilized materials. The achieved atomic% values for sodium, potassium, nitrogen, oxygen and boron, were ~8.9, ~4.1, ~23.2, ~55.3 and ~8.52, respectively. The same trends of the weight% and atomic% was acquired for binary molten salt-based hBN nanocomposites, from figure 1. (e, f) and figure 1. (g, h) which represents uniformity of the synthesized samples. The acquired atomic% for boron in the binary molten salt-based hBN nanocomposites with loading concentrations of 1 and 1.5 wt.% was ~11.1 and ~14.5, respectively that proved the accuracy of the synthesized samples. Fractal-like structures due to the presence of hBN nanoparticles are clear in the SEM images [25].
Figure 1. Scanning electronic microscopy (SEM) images for (a, b) pure binary molten salt (c,d) synthesized binary molten salt-based hBN nanocomposite with loading concentration of 0.5 wt.% (e,f) synthesized binary molten salt-based hBN nanocomposite with loading concentration of 1 wt.% (g,h) synthesized binary molten salt-based hBN nanocomposite with loading concentration of 1.5 wt.%

3.2 Specific heat capacity ($c_p$) characterization

Specific heat capacity ($c_p$) and melting temperature of the samples were measured using differential scanning calorimetry (DSC-8000, Perkin Elmer, USA). DSC curves for the binary molten salt and binary molten salt-based hBN nanocomposites are shown in Figure 2. The results are represented as a function of temperature. To verify the accuracy of the measurement method, the melting temperature of the pure eutectic binary molten salt was measured and compared with literature data. The estimation of measurement uncertainty is 1.5%. The measured value for melting temperature of binary molten salt was ~225.6 °C which is in good agreement with the reported value in literature (222 °C) [10]. The acquired melting temperature for the binary molten salt-based hBN nanocomposites with concentrations of 0.5, 1 and 1.5 wt.% was ~225 °C, which revealed that hBN nanoparticles do not affect the melting temperature of the synthesized samples. Figure 2. (a) demonstrates the obtained DSC curve for $c_p$ measurement of the binary molten salt with the average value of 1.14 J/g K (solid phase) and 1.13 J/g K (liquid phase). The achieved $c_p$ value for the binary molten salt is in agreement with the literature [24]. The measurement uncertainty of $c_p$ value in the present work is in the range of ~1% which is based on the higher operating temperature (up to ~500 °C). The experimentally achieved data for the average $c_p$ value of the binary molten salt-based hBN nanocomposite with loading concentration of 0.5 wt.% proved ~42% (1.62 J/g K) and ~110% (2.38
J/g K) enhancements compared with the binary molten salt in the solid and liquid phases, respectively (Fig 2. b). In the present research work, enhancements of ~44% (1.64 J/g K) and ~75% (2 J/g K) were obtained for average $c_p$ value in the solid phase of binary molten salt-based hBN nanocomposites with loading concentrations of 1 and 1.5 wt.% (Fig 2. (c, d)). The achieved average $c_p$ value for the binary molten salt-based hBN nanocomposite with loading concentration of 1 wt.% in the liquid phase revealed ~118% enhancement over the binary molten salt without nanoparticles (Fig 2. c). The measured average $c_p$ value of the binary molten salt-based hBN nanocomposite with loading concentration of 1.5 wt.% in the liquid phase represented promising enhancement of ~180 % in comparison with pure binary molten salt (Fig 2. d).

![DSC curve for $c_p$ measurement of binary molten salt](image1)

**Figure 2.** DSC curve for $c_p$ measurements of (a) binary molten salt (b) binary molten salt-based hBN nanocomposite (0.5 wt.%) (c) binary molten salt-based hBN nanocomposite (1 wt.%) (d) binary molten salt-based hBN nanocomposite (1.5 wt.%)

In this study, the addition of hexagonal boron nitride to the binary molten salt proved promising enhancements in the average value of specific heat capacity ($c_p$). The highest enhancement was obtained for the binary molten salt-based hBN nanocomposite with loading concentration of 1.5 wt.%. In a general model proposed by Shin, Tiznobaik and Banerjee [26], the enhancement in the $c_p$ value is associated with fractal-like structures in MSBNFs which is composed of ions of the inorganic salts. The fractal-like structures of the synthesized samples in this study are clear from SEM images in Figure 1, which represent the reasoning phenomenon in agreement with the proposed model by Shin et al. [26] for the specific heat capacity ($c_p$) enhancement mechanism.
3.3 Thermal stability characterization

Thermogravimetric analysis (TGA) was employed to measure mass loss and thermal stability. Heating rate was fixed at 10 °C/min and the measurements were performed at temperature range of 30-850 °C. The experimentally achieved results (Fig 3.) indicated increment of thermal stability for nanocomposites in compare with pure binary molten salt. Figure 3. revealed that the thermal decomposition in the binary molten salt starts from ~60°C, while the beginning of decomposition temperatures for binary molten salt-based hBN nanocomposites with loading concentrations of 0.5, 1 and 1.5 wt.% are ~639, ~642 and ~652°C. Smooth decomposition performance can be observed from figure 3. with introduction of more amount of hBN nanoparticles into the binary molten salt. Binary molten salt-based hBN nanocomposite with loading concentration of 1.5 wt.% represented ~16% enhancement in thermal stability over the binary molten salt. The chain-like structures (SEM images) due to presence of hBN nanoparticles and interfacial interacting between binary molten salt molecules and induced nanoparticles might be the consequent of enhancement in thermal stability.

![Figure 3.](image)

**Figure 3.** Thermal stability measurements of binary molten salt and binary molten salt-based hBN nanocomposites in three different concentrations (a) TGA curve for all samples (b) enlarged area of beginning of decomposition in TGA curve

4. Conclusions

In conclusion, the eutectic alkali binary molten salt-based hBN phase change materials with loading concentrations of 0.5, 1 and 1.5 wt.% and pure eutectic binary molten salt were synthesized using one-phase method. The alkali binary molten salt with/without nanoparticles were mixed physically (stirring), followed by mixing by using probe sonicator. The resultant samples were in well-dispersed circumstances. Scanning electronic microscopy (SEM) and energy-dispersive x-ray (EDX) indicated chain-like structures in the resultant nanofluid and elemental analysis using EDX proved good dispersion of hexagonal boron nitride nanoparticles. Specific heat capacity ($c_p$) and melting temperature measurements were performed by using DSC. The experimentally achieved data for melting temperature of the pure binary molten salt and binary molten salt-based hBN nanocomposites with concentrations of 0.5, 1 and 1.5 wt.% was ~225 °C, which revealed that hBN nanoparticles do not affect the melting temperature of the synthesized samples. The average specific
heat capacity ($c_p$) was measured for binary molten salt with/without nanoparticles in solid and liquid phases. The experimentally achieved data for average $c_p$ values of the binary molten salt in solid and liquid phases were 1.14 and 1.13 J/g K, respectively. While, the average $c_p$ values for the binary molten salt-based hBN nanocomposites with the highest loading concentration of nanoparticles (1.5 wt.%) in solid and liquid phases were 2 and 3.17 J/g K, respectively. The measured average $c_p$ value of the binary molten salt-based hBN nanocomposite with loading concentration of 1.5 wt.% in the liquid phase represented promising enhancement of ~180% in comparison with pure binary molten salt. Thermal stability measurements expressed enhancement of thermal stability in binary molten salt induced with hBN nanoparticles. Binary molten salt-based hBN nanocomposite with loading concentration of 1.5 wt.% represented ~16% enhancement in thermal stability over the binary molten salt.

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