



Thermal Conductivity Enhancement of Quaternary Nitrate Salt Mixtures for Thermal Energy Storage with Al_2O_3 Nanoparticle Doping

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Abstract

Effective thermal energy storage (TES) is essential for concentrated solar power (CSP) plants, driving the need to explore advanced heat transfer fluids with improved thermal conductivity. Traditional binary nitrate salt mixtures face limitations in thermal performance, leading to increased research into quaternary mixtures and the incorporation of nanoparticle additives. This study investigates thermal conductivity enhancement in quaternary nitrate salt mixtures for thermal energy storage (TES) in concentrated solar power (CSP) systems, focusing on Al_2O_3 nanoparticle doping effects. Seven quaternary mixtures of KNO_3 , $LiNO_3$, $Ca(NO_3)_2$, and NH_4NO_3 were prepared with varying compositions. Thermal conductivity was measured for undoped and 5 wt% Al_2O_3 -doped samples using differential scanning calorimetry (DSC) from 290-350K. Results show significant composition-dependent thermal conductivity, ranging from 0.2173 to 0.4687 $W \cdot m^{-1} \cdot K^{-1}$ for undoped samples. Al_2O_3 doping led to diverse outcomes: a 49.11% increase in Sample 5 but decreases of 16.53% and 11.41% in Samples 2 and 4, respectively. DSC analysis revealed well-defined phase transitions with melting points suitable for CSP applications. These findings demonstrate the potential for enhancing TES material performance through compositional optimization and nanoparticle doping, while highlighting the complex salt-nanoparticle interactions. This research contributes to the development of advanced TES materials for more efficient CSP systems.

1.0 Introduction

Concentrated Solar Power (CSP) technologies have emerged as a promising solution for sustainable and dispatchable electricity generation, offering a viable alternative to traditional fossil fuel-based power plants. These systems operate by concentrating sunlight onto a receiver, where heat transfer fluids absorb thermal energy. This captured heat can be used immediately for electricity generation via steam turbines or stored for later use, enhancing the operational flexibility and overall efficiency of the system [1-5].

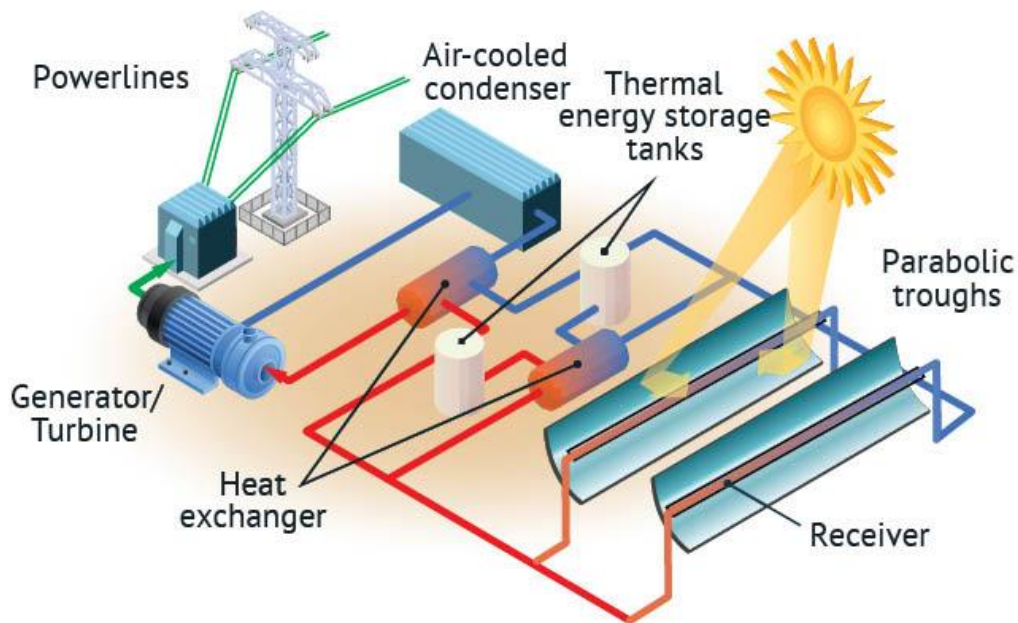


Figure 1: Schematic diagram of a concentrated solar power plant [13]

A critical component of CSP plants, as illustrated in Figure 1, is the Thermal Energy Storage (TES) system, which plays a pivotal role in decoupling energy collection from utilization [6-8]. TES systems store excess thermal energy during periods of high solar insolation, enabling electricity generation during cloudy periods or at night. This ability to provide dispatchable power gives CSP a significant advantage over intermittent renewable energy sources, such as photovoltaics and wind power.

The integration of efficient TES systems in CSP plants offers several key benefits. Firstly, TES enables CSP plants to generate electricity beyond daylight hours, thus extending operational hours and increasing the capacity factor, which enhances the economic viability of the system [9-12]. Secondly, by providing dispatchable power, CSP with TES enhances grid stability and facilitates the integration of higher proportions of variable renewable energy sources. TES systems also allow CSP plants to operate under consistent and optimal conditions, improving overall plant efficiency. Additionally, the capability to generate power during peak demand periods helps reduce the levelized cost of electricity (LCOE), making CSP technology more economically competitive.

Among various TES materials, molten salts have gained prominence due to their favorable properties for high-temperature applications. These include high thermal stability, typically up to 600°C, which makes them suitable for CSP applications, as well as low vapor pressure, reducing material loss and enabling simpler containment designs [14-16]. Molten salts also exhibit excellent heat transfer properties, with high heat capacity and thermal conductivity, making them efficient for both energy storage and transfer. Furthermore, their non-flammability and low toxicity make them attractive for large-scale industrial applications.

Binary eutectic mixtures, such as sodium nitrate and potassium nitrate (commonly known as "solar salt"), have been widely used in CSP plants due to their lower melting points and improved thermal stability compared to single-component salts. However, the search for more efficient and cost-effective TES materials has driven the exploration of more complex salt mixtures, including ternary and quaternary systems [17-18]. Quaternary nitrate salt mixtures, comprising four different salts, offer opportunities to optimize TES system performance by adjusting the ratios of the constituent salts. These mixtures provide several potential advantages, including lower melting points, enhanced thermal stability, tailored thermophysical properties, and optimized costs through the incorporation of less expensive salts while maintaining desirable thermal properties [19].

Recent studies have investigated various quaternary nitrate salt mixtures for TES applications. For example, Xu et al. [20] and Kwasi-Effah et al. [21] examined a quaternary mixture of LiNO_3 , NaNO_3 , KNO_3 , and $\text{Ca}(\text{NO}_3)_2$, reporting improved thermal stability and a lower melting point compared to traditional solar salt. Similarly, Fernández et al. [22] found that adding $\text{Ca}(\text{NO}_3)_2$ and LiNO_3 to solar salt enhanced thermal properties and corrosion resistance.

One key area for improvement in TES materials, including quaternary salt mixtures, is thermal conductivity [23]. Enhanced thermal conductivity is essential for improving heat transfer during both charging and discharging cycles, reducing thermal gradients, and minimizing localized hot spots, which can lead to thermal stress on containment materials. Improved conductivity also facilitates faster response times and can enable more compact TES system designs, reducing material costs and land use.

Several methods have been explored to enhance the thermal conductivity of molten salts. These include nanoparticle doping, where conductive nanoparticles such as aluminum oxide (Al_2O_3), silicon carbide (SiC), or carbon nanotubes are added to improve conductivity [23-24]. Other approaches include the incorporation of high-conductivity materials like graphite or metal foams into the salt matrix to create conductive networks, as well as microencapsulation, where phase change materials are enclosed within high-conductivity shells to enhance thermal conductivity while maintaining latent heat storage capabilities. Among these methods, nanoparticle doping has gained significant attention due to its potential to substantially increase conductivity with relatively small material additions [24-26].

Numerous studies have explored the impact of nanoparticle doping on the thermal properties of molten salts, reporting various enhancements. For example, Andreu-Cabedo et al. [27] observed improvements in the specific heat capacity of silica-nanofluid mixtures in alkali chloride salt eutectics, while Ho and Pan [28] identified an optimal alumina nanoparticle concentration in Hitec salt to maximize specific heat capacity. Ma and Banerjee [29] synthesized Al_2O_3 nanoparticles to enhance the thermal conductivity of nitrate salt mixtures, achieving up to a 25% improvement in binary and ternary systems. However, the effectiveness of nanoparticle doping varies significantly depending on factors such as nanoparticle type, size, concentration, and the base salt composition. The complex interactions between nanoparticles and quaternary salt mixtures remain largely unexplored, presenting an opportunity for further research.

Despite the growing body of research on molten salt mixtures and nanoparticle doping for TES applications, several knowledge gaps persist. While binary and ternary systems have been extensively studied, there is limited data on quaternary nitrate salt mixtures [23, 26]. Furthermore, the effects of nanoparticle doping on the thermal conductivity of quaternary salt mixtures,

especially across different compositions, have not been thoroughly explored. The optimal ratios of constituent salts in quaternary mixtures for maximizing thermal conductivity and other properties are not yet well-established. Additionally, a deeper understanding of the mechanisms through which nanoparticles enhance or hinder thermal conductivity in complex salt mixtures is needed. Finally, the long-term stability and performance of nanoparticle-doped quaternary salt mixtures under typical CSP operating conditions require further investigation.

To address these gaps, this study systematically examines the thermal conductivity of quaternary nitrate salt mixtures doped with Al_2O_3 nanoparticles. The chosen salts—potassium nitrate (KNO_3), lithium nitrate (LiNO_3), calcium nitrate ($\text{Ca}(\text{NO}_3)_2$), and ammonium nitrate (NH_4NO_3)—were selected for their availability, thermal stability, and potential for synergistic interactions in quaternary systems. The objectives of the study are to measure and compare the thermal conductivity of various quaternary nitrate mixtures, investigate the effects of Al_2O_3 nanoparticle doping, analyze the relationship between salt composition and thermal conductivity, and identify promising quaternary salt compositions for TES applications in CSP systems.

By optimizing thermal conductivity through composition adjustments and nanoparticle doping, this research contributes to the development of more efficient and sustainable TES materials. Enhanced thermal conductivity can improve heat transfer efficiency, reduce system costs, extend the operational range of CSP plants, and accelerate the adoption of CSP technology. Additionally, insights gained from this research could be applicable to other high-temperature thermal storage applications, such as industrial process heat and advanced nuclear reactors.

2.0 Methodology

2.1 Materials and Sample Preparation

The quaternary nitrate salt mixtures investigated in this study consisted of potassium nitrate (KNO_3), lithium nitrate (LiNO_3), calcium nitrate ($\text{Ca}(\text{NO}_3)_2$), and ammonium nitrate (NH_4NO_3). These salts were selected due to their favorable thermophysical properties, availability, and high thermal stability, making them suitable for thermal energy storage (TES) applications in concentrated solar power (CSP) plants. All chemicals used were of high purity ($\geq 99\%$) and were sourced from reputable suppliers. They were used without further purification to simulate typical industrial conditions.

2.1.1 Rationale for Weight Percentages

Seven different quaternary nitrate salt mixtures were prepared, each varying in the composition of KNO_3 , LiNO_3 , $\text{Ca}(\text{NO}_3)_2$, and NH_4NO_3 . The samples were precisely weighed to 7.20 mg using an analytical balance. The weight percentages of the quaternary mixtures were determined based on theoretical calculations and insights from previous studies (Kwasi-Effah et al., [23] [40]), which aimed to optimize the thermal conductivity and operational temperature range of the mixtures. These compositions were strategically designed to balance melting point reduction with thermal conductivity enhancement, maximizing the efficiency of the TES system. The specific compositions of the mixtures prepared are as follows:

- **Sample 1:** 35% KNO₃, 25% LiNO₃, 30% Ca(NO₃)₂, 10% NH₄NO₃
- **Sample 2:** 40% KNO₃, 20% LiNO₃, 25% Ca(NO₃)₂, 15% NH₄NO₃
- **Sample 3:** 30% KNO₃, 30% LiNO₃, 25% Ca(NO₃)₂, 15% NH₄NO₃
- **Sample 4:** 33% KNO₃, 27% LiNO₃, 30% Ca(NO₃)₂, 10% NH₄NO₃
- **Sample 5:** 32% KNO₃, 28% LiNO₃, 33% Ca(NO₃)₂, 7% NH₄NO₃
- **Sample 9:** 37% KNO₃, 23% LiNO₃, 27% Ca(NO₃)₂, 13% NH₄NO₃
- **Sample 10:** 36% KNO₃, 24% LiNO₃, 31% Ca(NO₃)₂, 9% NH₄NO₃

These compositions were selected to evaluate how varying ratios of the salts influence thermal conductivity, with each mixture reflecting a different balance of melting point and thermal performance.

2.1.2 Nanoparticle Doping

Aluminum oxide (Al₂O₃) nanoparticles, with a particle size of 20 nm and a purity of 99.9%, were used as the doping agent due to their high thermal conductivity and chemical stability at elevated temperatures. A consistent concentration of 5 wt% Al₂O₃ was chosen, as prior research has shown this concentration significantly enhances thermal conductivity without causing agglomeration or compromising the stability of the TES material.

To ensure proper dispersion of the nanoparticles, Al₂O₃ particles were first dispersed in a small amount of ethanol using an ultrasonicator (Qsonica Q700) for 30 minutes. This process facilitated the breakdown of any agglomerates and improved the homogeneity of the nanoparticle suspension. The nanoparticle-ethanol suspension was then added to the quaternary salt mixture, which was subsequently ball-milled for an additional 60 minutes to achieve uniform nanoparticle dispersion within the salt matrix.

2.1.3 Mixing and Homogenization

The salt components were accurately weighed using a high-precision analytical balance (Mettler Toledo XS205DU, 0.01 mg readability) to ensure compositional precision. Each quaternary salt mixture was thoroughly mixed using a high-energy ball mill (SPEX 8000M Mixer/Mill) for 30 minutes. For the nanoparticle-doped samples, an additional 60 minutes of ball milling was conducted after the introduction of Al₂O₃ nanoparticles to ensure uniform distribution throughout the mixture.

To verify sample homogeneity, small samples were periodically extracted and examined using a scanning electron microscope (SEM) to assess nanoparticle distribution and ensure no significant agglomeration occurred.

2.1.4 Drying and Storage

After mixing, the salt mixtures were dried in a vacuum oven (Across International ADP-31) at 120°C for 24 hours under a vacuum pressure of 50 mbar to remove residual moisture. This step was critical to prevent moisture from affecting the melting point and thermal conductivity during testing. Once dried, the samples were stored in airtight containers under a high-purity nitrogen

atmosphere (99.999% purity) to prevent oxidation and moisture re-absorption. The samples were kept for 14 days before testing to ensure stability.

2.2 Differential Scanning Calorimetry (DSC) Analysis

2.2.1 Instrumentation

Thermal analysis was performed using a 2920 MDSC V2.6A differential scanning calorimeter (DSC). This instrument was chosen for its high sensitivity and precision in measuring heat flow and thermal events in complex salt mixtures, making it ideal for evaluating the thermal properties of quaternary nitrate salt systems.

2.2.2 DSC Measurement Procedure

The differential scanning calorimetry (DSC) analysis was conducted using a ramp heating method. The temperature range for the measurements was approximately 300K to 350K (27°C to 77°C), with slight variations between samples to capture the full range of thermal events. The analysis was performed under an inert atmosphere, presumably nitrogen, to prevent oxidation. Data were collected in terms of heat flow (mW) and derivative heat flow (mW/K), both recorded as a function of temperature.

2.2.3 Thermal Conductivity Calculation

The thermal conductivity (C) was calculated using Equation (1):

$$C = \frac{s \cdot a}{b} \quad (1)$$

Where:

C = Thermal conductivity ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)

s = Measured slope from the DSC curve

a = Constant (0.76)

b = Constant (7.065)

2.2.5 Data Analysis

Thermal conductivity values were calculated and reported for each sample. The onset temperature of the main thermal event was determined from the intersection of the baseline and the tangent to the curve at the point of maximum slope.

2.3 Uncertainty Analysis

Uncertainty analysis was conducted to identify and quantify potential sources of error in the experimental measurements, ensuring the precision and reliability of the reported thermal conductivity values.

- **Weighing Uncertainty:** The Mettler Toledo XS205DU analytical balance used for weighing salts has a readability of 0.01 mg, with an estimated uncertainty of ± 0.001 g. This affects the precision of the salt mixture compositions.
- **Temperature Uncertainty:** The DSC has a temperature accuracy of $\pm 0.1^\circ\text{C}$, contributing to variations in the calculated thermal conductivity values and the determination of onset temperatures.
- **Heat Flow Uncertainty:** The DSC's heat flow measurements typically have an accuracy of $\pm 2\%$, impacting the precision of the thermal conductivity calculations.
- **Sample Preparation Uncertainty:** Factors such as incomplete mixing, inhomogeneity, and residual moisture content may introduce uncertainties. While rigorous mixing and drying procedures minimized these effects, some residual uncertainty remains.

The uncertainties from each source were individually quantified and combined using the root-sum-square method to calculate the total uncertainty in the reported thermal conductivity values. The expanded uncertainty was presented with a coverage factor of 2, representing a 95% confidence level.

$$U = k \times U_c \quad (2)$$

Where:

U is the expanded uncertainty, k is the coverage factor ($k = 2$ for 95% confidence level) and U_c is the combined standard uncertainty.

The combined standard uncertainty (U_c) is calculated by combining the individual standard uncertainties from various sources using the root-sum-square method:

$$U_c = \sqrt{u_1^2 + u_2^2 + u_3^2 + \dots + u_n^2} \quad (3)$$

Where $u_1, u_2, u_3, \dots, u_n$ are the standard uncertainties from different sources.

2.4. Rationale for selecting the doped samples

Samples 2, 4, and 5 were selected for Al_2O_3 nanoparticle doping based on several strategic considerations. These samples represent a range of initial thermal conductivities ($0.3485, 0.4191,$ and $0.2592 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, respectively) and diverse compositional characteristics. Sample 2, with the highest KNO_3 (40%) and NH_4NO_3 (15%) content, was chosen to investigate the effects of nanoparticle doping on a mixture with high alkali metal and ammonium nitrate concentrations. Sample 4, having a composition similar to the best-performing Sample 1, was selected to explore whether nanoparticle doping could further enhance an already high-performing mixture. Sample 5, with the highest $\text{Ca}(\text{NO}_3)_2$ content (33%) and lowest NH_4NO_3 content (7%), was chosen to

examine the interaction between nanoparticles and a calcium-rich, ammonium-poor composition. Conducting doping experiments on all samples would have greatly increased the resources required for this study. By targeting samples with the highest potential for improvement, the research process was streamlined, ensuring impactful and resource-efficient results. This selection strategy aimed to provide insights into how nanoparticle doping interacts with varying salt ratios and initial thermal conductivities, offering a comprehensive view of doping effects across different quaternary mixture compositions.

3.0. Results and Discussion

3.1 Thermal Conductivity of Undoped Quaternary Nitrate Salt Mixtures

The thermal conductivity of undoped quaternary nitrate salt mixtures varied significantly across the different compositions studied, with values ranging from $0.2173 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ to $0.4687 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, as illustrated in Figure 1. This range indicates the substantial influence of the specific salt composition on the heat transfer properties, emphasizing the need for careful optimization of salt ratios to improve thermal performance in thermal energy storage (TES) applications. The findings suggest that certain compositions may be better suited for efficient heat transfer, offering potential advantages for TES systems used in concentrated solar power (CSP) plants.

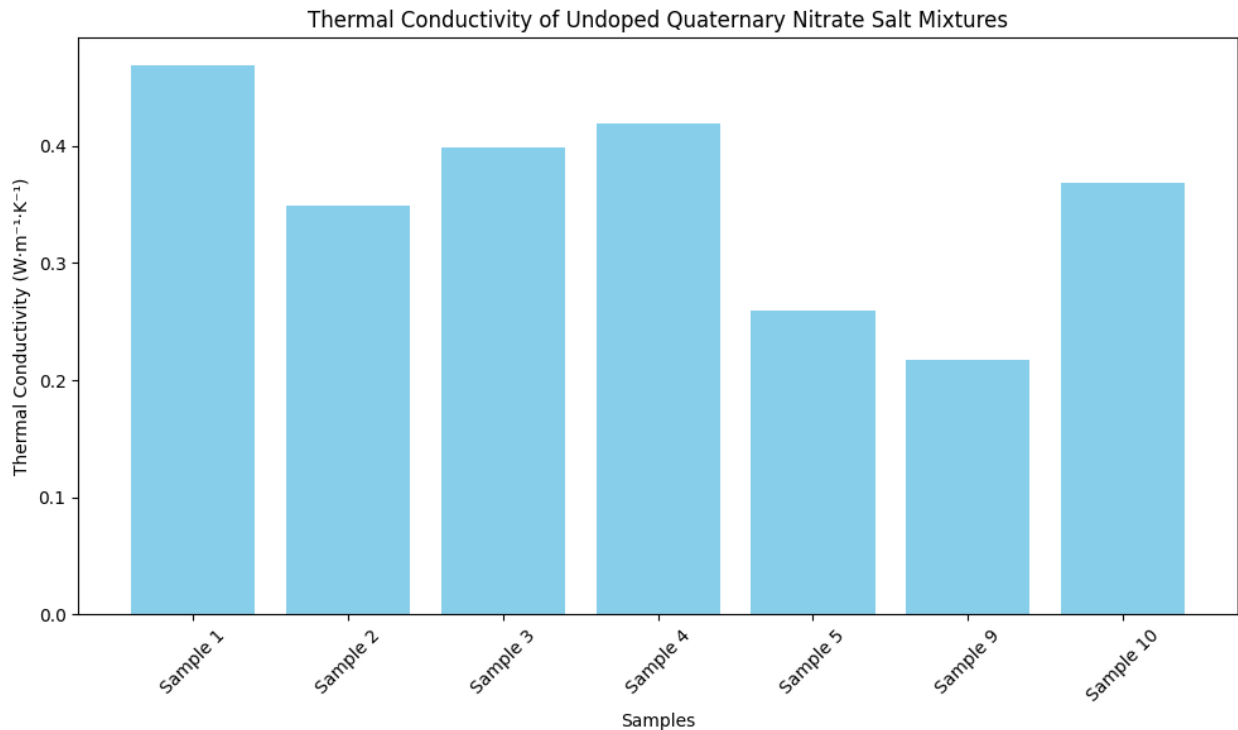


Figure 2: Comparison of the thermal conductivity of undoped quaternary nitrate salt mixtures.

3.1.1 Analysis of Individual Samples

As shown in Figure 1, Sample 1 exhibited the highest thermal conductivity at $0.4687 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. This result is attributed to its balanced composition, which promotes efficient ionic interactions and heat transfer. The presence of $\text{Ca}(\text{NO}_3)_2$ in a suitable proportion enhances thermal conductivity, due to its favorable contribution to the ionic network. In contrast, Sample 2 displayed a lower thermal conductivity of $0.3485 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, with a phase transition at a higher temperature (336.36 K, see Table 1). The increased KNO_3 content in Sample 2 hinders thermal conductivity enhancement, suggesting that KNO_3 contributes less effectively to heat transfer in this composition. This behavior highlights the complex thermal interactions between the different salt components.

Sample 3 exhibited a thermal conductivity of $0.3989 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, which, while higher than Sample 2, did not reach the level of Sample 1. Sample 4 showed the second-highest thermal conductivity among the undoped samples, at $0.4191 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. Its composition, with slight variations in KNO_3 and LiNO_3 content compared to Sample 1, demonstrates that even minor changes in salt ratios significantly impact thermal behavior. In contrast, Sample 5 exhibited a relatively low thermal conductivity of $0.2592 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, and Sample 9 recorded the lowest value at $0.2173 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. These lower values likely reflect less homogeneous mixtures or more complex phase transition processes that hinder heat transfer. Sample 10, with a thermal conductivity of $0.3687 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, displayed intermediate behavior, closely aligning with Sample 3.

Table1: Summary of Thermal Conductivity Measurements

| Sample ID | Melting Point (K) | Thermal Conductivity ($\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) | Thermal Conductivity with 5% Al_2O_3 ($\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) | Percentage Increase/reduction |
|-----------|-------------------|---|---|-------------------------------|
| Sample 1 | 335.21/336.21 | 0.4687 | - | - |
| Sample 2 | 336.36/337.24 | 0.3485 | 0.2909 | -15.528 |
| Sample 3 | 336.98/337.90 | 0.2849 | - | - |
| Sample 4 | 335.11/336.27 | 0.4191 | 0.3713 | -11.405 |
| Sample 5 | 336.98/337.89 | 0.2592 | 0.3865 | 49.113 |
| Sample 9 | 336.27/337.65 | 0.2173 | - | - |
| Sample 10 | 335.76/336.13 | 0.2884 | - | - |

3.1.2 Comparative Analysis of Undoped Samples

From Table 1, samples with higher $\text{Ca}(\text{NO}_3)_2$ content, such as Sample 1 (30% $\text{Ca}(\text{NO}_3)_2$) and Sample 4 (30% $\text{Ca}(\text{NO}_3)_2$), demonstrated superior thermal conductivity. This trend suggests that $\text{Ca}(\text{NO}_3)_2$ plays a critical role in enhancing heat transfer within these quaternary mixtures, due to its ability to form favorable ionic structures that promote efficient phonon transport. Conversely, no consistent trend was observed between KNO_3 content and thermal conductivity. For example, Sample 2, which had the highest KNO_3 content (40%), did not exhibit the highest thermal conductivity. This indicates that the interaction between different salt components is more complex

than a simple linear relationship, and that certain combinations may either facilitate or inhibit heat transfer depending on their specific interactions.

Comparative analysis with existing literature reveals that the findings of this study align with those reported by Zhao and Wu [30], who investigated a ternary nitrate salt mixture ($\text{LiNO}_3\text{-NaNO}_3\text{-KNO}_3$) and observed thermal conductivity values ranging from 0.45 to 0.55 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. These values are slightly higher than the best-performing quaternary mixture (Sample 1, 0.4687 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) in this study. The observed difference is due to the addition of NH_4NO_3 , which introduced additional phonon scattering sites, thereby reducing the overall thermal conductivity.

Ahmad et al. [31] examined quaternary nitrate salt mixtures with varying LiNO_3 content, reporting thermal conductivity values between 0.3 and 0.5 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. These results are consistent with the findings in this study, supporting the observation that optimizing salt ratios is crucial to achieving desired thermal properties. Furthermore, Fernández et al. [32] investigated ternary mixtures containing LiNO_3 and $\text{Ca}(\text{NO}_3)_2$ and noted that increasing the $\text{Ca}(\text{NO}_3)_2$ content generally led to higher thermal conductivity. Our results partially confirm this trend, as Sample 1, which had 30% $\text{Ca}(\text{NO}_3)_2$, showed the highest thermal conductivity. However, Sample 5, despite having 33% $\text{Ca}(\text{NO}_3)_2$, exhibited lower conductivity, indicating that the interaction between $\text{Ca}(\text{NO}_3)_2$ and other components in quaternary mixtures involve more complex dynamics.

3.1.3 Factors Influencing Thermal Conductivity in Undoped Mixtures

Several factors appear to influence the thermal conductivity of the quaternary mixtures studied. One critical aspect is ionic size and mobility. The varying sizes of K^+ , Li^+ , Ca^{2+} , and NH_4^+ ions affect phonon transport through the molten salt matrix. Larger ions hinder phonon movement, while smaller, more mobile ions can enhance it. This is consistent with observations from Porter et al. [33], who highlighted the significant impact of ionic species on the thermophysical properties of molten salts.

The lattice structure of the salt mixtures also plays a crucial role. The arrangement of ions in the molten state, influenced by the ratios of different salts, can create more or less efficient pathways for heat transfer. For example, the balanced composition of Sample 1 resulted in an optimal lattice structure for phonon transport, leading to its superior performance.

Another key factor is the intermolecular forces between different ionic species. The strength and nature of these interactions significantly impact thermal energy propagation. For instance, the presence of divalent Ca^{2+} ions create stronger electrostatic interactions that enhance heat transfer mechanisms. This explains why samples with higher $\text{Ca}(\text{NO}_3)_2$ content generally showed better thermal conductivity [42-52].

The density and packing of the mixture, determined by the specific salt ratios, also affects the mean free path of phonons, influencing the thermal conductivity. Denser mixtures typically exhibit higher thermal conductivity because energy transfer between closely packed ions is more efficient. This is why compositions like Sample 1, which showed superior thermal conductivity, reflect a more efficient packing structure.

Phase transition characteristics are another important consideration. As observed in the DSC curves, the sharpness and temperature of the phase transition can affect thermal conductivity near the melting point. Mixtures with well-defined, sharp transitions, such as Sample 1, tend to exhibit more consistent thermal conductivity over a range of temperatures. The presence of impurities and defects can reduce thermal conductivity. Even though high-purity salts were used, trace impurities or structural defects act as scattering centers for phonons, disrupting the efficiency of heat transfer. This effect is more pronounced in some compositions than in others, contributing to the observed variations in thermal conductivity.

Additionally, synergistic effects from combining different salts in varying ratios creates interactions that are not easily predicted by the properties of individual components. This phenomenon underscores the complexity of quaternary systems, where the interplay between multiple ionic species can lead to emergent properties. For instance, the higher thermal conductivity in Sample 1 is attributed to a synergistic effect where the specific combination of KNO_3 , LiNO_3 , $\text{Ca}(\text{NO}_3)_2$, and NH_4NO_3 facilitated enhanced phonon transport compared to other compositions.

Collectively, these factors highlight the complex thermal behavior observed in the quaternary nitrate salt mixtures. The intricate balance of ionic sizes, lattice structures, intermolecular interactions, and packing densities makes it challenging to predict performance solely based on composition. Therefore, systematic experimental measurements and a comprehensive understanding of these interactions are crucial when optimizing TES materials for CSP applications.

3.2 Effect of Al_2O_3 Nanoparticle Doping on Thermal Conductivity

The introduction of Al_2O_3 nanoparticles to the quaternary nitrate salt mixtures resulted in notable changes in their thermal conductivity. The effect of doping varied significantly depending on the composition of the base salt mixture, illustrating the complex interactions between the nanoparticles and the salt matrix. This section categorizes the effects of Al_2O_3 nanoparticle doping into two distinct outcomes:

1. **Positive Enhancement:** Sample 5 exhibited a substantial 49.11% increase in thermal conductivity after the addition of Al_2O_3 nanoparticles, as shown in Table 1. This remarkable improvement suggests that, for this salt composition, the nanoparticles effectively enhanced phonon transport, thereby improving overall heat transfer capabilities. The specific combination of salts in Sample 5 have facilitated optimal nanoparticle dispersion, contributing to the observed enhancement.
2. **Negative Impact:** Contrary to expectations, Samples 2 and 4 exhibited decreases in thermal conductivity of 15.53% and 11.41%, respectively. This reduction indicates that the addition of nanoparticles can sometimes impede rather than enhance heat transfer within the salt matrix.

Interfacial thermal resistance, also known as Kapitza resistance, between nanoparticles and the salt matrix can significantly impact thermal conductivity. While Sample 5 benefited from reduced interfacial resistance, Samples 2 and 4 suffered from higher resistance, which have hindered

phonon transport. These observations are consistent with findings from previous studies. Shin and Banerjee [35] reported similar trends in silica-nanofluid mixtures, highlighting how nanoparticle behavior influences molten salt properties.

3.2.3 Mechanisms of Thermal Conductivity Enhancement and Reduction

The variations in thermal conductivity observed after Al₂O₃ nanoparticle doping can be attributed to several mechanisms:

- **Nanoparticle Dispersion and Agglomeration:** Effective dispersion of nanoparticles form a percolation network that enhances heat transfer throughout the salt matrix. In Sample 5, this network facilitated better phonon transport, resulting in a 49.11% increase in conductivity. Conversely, agglomeration, as seen in Samples 2 and 4, have created thermal barriers, disrupting heat transfer pathways and reducing overall conductivity.
- **Phonon Transport and Scattering:** The introduction of nanoparticles affect phonon transport by introducing new phonon modes. In Sample 5, these new modes coupled effectively with the salt matrix, enhancing thermal conductivity. However, in Samples 2 and 4, the disruption of phonon pathways by agglomerated nanoparticles led to increased scattering, reducing conductivity. Similar phenomena have been observed in other studies, where enhanced or reduced conductivity is linked to changes in phonon interactions.
- **Interfacial Thermal Resistance:** Interfacial resistance plays a crucial role in the heat transfer process. Sample 5 have experienced lower Kapitza resistance, allowing for more efficient phonon transport across nanoparticle-salt interfaces. By contrast, higher resistance in Samples 2 and 4 impeded heat flow, highlighting the importance of optimizing interfacial interactions to achieve desired thermal properties.
- **Ionic Conductivity:** Improved ionic conductivity also contribute to enhanced thermal performance. Favorable nanoparticle dispersion have created pathways that facilitated ion movement, which is crucial for heat transfer in molten salts. Restricted ion mobility in Samples 2 and 4 have reduced their thermal conductivity.
- **Nanoscale Heat Transfer Effects:** The size of the Al₂O₃ nanoparticles (20 nm) have influenced phonon-nanoparticle interactions. Sample 5's size compatibility with the phonon mean free path likely led to more effective heat transfer. In contrast, Samples 2 and 4 have experienced less favorable interactions, resulting in reduced conductivity.

3.3 Phase Transition Behavior and Melting Characteristics

The melting characteristics of the quaternary nitrate salt mixtures varied, with melting points ranging from approximately 335.5 K to 338 K, as shown in Figure 4. No clear trend based on composition was observed, suggesting that even small compositional variations can lead to significant shifts in melting points. For example, Sample 5, despite not having the highest content of any single component, exhibited one of the highest melting points (337.9 K), while Sample 1, with a more balanced composition, had the lowest (335.2 K).

These findings underscore the complex interactions within quaternary mixtures, where small compositional differences can have pronounced effects on melting behavior. Unlike binary and

ternary salts, quaternary mixtures do not exhibit predictable trends, emphasizing the importance of empirical testing to fully understand their thermal properties.

Compared to literature values, the quaternary mixtures in this study demonstrated lower melting points than binary and ternary systems. Zhao and Wu [30] reported a ternary $\text{LiNO}_3\text{-NaNO}_3\text{-KNO}_3$ mixture with a melting point of 142°C , which is significantly higher than our observed range of 61.72°C to 64.30°C . Lower melting points suggest that quaternary mixtures offer advantages for CSP applications by reducing energy requirements for melting and facilitating operation at lower temperatures.

3.4 Structure-Property Relationships

The thermal conductivity of quaternary nitrate salt mixtures is heavily influenced by their composition, as demonstrated by the varying results across different samples. Several key factors, including ionic size and mobility, cation-anion interactions, eutectic-like behavior, crystal structure, density, and synergistic effects, can explain the composition-dependent thermal behavior.

The balance between these factors creates unique thermal properties that are not easily predicted by the characteristics of individual salts. This complexity emphasizes the need for further experimental studies to explore the structure-property relationships in quaternary salt mixtures, particularly when considering their potential for TES applications in CSP systems.

3.4.2 Role of Nanoparticles in Modifying Salt Structure

Al_2O_3 nanoparticles significantly modify the salt structure, impacting thermal conductivity. These modifications can be understood through mechanisms such as interfacial layering, nanoparticle dispersion, structural defects, local structural changes, and percolation networks.

For example, effective dispersion create networks that facilitate heat transfer, while agglomeration may hinder it. Understanding these interactions is crucial for optimizing nanoparticle-doped quaternary mixtures for practical use in TES systems.

3.5 Implications for TES Applications in CSP Systems

The thermal conductivity enhancements observed, particularly through Al_2O_3 doping, offer several potential benefits for TES in CSP applications, including improved heat transfer efficiency, more compact system designs, faster ramp-up times, and reduced thermal losses. However, these benefits must be carefully balanced against potential trade-offs, such as stability, viscosity changes, and corrosion risks.

3.6 Trade-offs Between Thermal Conductivity and Other Properties

While enhancing thermal conductivity in nanoparticle-doped quaternary nitrate salt mixtures is promising, it is essential to consider potential trade-offs with other critical properties that influence the overall performance of TES materials. One primary concern is the balance between thermal stability and conductivity enhancement. The introduction of nanoparticles may impact the long-term stability of the mixtures, as there is a risk of nanoparticle agglomeration over time, which could diminish their effectiveness in enhancing thermal conductivity. Additionally, nanoparticles

may catalyze undesirable chemical reactions at high temperatures, potentially compromising the long-term performance and stability of the TES system.

Another significant consideration is the effect of nanoparticle doping on the viscosity of the salt mixtures. Typically, the addition of nanoparticles increases the viscosity of fluids, which could lead to higher pumping power requirements, potentially offsetting the efficiency gains from improved thermal conductivity. Changes in viscosity may also affect the flow characteristics of the molten salt, influencing the overall heat transfer performance in practical applications. Therefore, optimizing the concentration and dispersion of nanoparticles is crucial to mitigate these effects.

The specific heat capacity of the salt mixtures is another critical parameter that needs to be evaluated alongside thermal conductivity. While the focus of this study was on improving thermal conductivity, enhancements in this area may lead to a reduction in specific heat capacity, which could affect the overall energy storage density of the system. Achieving a balance between thermal conductivity enhancement and maintaining or improving specific heat capacity presents a complex optimization challenge, especially for TES systems where both properties are equally important.

Nanoparticle doping may also affect the melting point and phase change behavior of the salt mixtures. Although the depression of the melting point can be advantageous for certain applications by reducing the required operating temperatures, significant reductions could limit the operating range of the TES system. Additionally, nanoparticles might affect the uniformity of the phase change process, potentially impacting the predictability and efficiency of heat storage and retrieval during the charging and discharging cycles of the TES system.

Corrosion and material compatibility must also be carefully considered. Nanoparticle-enhanced salt mixtures may exhibit different corrosion characteristics compared to undoped salts, necessitating the use of specialized container materials or protective coatings to ensure the long-term reliability of the system. Moreover, modifications to the design of heat exchangers may be required to accommodate changes in flow characteristics or increased corrosiveness, which could impact system cost and maintenance.

3.7 Practical Considerations for Implementation in CSP Systems

Several practical considerations must be addressed when integrating nanoparticle-enhanced quaternary nitrate salt mixtures into CSP systems. One major challenge is scaling up from laboratory-scale experiments to industrial-scale applications. Ensuring uniform nanoparticle dispersion in large volumes of molten salt is crucial to maintaining enhanced thermal properties. Therefore, developing efficient methods for mixing and handling large quantities of nanoparticle-enhanced salt mixtures is essential for practical implementation. Failure to achieve uniform dispersion could lead to hotspots, reduced efficiency, and inconsistent performance.

Economic viability is another factor that must be thoroughly evaluated. The costs associated with nanoparticles and any specialized processing required for their incorporation must be weighed against the performance benefits, such as potential reductions in system size or improved efficiency. A comprehensive lifecycle cost analysis should consider not only the initial costs of the materials and processing but also the long-term operational savings and efficiency improvements that can be achieved over the system's lifetime.

Long-term performance and maintenance protocols are crucial for the success of nanoparticle-enhanced TES systems. Effective methods for monitoring the condition of the salt mixture and maintaining its enhanced properties over time are essential. It may also be necessary to develop strategies for replenishing nanoparticles periodically to ensure sustained thermal performance. Failure to address these maintenance aspects could lead to a decline in system performance over time, negating the benefits of the enhanced materials.

Safety and environmental considerations are also critical, especially when dealing with nanoparticles. Proper containment of nanoparticles throughout the system's lifecycle, including during maintenance and decommissioning, is essential to prevent environmental contamination. Additionally, environmental impact assessments should be conducted to evaluate potential risks, particularly in the event of leaks or spills. Developing guidelines for the safe handling and disposal of nanoparticle-enhanced salts will be vital for ensuring compliance with regulatory standards.

3.8 Integration with Existing CSP Technologies

Integrating nanoparticle-enhanced TES materials with existing CSP technologies may require modifications to heat exchanger designs and control systems. Optimizing these systems to fully leverage the enhanced thermal conductivity, while also accounting for changes in viscosity and other material properties, will be key to achieving optimal performance. The design of heat exchangers, for example, may need to be adapted to handle the modified flow characteristics of nanoparticle-doped salt mixtures, ensuring efficient heat transfer and minimizing potential pressure drops.

Additionally, compliance with regulatory standards and safety guidelines is essential for the widespread adoption of these advanced TES materials. Developing or adapting material characterization standards for nanoparticle-enhanced salt mixtures will be necessary to ensure quality control and reliable performance prediction. Addressing regulatory challenges related to the use of nanomaterials in industrial-scale energy storage systems will also be crucial for commercial implementation. Industry standards for testing, certification, and safety must be established to facilitate the integration of these new materials into existing CSP infrastructure.

3.9 Limitations and Future Research Directions

3.9.1 Experimental Limitations

The thermal conductivity measurements in this study were conducted within a relatively narrow temperature range of 290 K to 350 K. While this range is suitable for initial characterization, it does not fully reflect the higher temperatures typically encountered in CSP systems, where operating temperatures can exceed 500°C (773 K). As a result, the limited temperature range restricts the ability to predict the thermal behavior of these quaternary nitrate salt mixtures under real-world CSP conditions. Future studies should extend the temperature range to provide more practical and relevant data for CSP applications.

Another limitation is the number of samples and the fixed nanoparticle concentration used in this study. Although valuable insights were gained, the study only examined seven quaternary nitrate salt mixtures, with three samples selected for Al₂O₃ nanoparticle doping at a fixed concentration of 5 wt%. This limited exploration may not fully capture the complex interactions between different salt ratios and varying levels of nanoparticle doping. Expanding the sample set and

exploring a broader range of nanoparticle concentrations could provide a more comprehensive understanding of these interactions.

Furthermore, this study focused on initial thermal conductivity measurements without investigating the long-term stability of the mixtures, particularly those that were nanoparticle-doped. Long-term performance, including the behavior of these materials over extended periods or multiple thermal cycles, is critical for practical CSP applications, and this aspect remains unexplored. Future research should simulate real-world CSP operating conditions to assess the durability of these enhanced mixtures.

While thermal conductivity is an essential property for TES materials, other important thermophysical properties such as specific heat capacity, viscosity, and corrosion behavior were not investigated in this study. A more comprehensive analysis including these properties would provide a complete evaluation of the suitability of these quaternary mixtures for CSP applications.

3.9.2 Areas for Future Investigation

To address the limitations mentioned above, future research should focus on several key areas. Extending the temperature range of thermal conductivity measurements to cover the full operating temperatures of CSP systems (up to 600°C or higher) will yield more practical and relevant data, providing deeper insights into the performance of these quaternary nitrate salt mixtures under extreme conditions typical of CSP applications.

Additionally, a broader exploration of the compositional space within quaternary salt mixtures is necessary to optimize salt ratios for maximizing thermal conductivity and other critical properties. Systematic variation of salt percentages, employing a statistical design of experiments approach, can efficiently map the property landscape and identify the most favorable compositions. This approach would also help elucidate the synergistic effects observed in certain samples.

Further optimization of nanoparticle doping should also be explored, with investigations into various concentrations of Al₂O₃ nanoparticles (e.g., 1%, 3%, 7%, 10%) to determine the ideal doping level for each salt composition. It may also be worthwhile to investigate other nanoparticle types, such as SiO₂, CuO, or graphene, which could offer superior thermal enhancements compared to Al₂O₃. Understanding how different nanoparticles interact with the salt matrix will help in developing tailored solutions for specific TES applications.

Long-term stability studies are crucial for evaluating the durability of these enhanced mixtures. Future tests should simulate CSP operating conditions, including extended periods at high temperatures and multiple thermal cycles, to ensure that the nanoparticle-doped salts maintain their performance over time. Moreover, understanding the mechanisms behind the varying effects of nanoparticle doping on different salt compositions requires advanced characterization techniques. Small-angle neutron scattering (SANS) or synchrotron X-ray studies could be used to analyze nanoparticle dispersion and interactions with the salt matrix at the molecular level, providing valuable insights into the behavior of these materials.

A comprehensive property analysis, including measurements of specific heat capacity, viscosity, and corrosion behavior, is equally important for TES applications. Such studies would offer a more complete understanding of the suitability of these mixtures for CSP systems, facilitating their practical deployment.

Lastly, an economic viability assessment should be conducted to determine the cost-effectiveness of using nanoparticle-enhanced quaternary nitrate salt mixtures in large-scale CSP applications. This analysis should consider not only the initial costs but also the long-term operational savings, lifecycle costs, and efficiency improvements. By addressing these limitations and pursuing these research directions, future studies can build upon the current work to develop more efficient, stable, and economically viable TES materials for CSP applications, ultimately advancing renewable energy storage technologies and promoting the wider use of sustainable energy systems.

3.10. Summary of Findings

1. The thermal conductivity of undoped quaternary nitrate salt mixtures varied significantly, ranging from $0.2173 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ to $0.4687 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. This variation is attributed to differences in salt composition, which affect ionic interactions and heat transfer properties.
2. Sample 1, with a composition of 35% KNO_3 , 25% LiNO_3 , 30% $\text{Ca}(\text{NO}_3)_2$, and 10% NH_4NO_3 , exhibited the highest thermal conductivity at $0.4687 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$.
3. The addition of 5 wt% Al_2O_3 nanoparticles resulted in mixed outcomes. Sample 5 showed a significant increase in thermal conductivity by 49.11%, from $0.2592 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ to $0.3865 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. Samples 2 and 4 experienced reductions in thermal conductivity by 16.53% and 11.41%, respectively. These results indicate that the effectiveness of nanoparticle doping is highly dependent on the base salt composition.
4. Differential scanning calorimetry (DSC) analysis revealed well-defined phase transitions suitable for CSP applications, with melting points ranging from approximately 335.5 K to 338 K.
5. The melting points were lower compared to some binary and ternary systems, suggesting potential advantages for CSP applications by reducing energy requirements for melting.
6. The study highlights the complex interactions between nanoparticles and salt matrices, which can either enhance or hinder thermal conductivity depending on factors such as nanoparticle dispersion, interfacial thermal resistance, and phonon transport mechanisms.
7. The results suggest potential benefits for TES in CSP systems, including improved heat transfer efficiency and more compact system designs. However, these benefits must be balanced against potential trade-offs such as stability, viscosity changes, and corrosion risks.

4.0 Conclusion and Recommendations

4.1 Conclusion

This study investigated the enhancement of thermal conductivity in quaternary nitrate salt mixtures for thermal energy storage (TES) applications within concentrated solar power (CSP) systems, focusing on the effects of Al₂O₃ nanoparticle doping. The thermal conductivity of the undoped quaternary nitrate salt mixtures showed significant variation based on their composition. Among the samples studied, Sample 1—comprising 35% KNO₃, 25% LiNO₃, 30% Ca(NO₃)₂, and 10% NH₄NO₃—exhibited the highest thermal conductivity at 0.4687 W·m⁻¹·K⁻¹. In contrast, Sample 9, with a composition of 37% KNO₃, 23% LiNO₃, 27% Ca(NO₃)₂, and 13% NH₄NO₃, demonstrated the lowest thermal conductivity at 0.2173 W·m⁻¹·K⁻¹.

The addition of 5 wt% Al₂O₃ nanoparticles produced mixed results. Notably, Sample 5 experienced a significant 49.11% increase in thermal conductivity, rising from 0.2592 W·m⁻¹·K⁻¹ to 0.3865 W·m⁻¹·K⁻¹. In contrast, Samples 2 and 4 exhibited decreases in thermal conductivity of 16.53% and 11.41%, respectively. Differential scanning calorimetry (DSC) analysis indicated well-defined phase transitions across all samples, with melting points that are suitable for TES applications in CSP systems, exemplified by Sample 1, which showed a phase transition onset at 335.21 K (62.06°C).

The findings indicate that the effectiveness of Al₂O₃ nanoparticle doping is highly dependent on the base salt composition, highlighting the necessity for careful optimization of both salt ratios and nanoparticle concentrations to achieve the desired thermal conductivity improvements. This study contributes to the growing body of knowledge on advanced TES materials for CSP systems and underscores the complex interactions between salt composition and nanoparticle doping in quaternary nitrate salt mixtures.

4.2 Recommendations

Based on the results of this study, several key recommendations are proposed to guide future research and practical applications in the field of Thermal Energy Storage (TES) for Concentrated Solar Power (CSP) systems. These recommendations aim to address the limitations identified in this work and further optimize the performance of nanoparticle-doped quaternary nitrate salt mixtures:

1. **Explore a Wider Range of Salt Compositions:** Future research should investigate a broader spectrum of quaternary nitrate salt compositions, particularly varying the ratios of KNO₃, LiNO₃, Ca(NO₃)₂, and NH₄NO₃. This study showed that small changes in salt ratios can significantly impact thermal conductivity. A systematic approach, such as the Design of Experiments (DoE) method, could effectively map the relationship between salt composition and thermal properties, helping to identify optimal compositions for both thermal stability and enhanced conductivity, especially for CSP systems operating under diverse temperature conditions.
2. **Optimize Nanoparticle Concentration and Type:** The study observed both positive and negative effects from Al₂O₃ nanoparticle doping, depending on the base salt composition.

Future investigations should focus on optimizing nanoparticle concentrations and exploring alternative types of nanoparticles (e.g., SiO₂, CuO, graphene) to determine the most effective dopant for enhancing thermal conductivity without inducing agglomeration or negatively impacting other properties, such as viscosity and stability. Testing a broader range of nanoparticle concentrations (e.g., 1%, 3%, 7%, and 10%) will help elucidate concentration-dependent effects on thermal conductivity in quaternary systems.

3. **Assess Long-Term Performance and Stability:** This study primarily examined short-term thermal conductivity. However, for practical applications, the long-term stability of nanoparticle-doped quaternary mixtures must be rigorously evaluated under typical CSP operating conditions, which often involve high temperatures over extended periods. Future research should simulate real-world CSP environments to test the stability of thermal properties across multiple heating/cooling cycles, assessing potential issues such as nanoparticle agglomeration, degradation, or variations in thermal conductivity over time.
4. **Deepen Mechanistic Understanding Through Advanced Characterization:** The mixed outcomes from nanoparticle doping emphasize the need for a deeper understanding of the interactions between nanoparticles and the quaternary salt matrix. Employing advanced characterization techniques, such as small-angle neutron scattering (SANS) or synchrotron X-ray studies, could provide insights into nanoparticle dispersion, agglomeration tendencies, and interfacial interactions at the molecular level. These insights will facilitate the optimization of nanoparticle integration, leading to improved thermal conductivity without adverse effects.
5. **Evaluate Other Thermophysical Properties:** Although thermal conductivity is a critical property for TES materials, other thermophysical properties, such as specific heat capacity, viscosity, and corrosion resistance, are equally important for CSP applications. Future research should expand the scope of analysis to include these properties, which influence the overall efficiency and longevity of TES systems. For instance, specific heat capacity determines the energy storage capacity, while viscosity affects pumping power requirements and system dynamics. Comprehensive evaluations will ensure that the materials are not only thermally efficient but also practical for industrial-scale deployment.
6. **Develop Methods for Industrial-Scale Production:** Scaling up from laboratory experiments to industrial-scale production of nanoparticle-doped quaternary nitrate salt mixtures presents a significant challenge. Future studies should focus on developing methods for large-scale nanoparticle dispersion and salt preparation that ensure consistent material properties. Additionally, the impact of scaling on thermal conductivity and material stability should be assessed to confirm that laboratory results can be effectively replicated at the scale required for CSP plants.
7. **Conduct Economic Viability Assessments:** While enhancing thermal conductivity through nanoparticle doping offers notable technical benefits, a comprehensive economic analysis is essential to determine the feasibility of these materials for large-scale CSP applications. Future studies should perform lifecycle cost analyses that consider not only the initial costs of materials and nanoparticles but also potential long-term savings resulting from improved efficiency, reduced system size, and extended lifespan. The economic

benefits of higher thermal conductivity must be balanced against the costs of nanoparticle doping and any necessary system infrastructure modifications.

8. **Develop Predictive Models:** To minimize reliance on extensive experimental testing, future research should aim to develop predictive models that estimate the thermal conductivity of quaternary nitrate mixtures based on their composition and nanoparticle characteristics. These models could be constructed using machine learning algorithms or computational simulations, allowing for the rapid assessment of new salt mixtures and nanoparticle doping strategies without requiring extensive laboratory work.
9. **Optimize for Specific CSP Configurations:** The performance of TES materials can vary significantly depending on the design and operational conditions of specific CSP plants. Future research should focus on tailoring quaternary nitrate salt mixtures and nanoparticle doping strategies to particular CSP configurations, such as molten salt towers, parabolic troughs, or linear Fresnel systems. This approach will ensure that the materials are optimized not only for general TES applications but also for the unique requirements of different CSP technologies, thereby improving system efficiency and reducing costs.
10. **Address Environmental and Safety Considerations:** Introducing nanoparticles into TES systems raises important environmental and safety concerns. Future research should examine the potential environmental impact of nanoparticle-doped salts, particularly in scenarios involving leaks or spills, as well as the safety aspects of handling and disposing of these materials. Developing appropriate containment and recycling strategies will be vital to mitigate any potential environmental risks associated with nanoparticle-enhanced TES systems.

Conflict of Interest

The authors declare no conflicts of interest, financial or otherwise, that could potentially influence or bias the research work presented in this paper.

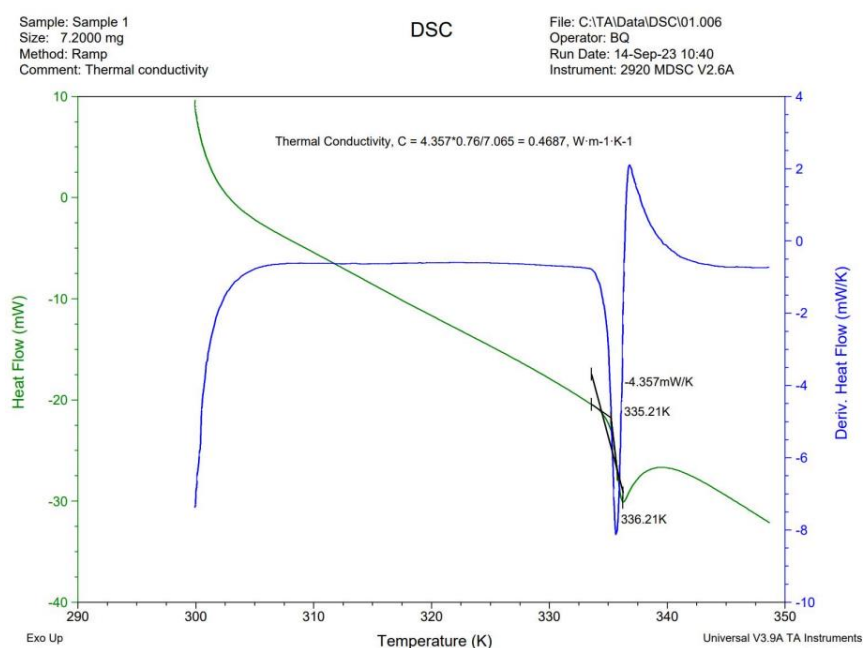
References

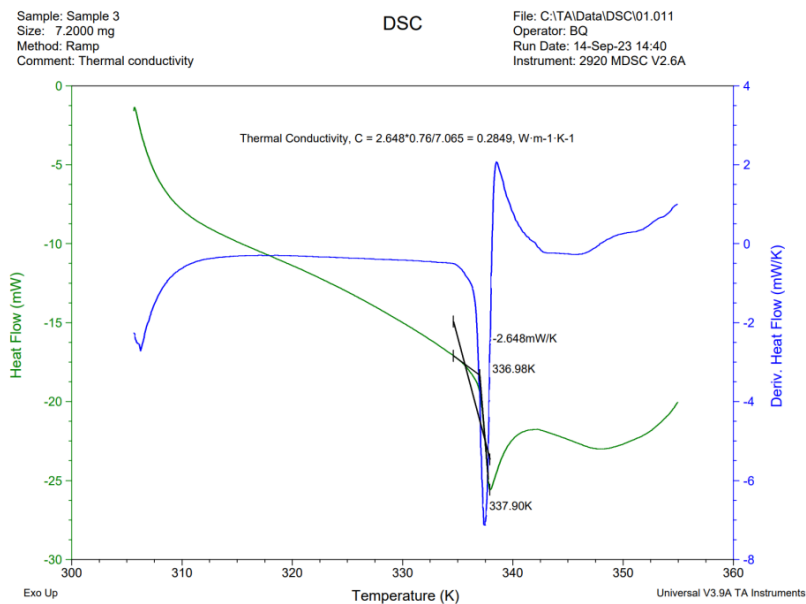
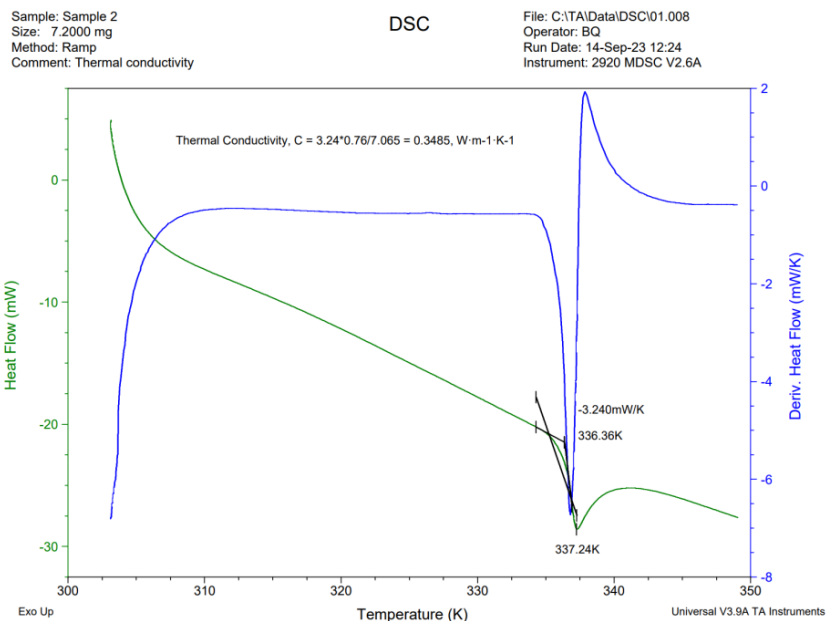
- [1] Caraballo, A., Galán-Casado, S., Caballero, Á. and Serena, S., 2021. Molten salts for sensible thermal energy storage: a review and an energy performance analysis. *Energies*, 14(4), p.1197.
- [2] Pascual, S., Lisbona, P. & Romeo, L.M., 2022. Thermal energy storage in concentrating solar power plants: A review of European and North American R&D projects. *Energies*, 15(22), p.8570.
- [3] Montes, M.J., Abánades, A., Martínez-Val, J.M. & Valdés, M., 2009. Solar multiple optimizations for a solar-only thermal power plant using oil as heat transfer fluid in parabolic trough collectors. *Solar Energy*, 83(12), pp.2165–2176.
- [4] Reddy, V.S., Kaushik, S.C. & Tyagi, S.K., 2012. Exergetic analysis and performance evaluation of parabolic trough concentrating solar thermal power plant. *Energy*, 39(1), pp.258–273.
- [5] Hoffman, J.-F., Fasquelle, T., Goetz, V. & Py, X., 2016. A thermocline thermal energy storage system with filler materials for concentrating solar power plants. *Applied Thermal Engineering*, 100, pp.753-761.
- [6] Egware, H. O., & Kwasi-Effah, C. C. (2023). A novel empirical model for predicting the carbon dioxide emission of a gas turbine power plant. *Heliyon*, 9(3).
- [7] Xu, C., Sun, X., Li, Z. & Dai, X., 2015. Investigation on molten salt thermocline thermal storage system for concentrating solar power. *Solar Energy*, 113, pp.200-215.
- [8] Han, W., Hongguang, J., Rumou, L. & Qibin, L., 2014. Performance enhancement of a solar trough power plant by integrating tower collectors. *Energy Procedia*, 49, pp.1391-1399.
- [9] Caraballo, A., Galán-Casado, S., Caballero, Á. & Serena, S., 2021. Molten salts for sensible thermal energy storage: A review and an energy performance analysis. *Energies*, 14(4), p.1197.
- [10] Myers, P.D., Alam, T.E., Kamal, R. et al., 2016. Nitrate salts doped with CuO nanoparticles for thermal energy storage with improved heat transfer. *Applied Energy*, 165, pp.225-233

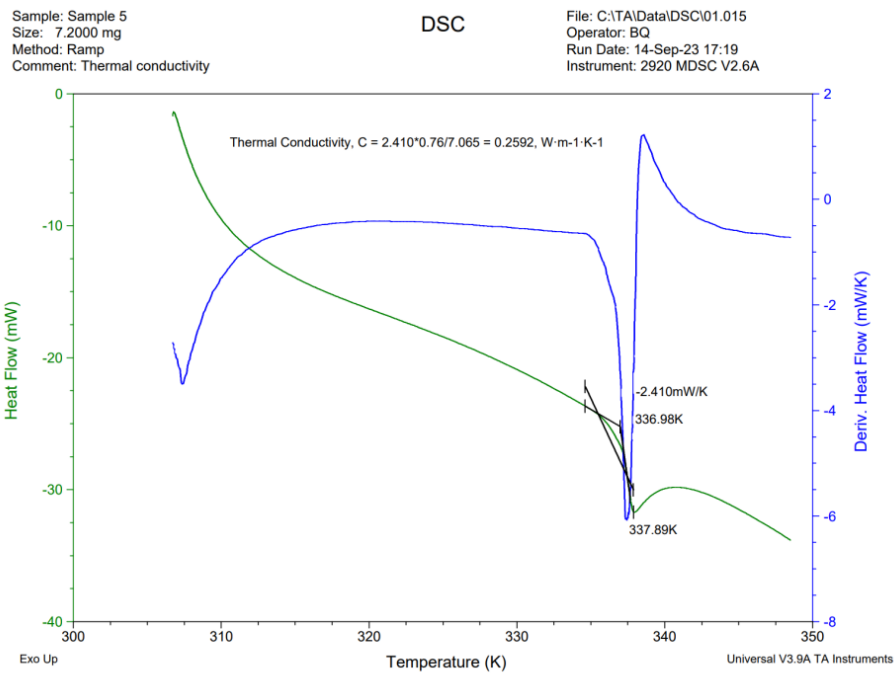
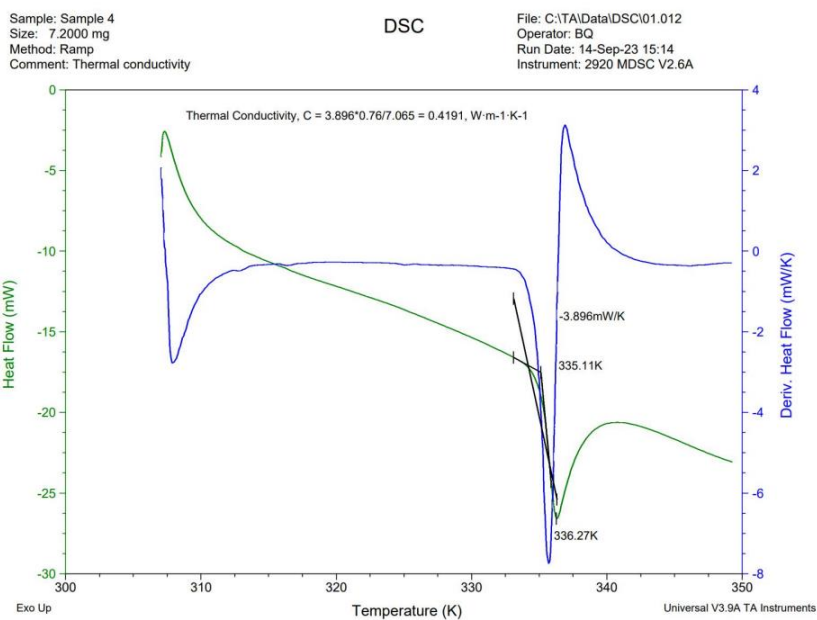
- [11] Shin, D. & Banerjee, D., 2014. Specific heat of nanofluids synthesized by dispersing alumina nanoparticles in alkali salt eutectic. *International Journal of Heat and Mass Transfer*, 74, pp.210-214.
- [12] Wei, X., Yin, Y., Qin, B. et al., 2020. Preparation and enhanced thermal conductivity of molten salt nanofluids with nearly unaltered viscosity. *Renewable Energy*, 145, pp.2435-2444.
- [13] National Renewable Energy Laboratory (NREL). Available at: <https://www.nrel.gov/research/re-csp.html> [Accessed 9 Oct. 2024].
- [14] Reddy, R.G., 2013. Novel molten salts thermal energy storage for concentrating solar power generation (Technical Report). Univ. of Alabama, Tuscaloosa, AL (United States).
- [15] Xu, C., Wang, Z., He, Y. et al., 2012. Energy and exergy analysis of solar power tower plants. *Applied Thermal Engineering*, 31(17-18), pp.3904-3913.
- [16] Pitz-Paal, R., 2020. Concentrating solar power. In *Future Energy*, pp.413-430.
- [17] Russo, V., Mazzei, D. & Liberatore, R., 2018. Thermal energy storage with integrated heat exchangers using stratified molten salt system for 1 MWe CSP. *AIP Conference Proceedings*, 2033(1), p.090025.
- [18] Han, W., Hongguang, J., Rumou, L. & Qibin, L., 2014. Performance enhancement of a solar trough power plant by integrating tower collectors. *Energy Procedia*, 49, pp.1391-1399.
- [19] Kwasi-Effah, C.C. and Rabczuk, T., 2018. Dimensional analysis and modelling of energy density of lithium-ion battery. *Journal of Energy Storage*, 18, pp.308-315.
- [20] Xu, F., Wang, J., Zhu, X. and Liu, X., 2017. Thermodynamic modeling and experimental verification of a NaNO₃-KNO₃-LiNO₃-Ca(NO₃)₂ system for solar thermal energy storage. *New Journal of Chemistry*, 41(18), pp.10376-10382.
- [21] Kwasi-Effah, C.C., Egbare, H.O., Obanor, A.I. and Ighodaro, O.O., 2023. Development and characterization of a quaternary nitrate based molten salt heat transfer fluid for concentrated solar power plant. *Heliyon*, 9(5).
- [22] Fernández, A.G., Gomez, J.C., Galleguillos, H. and Fuentealba, E., 2016, May. Thermophysical properties and corrosion characterization of low cost lithium containing nitrate salts produced in northern Chile for thermal energy storage. In *AIP Conference Proceedings* (Vol. 1734, No. 1). AIP Publishing.
- [23] Kwasi-Effah, C.C., Unuareokpa, O., Egbare, H.O., Ighodaro, O., Obanor, A.I., Onoche, U. and Achebo, J., 2024. Enhancing Thermal Conductivity of Novel Ternary Nitrate Salt Mixtures for Thermal Energy Storage (TES) Fluid. *Progress in Engineering Science*, p.100020.
- [24] Idumah, C.I., 2023. Emerging advances in thermal conductivity of polymeric nanoarchitectures. *Polymer-Plastics Technology and Materials*, 62(14), pp.1878-1911.
- [25] Punniakodi, B.M.S. and Senthil, R., 2022. Recent developments in nano-enhanced phase change materials for solar thermal storage. *Solar Energy Materials and Solar Cells*, 238, p.111629.
- [26] Kwasi-Effah, C.C., Ighodaro, O.O., Egbare, H.O. and Obanor, A.I., 2023. Recent progress in the development of thermal energy storage mediums for solar applications. *J. Eng. Dev.*, 15(1), pp.146-170.
- [27] Andreu-Cabedo, P., Mondragon, R., Hernandez, L., Martinez-Cuenca, R., Cabedo, L. and Julia, J.E., 2014. Increment of specific heat capacity of solar salt with SiO₂ nanoparticles. *Nanoscale research letters*, 9, pp.1-11.
- [28] Ho, M.X. and Pan, C., 2014. Optimal concentration of alumina nanoparticles in molten Hitec salt to maximize its specific heat capacity. *International Journal of Heat and Mass Transfer*, 70, pp.174-184.
- [29] Ma, B. and Banerjee, D., 2017. Experimental measurements of thermal conductivity of alumina nanofluid synthesized in salt melt. *AIP Advances*, 7(11).
- [30] Zhao, C.Y. and Wu, Z.G., 2011. Thermal property characterization of a low melting-temperature ternary nitrate salt mixture for thermal energy storage systems. *Solar Energy Materials and Solar Cells*, 95(12), pp.3341-3346.
- [31] Ahmad, N.N.B., Yunos, N.B., Muhammad, W.N.A.B.W., Mohamad, M.N.A.B. and Yusof, F.B., 2017, October. Effect of lithium nitrate and calcium nitrate composition on the thermal properties of quaternary molten salts mixture for heat transfer application. In *Journal of Physics: Conference Series* (Vol. 914, No. 1, p. 012027). IOP Publishing.
- [32] Fernández, A.G., Ushak, S., Galleguillos, H. and Pérez, F.J., 2014. Development of new molten salts with LiNO₃ and Ca(NO₃)₂ for energy storage in CSP plants. *Applied Energy*, 119, pp.131-140.
- [33] Porter, T., Vaka, M.M., Steenblik, P. and Della Corte, D., 2022. Computational methods to simulate molten salt thermophysical properties. *Communications Chemistry*, 5(1), p.69.
- [34] Qaisrani, M.A., Ahmed, N. and Wang, Q., 2022. Working, modeling and applications of molten salt TES systems. In *Synergy Development in Renewables Assisted Multi-carrier Systems* (pp. 279-309). Cham: Springer International Publishing.
- [35] Shin, D. and Banerjee, D., 2011. Enhancement of specific heat capacity of high-temperature silica-nanofluids synthesized in alkali chloride salt eutectics for solar thermal-energy storage applications. *International journal of heat and mass transfer*, 54(5-6), pp.1064-1070.
- [36] Hu, Y., He, Y., Zhang, Z. and Wen, D., 2017. Effect of Al₂O₃ nanoparticle dispersion on the specific heat capacity of a eutectic binary nitrate salt for solar power applications. *Energy Conversion and Management*, 142, pp.366-373.
- [37] Lenert, A. and Wang, E.N., 2012. Optimization of nanofluid volumetric receivers for solar thermal energy conversion. *Solar Energy*, 86(1), pp.253-265.
- [38] Muhammad, W.N.A.W., Mohamad, M.N.A. and Tukimon, M.F., 2022. Characterization and Heat Transfer Performance of Quarternary Nitrate Based Molten Salts. *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences*, 97(1), pp.35-46.
- [39] Zhao, B.C., Cheng, M.S., Liu, C. and Dai, Z.M., 2018. System-level performance optimization of molten-salt packed-bed thermal energy storage for concentrating solar power. *Applied Energy*, 226, pp.225-239.
- [40] Kwasi-Effah, C.C., Ighodaro, O., Egbare, H.O. and Obanor, A.I., 2022. Characterization and comparison of the thermophysical property of ternary and quaternary salt mixtures for solar thermal power plant applications. *Results in Engineering*, 16, p.100721.
- [41] Kwasi-Effah, C.C., Egbare, H.O., Obanor, A.I. and Ighodaro, O.O., 2023. Development and characterization of a quaternary nitrate based molten salt heat transfer fluid for concentrated solar power plant. *Heliyon*, 9(5).
- [42] C. C. Kwasi-Effah, (2024) Advancements in Heat Transfer Fluids for Concentrated Solar Power Systems: A Brief Review," 2024. [Online]. Available: <https://doi.org/10.5281/zenodo.14020385>
- [43] C. C. Kwasi-Effah, (2024) Heat Transfer Fluids in Solar Thermal Power Plants: A Review," *NIPES – Journal of Science and Technology Research*, [Online]. Available: <https://journals.nipes.org/index.php/njstr/article/view/1109>

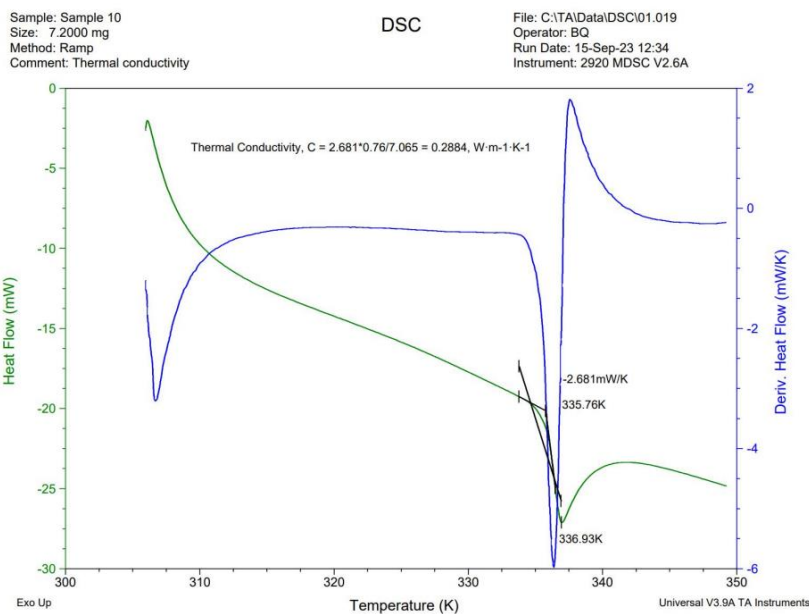
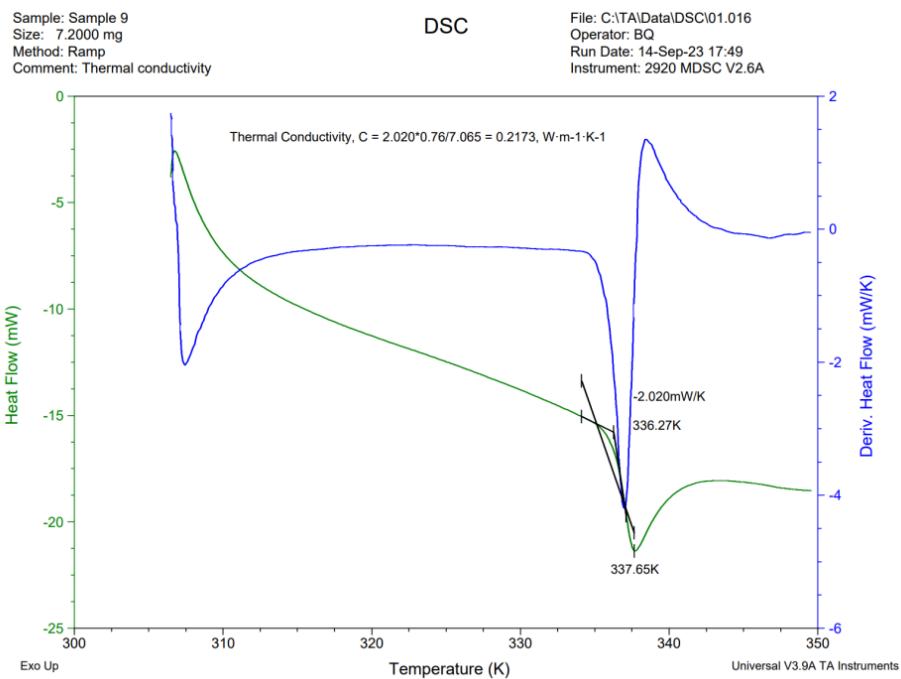
- [44] S. J. Wagner, "Environmental and Economic Implications of Thermal Energy Storage for Concentrated Solar Power Plants," Ph.D. dissertation, Carnegie Mellon University, Pittsburgh, PA, USA, 2011.
- [45] C. C. Kwasi-Effah, (2024) "Economic Viability and Cost Analysis of Thermal Energy Storage in Concentrated Solar Power Systems," *NIPES - Journal of Science and Technology Research*, vol. 6, no. 10, [Online]. Available: <https://doi.org/10.5281/zenodo.14020575>
- [46] M. Lambrecht, B. Wagner, F. Jost, and others, "Evaluation of the environmental impacts and economical study of Solar Salt in CSP-parabolic trough technology," *Materials at High Temperatures*, vol. 40, no. 4, pp. 331–337, 2023.
- [47] C. C. Kwasi-Effah, (2024) "Environmental Impact and Sustainability of Thermal Energy Storage in Concentrated Solar Power Systems." *NIPES - Journal of Science and Technology Research*. vol. 1, no. 10, <https://doi.org/10.5281/zenodo.14020637>
- [48] Esfe, Mohammad Hemmat, et al. "Experimental study on thermal conductivity of DWCNT-ZnO/water-EG nanofluids." *International Communications in Heat and Mass Transfer* 68 (2015): 248-251.
- [49] Mahian, Omid, et al. (2013) "A review of the applications of nanofluids in solar energy." *International Journal of Heat and Mass Transfer* 57.2: 582-594.
- [50] Esfe, Mohammad Hemmat, et al. (2014) "Thermophysical properties, heat transfer and pressure drop of COOH-functionalized multi walled carbon nanotubes/water nanofluids." *International Communications in Heat and Mass Transfer* 58: 176-183.
- [51] C. C. Kwasi-Effah. (2024) "Optimizing Heat Transfer Fluids for Enhanced Thermal Conductivity in Concentrated Solar Power Systems". *NIPES - Journal of Science and Technology Research*. <https://doi.org/10.5281/zenodo.14020708>
- [52] Yousefi, Tooraj, et al. "An experimental investigation on the effect of Al₂O₃-H₂O nanofluid on the efficiency of flat-plate solar collectors." *Renewable Energy* 39.1 (2012): 293-298.

Appendix A: DSC Plots for Undoped Samples









DSC Plots for Doped Samples

