# Enhanced Thermal Performance of Nitrate Salts Composite with Compressed Expanded Graphite for Solar Thermal Energy Storage

Narender Kumar[1] iD, and Prodyut R. Chakraborty[1,*] iD

[1] Indian Institute of Technology Jodhpur, India

*Correspondence: Prodyut R. Chakraborty, pchakraborty@iitj.ac.in

**Abstract.** This research endeavors to enhance the performance of nitrate salts by incorporating expanded graphite (EG) to develop efficient and sustainable energy storage solutions tailored for medium-temperature range applications. The targeted domains for application encompass industrial processes, solar cooking, and solar power generation. In order to achieve this, a composite phase change material (PCM) is developed by saturating a compressed expanded graphite (CEG) matrix with molten PCM, and CEG is created by compressing EG to achieve the desired porosity. The primary goal is to leverage expanded graphite's high thermal conductivity to improve the composite PCM's overall heat transfer capabilities. The research involves characterizing the thermal properties of nitrate salts and the composite PCM, including measurements of melting and solidification temperatures, latent heat capacity, and thermal conductivity. These measurements are carried out using established experimental techniques to ensure accuracy and reliability. Notably, the study evaluates the thermo-physical properties of PCM-CEG composites across various temperature ranges of nitrate salts. The findings reveal a significant enhancement in thermal conductivity when expanded graphite is introduced into the composite. Differential scanning calorimetry (DSC) is used to assess the effective latent heat capacity and melting temperature of the PCM-CEG composite. It is observed that the effective latent heat capacity closely corresponds to the mass fraction of PCM in the composite, and the incorporation of graphite does not significantly impact the melting temperature of the PCM.

**Keywords:** Phase Change Materials, Expanded Graphite, Thermal Conductivity, Latent Heat

## 1. Introduction

The stability and reliability of energy systems that rely on solar energy are often compromised due to the time-dependent nature of solar energy availability. To address the time inconsistencies between energy demand and supply, thermal energy storage has emerged as a valuable method, facilitating the widespread utilization of solar energy [1, 2]. In this regard, latent thermal energy storage (LTES) utilizing phase change materials (PCMs) has gained significant attention due to its high energy storage density and minimal temperature variation [3]. Notably, molten salt has been recognized as a promising LTES medium for medium-temperature applications, typically 200 to 300°C, in solar thermal power systems [4]. Nitrates and their binary mixtures, known for their suitable melting points, cost-effectiveness, desirable phase-change temperature range, high heat capacity, and energy storage density, have been extensively utilized as PCMs for solar energy applications in the medium-temperature range of 200–300°C [5]. Tufen et al. [6] conducted a study employing the coaxial cylinder method to

measure the thermal conductivities of various molten salts, such as $NaNO_3$, $KNO_3$, and an equimolar mixture of $NaNO_3$–$KNO_3$. The experimental results indicated that the measured data for the salt mixtures aligned well with the calculated values obtained through a straightforward linear mixing law. Most pure inorganic salts exhibit low thermal conductivity, typically from 0.4 to 1.0 W/(mK), resulting in limited charging and discharging rates for LTES systems [7]. Various techniques have been adopted over the last few decades to enhance the thermal transport properties of PCMs. In recent years, researchers have explored the use of expanded graphite (EG), a modified form of graphite known for its layered structure and inter-layer space, as a promising heat transfer enhancement material for PCMs with inherently low thermal conductivity. Compared to metal promoters, EG offers several advantages, including higher thermal conductivity, compatibility with PCMs, stability, cost-effectiveness, and reduced density and weight [8]. Acem et al. [9] conducted a study to examine the thermal properties of cold-compressed nitrate/expanded graphite (EG) composites. Zhang et al. [10] conducted an experimental and theoretical analysis of the effectiveness of an LTES system. They examined the performance of a mixture of $NaNO_3$ and $KNO_3$ contained within an AISI 321 tube. In a study by Lu et al. [11], the thermo-physical properties of $KNO_3$-$LiNO_3$-$Ca(NO_3)_2$ with various proportions were investigated as PCMs for thermal energy storage. Additionally, EG was utilized as an additive to enhance the thermal conductivity of the PCMs. The investigations mentioned above suggest that the nitrate/expanded graphite (EG) composite PCMs possess significant thermo-physical properties that make them suitable for implementation as storage media in various solar applications. However, the existing knowledge regarding the thermal conductivity of these composite PCMs remains limited due to uncertainties associated with the available test methods. Considering a wide gap in the above literature, this study presents an experimental investigation focused on exploring the feasibility and performance of utilizing nitrate salts and compressed expanded graphite (CEG) as a composite material for medium-temperature thermal energy storage applications. The research aims to enhance the performance of nitrate salts with the addition of EG to develop efficient and sustainable energy storage solutions for medium-temperature range applications, such as industrial processes and solar power generation. The composite PCM is created by saturating the compressed expanded graphite matrix with molten PCM, and CEG is obtained by compressing expanded graphite (EG) for the required porosity. The primary objective is to leverage expanded graphite's high thermal conductivity to enhance the composite PCM's overall heat transfer capabilities. The characterization of the thermal properties involves measurements of the melting and solidification temperatures, latent heat capacity, and thermal conductivity of the nitrate salts and the composite PCM. These measurements are conducted using established experimental techniques, ensuring accuracy and reliability. The effective thermo-physical properties of PCM-CEG composites are experimentally measured across various temperature ranges of nitrate salts. Differential scanning calorimetry (DSC) assesses the PCM-CEG composite's effective latent heat capacity and melting temperature.

## 2. Preparation of material

In this study, Sodium Nitrate ($NaNO_3$), Solar Salt (60% $NaNO_3$ + 40% $KNO_3$), and Hitec Salt (7% $NaNO_3$+53% $KNO_3$+40% $NaNo_2$) with different melting ranges are considered as phase change materials. The solar salt and Hitec salt preparation involved a static mixed melting approach. To ensure accurate measurements, a 20 g mass of the prepared phase change material (PCM) was used, with the components weighed in a 60:40 ratio after being dried in an oven at 110 ℃ for 24 hours. Subsequently, the blended salt mixture was placed into a stainless-steel crucible within a muffle furnace, where it was gradually heated from room temperature to 370 ℃ at a rate of 10 ℃/min and held at 370 ℃ for 2 hours. Following this, the furnace was allowed to cool to room temperature, and the material was further dried in an oven at 110 ℃ for an additional 24 hours. The same procedure with the earlier mentioned combination is considered for the Hitec salt preparation. Expandable graphite is procured from Sigma Aldrich with mesh 50 in the second part. Expanded graphite, also known as exfoliated graphite or graphite intercalation compound (GIC), is prepared by subjecting expandable

graphite (which is treated with the sulphuric acid and oxidizing agent) to a high-temperature treatment that causes it to expand and separate into layers. The process typically involves heating the expandable graphite to 900-1000 ℃ for 60 seconds. This causes the intercalation compounds between the graphite layers to expand, resulting in the separation of these layers and the formation of expanded graphite. The expanded graphite material has a highly porous and vermicular structure, which imparts desirable properties such as high thermal and electrical conductivity, low density, and chemical resistance. Expanded graphite (EG) exhibits an exceptionally high specific surface area (surface area per unit volume), synonymous with a very high porosity level within its structure. Consequently, the transition from GIC to EG results in a substantial volumetric expansion, typically magnifying its bulk volume by a factor of around 300 times compared to that of GIC, as shown in *Figure 1*.



*Figure 1. The exfoliation process of Graphite*

Then, this expanded graphite powder is poured into a cylindrical mold with a 25mm diameter and then pressed to obtain the porous graphite matrix with 60% compression by volume. Upon compression, EG's unique vermicular (worm-like) structure enables natural mechanical interlocking within the framework. This phenomenon culminates in creating a form-stable foam known as compressed expanded graphite (CEG), characterized by its self-sustaining nature and devoid of the necessity for supplementary binding agents. Once generated, the CEG foam is utilized by soaking it with PCM to occupy the pores within the graphite matrix effectively. This results in a composite PCM (CPCM) having highly enhanced thermal conductivity. During the soaking process, the molten PCM permeates the graphite matrix due to capillary forces [12]. The porous structure within the CEG matrix absorbs and retains a substantial quantity of PCM, such as (*Figure 2*). The entire procedure for creating this excellent thermal conductivity enhancer is cost-effective, simpler, and more lightweight than other contemporary options, such as metal foam.
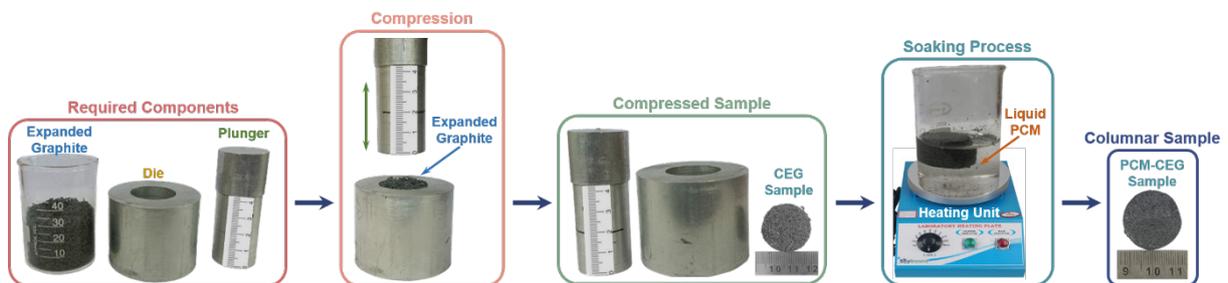


*Figure 2. Preparation of PCM-CEG Composite*

## 2.1 Characterization and measurement techniques

Scanning Electron Microscopy (SEM) uses the SEM-Carl Zeiss instrument model SEM-EVO 18 and EDS-51-ADDD-0048 to examine the morphology and structure of both pure EG and the PCM composite. The sample rack is positioned appropriately within the instrument during

the testing process. Vacuum treatment is initially carried out, followed by sequential selection and scanning photography for each sample individually.

DSC Differential Scanning Calorimetry), a Perkin Elmer instrument (Model: DSC-4000), was employed to determine the sample's phase change temperature and latent heat. Temperature measurements had an accuracy of less than ±0.1 °C, and calorimetric measurements were accurate to within ±1%. The sample quantity for each test was controlled to be between 5 to 10 mg. Three consecutive measurements were conducted on the same sample. The second or third measurement was typically chosen if these three measurements exhibited relatively stable and minimally deviating results. The testing conditions for the prepared phase change thermal storage materials were defined as follows: temperature range: 50 to 300 °C; heating rate: 10 °C/min; and a protective atmosphere of $N_2$.

The thermal conductivity of pure PCM $(k_{pcm})$ and the effective thermal conductivity of the composite PCMs (PCM-CEG composites) $(k_{eff})$ at room temperature is measured using a Hot Disk Thermal Constant Analyzer (Hot Disk TPS2500s). This analyzer employs the transient plane source (TPS) method to capture the thermal transport behavior of the sample. A probe with a radius of $3.189\ mm$ is used for all the experiments, and the thermal conductivity is estimated by inserting it between two identical pieces of the same composite sample. To ensure that the probe makes close and even contact with the samples so that the contact resistance is minimized to the best possible extent, the surfaces of the specimens are polished before the experiments. The accuracy of the thermal conductivity measurement from Hot Disk TPS2500s is within $\pm3\%$. The probe contains two identical insulating layers of thin polyimide (KaptonTM) films with a thickness of about $25\ \mu m$ and an electrically conductive pattern of thin nickel foil with a thickness of about $30\ \mu m$ in the form of a double spiral between the two layers (hot disc). We performed three measurements for each sample to ensure reliability, and the average value from these three measurements is considered. The thin nickel foil functions as a heat source as well as a temperature sensor. The samples with a diameter of $25\ mm$ and a thickness of $25\ mm$ are considered for the measurements. The transient plane source (TPS) method utilizes a thermal-conduction model to estimate the values of thermal conductivity ($k$ with unit $W/mK$). This method assumes a flat heat source within an infinite material [13,14].

## 3. Results and Discussion

This section presents the primary outcomes of our experimental inquiries, categorized into three main groups: structural analysis, phase change behaviour analysis, and analysis of effective thermal conductivity. It is important to emphasize that structural analysis is predominantly qualitative and observational. We analyzed the SEM images to verify the presence of PCM within the pores of the CEG foam during the soaking procedure. In contrast, the remaining two analyses, which center on the thermo-physical properties of the composite PCM (CPCM), provide quantitative insights into how the compression ratio of CEG impacts the thermos-physical attributes of CPCM.

### 3.1 Morphology Structure of PCM and Composite

The micrographs of porous expanded graphite and the heterogeneous composite phase change materials are shown in *Figure 3*. *Figure 3(a)* shows the microscopic morphology of EG with 500 and 3000 times magnification, respectively. The morphology of the EG is a vermicular network composed of graphite flakes and very highly porous in nature, which is consistent with the literature. There are a large number of micro-pores in it, which also enables EG to absorb PCM better. *Figure 3(b)* shows the microstructure of composite phase change materials after 1000 times magnification for solar salt and Hitec salt. It can be clearly observed that the fine-grained nitrate salt particles are absorbed into the pores by EG. Due to the rich pore structure of EG, under the joint action of pore capillary force and surface tension, the mixed molten salt can better penetrate into the porous skeleton structure of EG. From *Figure 3(b)*, we observe the

near-perfect filling of CEG pores with paraffin. However, some traces of air pockets are also found in the SEM image. With a 60 % compression ratio (CR) by volume, the porosity calculation comes out to be 75.6 % by liquid displacement method. The density and PCM mass fraction of pure and composite PCM are calculated by mass and volume measurements, shown in *Table 1*.
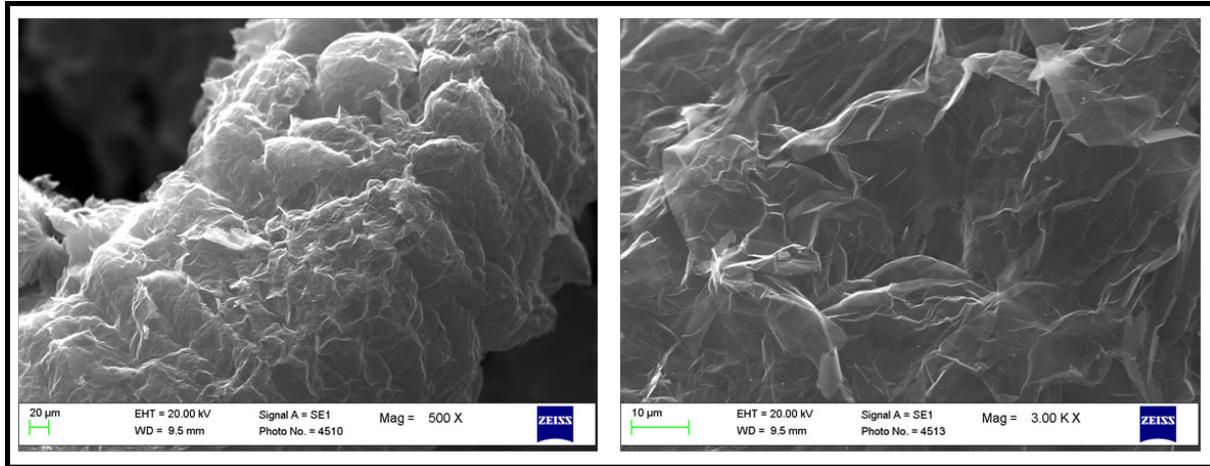


*(a)*
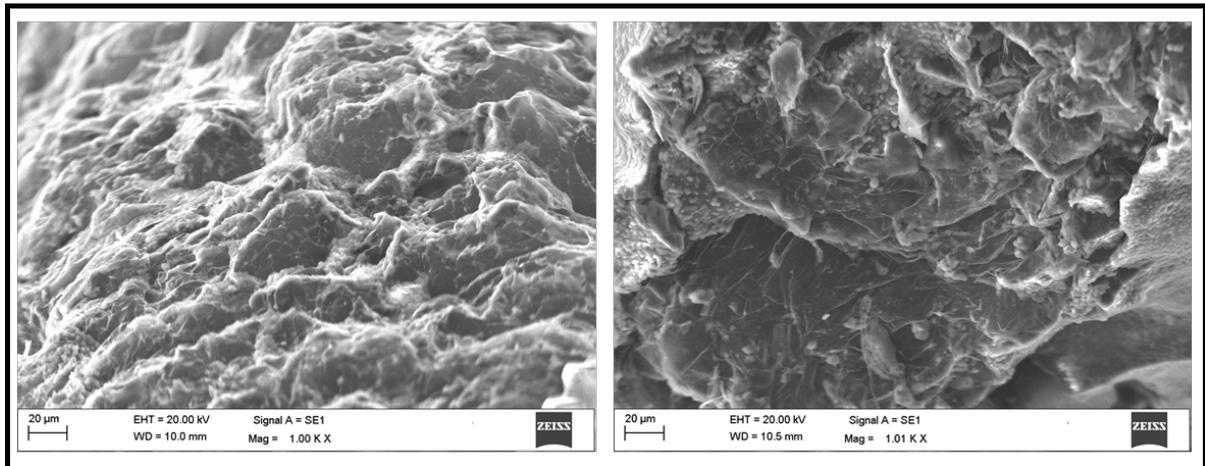


*(b)*

**Figure 3**. *SEM Images of (a) EG at 500 & 3000 Magnification & (b) PCM-CEG Composite*

## 3.2 Phase change behavior of PCM and composite

The phase change behavior of PCM and PCM-CEG composite is depicted from the DSC curve during melting, as shown in *Figure 4* for pure and prepared PCM-CEG composite. The positive heat flow curve shows the heat absorption by PCM during melting. The curve shows two peaks: a sharp, principal peak relating to the solid-to-liquid phase transition, which is the primary source of latent heat, and a small peak due to the solid-to-solid phase transition.

It is evident that both materials show similar thermal characteristics, as graphite and PCM do not undergo any chemical reactions. The melting temperature of various composites exhibits negligible difference when compared to the melting point of pure phase change material (PCM), as illustrated in *Figure 4*. The observed variation can be attributed to the existence of trace contaminants or the inclusion of expanded graphite.

The DSC curve for the PCM-CEG composite displayed a distinct melting peak, signifying the transition from a solid to a liquid phase within the material. To determine the latent heat of the PCM-CEG composite, we employed the baseline method, which involved drawing a tangent baseline along the steepest section of the curve and then calculating the area between this baseline and the curve using Origin 2018b. *Table 1* shows the melting temperature and latent heat storage values for pure PCM and composite PCMs. The melting temperature values for pure and composite PCMs are very close, and the salient change can be due to the impurities with the addition of expanded graphite, but the difference is minimal. The latent heat values of composites are small compared to the pure PCM, which is very close to the latent heat value of the mass fraction of PCM present in the composite.

*Table 1. Measured thermal properties of pure and composite PCM by DSC*

| PCM | $NaNO_3$ | | Solar Salt | | Hitec Salt | |
|---|---|---|---|---|---|---|
| **Thermal Properties** | **Pure** | **Composite** | **Pure** | **Composite** | **Pure** | **Composite** |
| Melting Temperature (℃) | 307.51 | 307.48 | 222 | 223 | 142 | 140 |
| Latent Heat (kJ/Kg) | 172 | 148.75 | 133 | 124.75 | 91 | 85.70 |
| Density (kg/m³) | 2260 | 1690 | 1890 | 1420 | 1640 | 1235 |
| PCM to CEG ratio (%) (60% CR) | 100 | 95.4 | 100 | 95.6 | 100 | 94.7 |
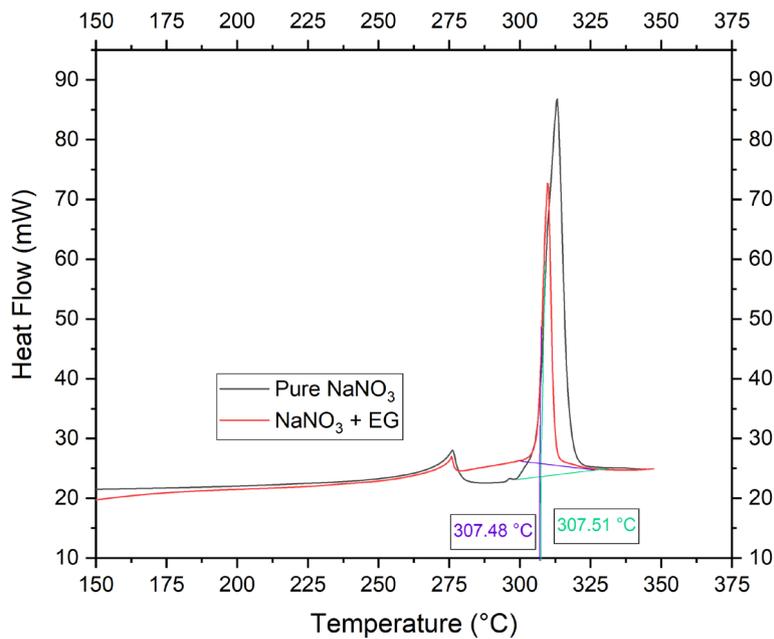


*Figure 4. DSC curve for pure $NaNO_3$ and composite $NaNO_3$*

## 3.3 Thermal Conductivity

The thermal conductivity of materials used for thermal storage is crucial in determining the rate at which heat is transported within a thermal storage system. When a material has low thermal conductivity, it places practical limitations on its use. Enhancing heat transfer by incorporating EG into PCMs can significantly increase their thermal conductivity to address this challenge.

This study examined the thermal conductivity of pure $NaNO_3$, Solar Salt, Hitec salt, and their composites. To ensure the accuracy of the results, three tests were conducted for each material, and the average value with error bars is presented in *Figure 5*. It is evident that composite PCMs exhibit significantly higher thermal conductivity compared to pure PCMs,

which consequently helps in increasing thermal performance enhancement of the latent heat storage systems.
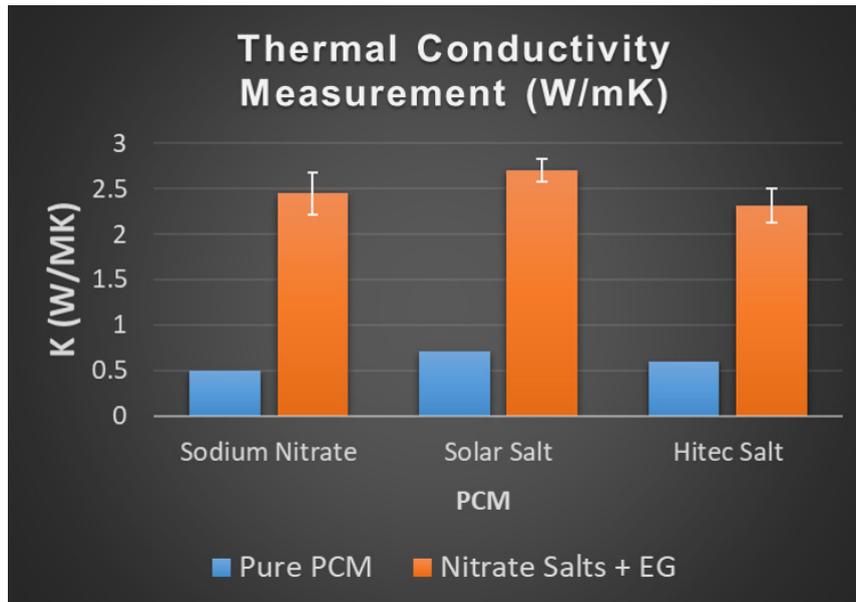


***Figure 5***. *Thermal Conductivity for Different PCMs and Composites*

## 4. Conclusion

This study primarily concentrated on enhancing heat transfer in latent heat storage systems using Phase Change Materials (PCMs). Expanded graphite was explored as a heat transport enhancer for various nitrate salts across a range of melting temperatures. The PCM composite was created by immersing the CEG matrix in the molten PCM. This soaking technique is a practical method, particularly suitable for shell-and-tube-type heat exchanger storage systems.

Various thermal characteristics were analyzed, including the thermal conductivity, melting temperature, and latent heat of both PCM and PCM-CEG composites. The introduction of graphite into the paraffin composite led to a noticeable increase in thermal conductivity, which exhibited a direct correlation with the quantity of added graphite. Specifically, the thermal conductivity was enhanced by a factor of 3-4 when incorporating 60% CEG by volume, characterized by approximately 80% porosity in the CEG. The melting temperature remained largely unaffected, as no significant chemical reactions occurred between the nitrate salts and graphite.

## Data availability statement

Data will be made available on request.

## Underlying and related material

No supporting material is deposited in a repository.

## Author Contributions

**Narender Kumar:** Methodology, Investigation, Validation, Data curation, Formal Analysis, Writing – original draft, Writing – review and editing, Visualization. **Prodyut R. Chakraborty**:

Conceptualization, Funding acquisition, Resources, Writing - Review Editing, Supervision, Project administration.

## Competing Interests

The authors declare that they have no financial or personal interests that may have influenced the research presented in this manuscript. Specifically, the authors have no financial interests in any products or services discussed in this manuscript and no personal relationships that may have influenced their research.

## Funding

## Acknowledgment

## References

[1] S.J. Wagner, E.S. Rubin, Economic implications of thermal energy storage for concentrated solar thermal power. Renewable Energy 61 (2014) 81–95. doi: https://doi.org/10.1016/j.renene.2012.08.013.

[2] H. Tyagi, A. K. Agarwal, P. R. Chakraborty, S.Powar, (2023). Applications of Solar Energy, Springer. https://www.springerprofessional.de/introduction-to-applications-of-solar-energy/15266690.

[3] R. K. Sharma, P. Ganesan, V. V. Tyagi, H. S. C. Metselaar, S. C. Sandaran, Developments in organic solid–liquid phase change materials and their applications in thermal energy storage, Energy Conversion and Management 95 (2015) 193–228. doi: https://doi.org/10.1016/j.enconman.2015.01.084.

[4] S. Boudaoud, A. Khellaf, K. Mohammedi, O. Behar, Thermal performance prediction and sensitivity analysis for future deployment of molten salt cavity receiver solar power plants in Algeria, Energy Conversion and Management 89 (2015) 655–664. doi: https://doi.org/10.1016/j.enconman.2014.10.033.

[5] H. Shabgard, T. L. Bergman, N. Sharifi, A. Faghri, High temperature latent heat thermal energy storage using heat pipes, Int J Heat Mass Transfer 53 (2010) 2979–2988. doi: https://doi.org/10.1016/j.ijheatmasstransfer.2010.03.035.

[6] R.Tufen, J. P. Petitet, I. Denielou, Le. B. Neindre, Experimental determination of the thermal conductivity of molten pure salts and salt mixtures, Int J Thermophys 6 (1985) 315–330. doi: https://doi.org/10.1007/BF00500266.

[7] Q. Peng, X. Wie, J. Ding, J. Yang, X. Yang, High-temperature thermal stability of molten salt materials, International Journal of Energy Research 32 (12) (2008), 1164-1174. doi: https://doi.org/10.1002/er.1453.

[8] A. Sarı, A. Karaipekli, Preparation, thermal properties and thermal reliability of palmitic acid/expanded graphite composite as form-stable pcm for thermal energy storage, Solar Energy Materials and Solar Cells 93 (5) (2009) 571–576. doi: https://doi.org/10.1016/j.solmat.2008.11.057.

[9] Z. Acem, J. Lopez, E.P. D. Barrio, KNO3/NaNO3–Graphite materials for thermal energy storage at high temperature: Part I. – Elaboration methods and thermal properties, Applied

Thermal Engineering 30 (2010) 1580–1595. doi: https://doi.org/10.1016/j.applthermaleng.2010.03.014.

[10]  H.L. Zhang, J. Baeyens, J. Degrève, G. Cáceres, R. Segal, F. Pitié, Latent heat storage with tubular encapsulated phase change materials (PCMs),  Energy 76 (2014) 66–72. doi: https://doi.org/10.1016/j.energy.2014.03.067.

[11]  W. Lu, L. Guizhi, X. Zhibo, W. Zhigen, Z. Guanhua, An experimental investigation of composite phase change materials of ternary nitrate and expanded graphite for medium-temperature thermal energy storage, Solar energy 195 (2020) 573-580. doi: 10.1016/j.solener.2019.11.102.

[12]  X. Py, R. Olives, S. Mauran, Paraffin/porous-graphite-matrix composite as a high and constant power thermal storage material, International Journal of heat and mass transfer 44 (14) (2001) 2727–2737. doi: https://doi.org/10.1016/S0017-9310(00)00309-4.

[13]  Y. He, Rapid thermal conductivity measurement with a hot disk sensor: Part 1. theoretical considerations, Thermochimica acta 436 (1-2) (2005) 122–129. doi: https://doi.org/10.1016/j.tca.2005.06.026.

[14]  Y. He, Rapid thermal conductivity measurement with a hot disk sensor: Part 2. characterization of thermal greases, Thermochimica acta 436 (1-2) (2005) 130–134. doi: https://doi.org/10.1016/j.tca.2005.07.003.