

Effect of SiO₂ Nanoparticle in Low-Temperature Molten Salts as Heat Transfer Fluid for Heat Recovery System

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Abstract

The utilization of low-temperature molten salts as heat transfer fluids in heat recovery systems has gained significant attention due to their advantageous physical and thermal properties. The relatively low thermal conductivity of molten salts limits their overall efficiency in transferring heat. The objective of this research to study the characteristic and thermal properties of quaternary molten with addition of SiO₂ nanoparticle. Quaternary molten salt mixture of substance are LiNO₃, KNO₃, Ca(NO₃)₂, NaNO₃ with combination of nanoparticle, SiO₂ were used. Thermo Gravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), Differential Thermal Analysis (DTA) and X-Ray Diffraction (XRD) testing were conducted. Based on the results and data discussion, the best composition of SiO₂ nanoparticles in the quaternary molten salt for heat transfer fluid and heat storage was determined. Sample B exhibited the lowest melting point of 87.3°C, sample B had the highest heat capacity of 1.6 J/K.g, and sample C demonstrated the best thermal stability with the lowest mass change of -0.538917mg. Therefore, it can be concluded that Sample B had the optimal composition of SiO₂ in the quaternary molten salt, providing a low melting point and high heat capacity.

1. Introduction

The integration of SiO₂ nanoparticles into low-temperature molten salts as heat transfer fluids (HTFs) for heat recovery systems has shown promising results in enhancing thermal properties and system efficiency. The addition of SiO₂ nanoparticles to molten salts, such as quaternary mixed nitrates, has been experimentally demonstrated to improve the fluidity and thermal performance of these salts. Specifically, the presence of nanoparticles reduces the time required to achieve uniform temperature during heat storage by 17.9%, delays the rapid temperature drop near heat exchangers, and enhances convective heat transfer. This results in a 16% extension in effective heat release time and a 13.8% increase in cumulative heat release, providing a theoretical basis for optimizing single-tank heat storage systems [1].

The thermal properties of molten salts are significantly influenced by the inclusion of SiO₂ nanoparticles. Studies have shown that the thermal conductivity of molten salts can be increased by up to 54.5% with a 10% weight loading of SiO₂ nanoparticles. This enhancement is attributed to the improved probability and frequency of ion collisions within the molten salt, as evidenced by changes in potential energy. Additionally, the specific heat capacity of molten salt-based nanofluids is higher than that of pure base salts, which is not solely due to the higher specific heat capacity of the nanoparticles themselves. Instead, the forces between nanoparticle atoms and base salt ions create a more stable state that requires more energy to deform, thus improving the heat storage properties of the nanofluids [2,3]. The stability and size of SiO₂ nanoparticles also play a crucial role in the

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performance of molten salt-based nanofluids. Nanoparticles larger than 450 nm demonstrate superior stability compared to smaller particles, with negligible increases in viscosity. However, the enhancement of specific heat capacity and thermal conductivity is not observed for larger nanoparticles, indicating a trade-off between stability and thermophysical property improvement. This suggests that optimizing the size of nanoparticles is essential for developing stable and efficient molten salt-based nanofluids [4].

Furthermore, the use of SiO₂ nanoparticles in molten salts offers additional benefits, such as reduced corrosion rates. Silica nanoparticle suspensions have been shown to lower corrosion rates of copper substrates by up to four times compared to neat molten salts. This is due to the negative surface potential of silica nanoparticles, which form surface 'nano-fins' that prevent negatively charged ions from approaching the metal surface, thereby reducing metal dissolution rates. This phenomenon, known as the 'nano-Fin Effect,' highlights the multifaceted advantages of incorporating SiO₂ nanoparticles into molten salts for heat recovery systems [5].

In summary, the incorporation of SiO₂ nanoparticles into low-temperature molten salts significantly enhances their thermal properties, stability, and corrosion resistance, making them highly effective as heat transfer fluids in heat recovery systems. The improvements in fluidity, thermal conductivity, specific heat capacity, and reduced corrosion rates underscore the potential of these nanofluids in optimizing thermal energy storage and transfer processes. Future research should focus on optimizing nanoparticle size and concentration to balance stability and thermophysical property enhancement, further advancing the application of SiO₂ nanoparticle-doped molten salts in various thermal systems.

2. Experimental Method

Several compositions were prepared utilizing the range of compositions shown in Table 1 determine the optimal mix of quaternary nitrate salts.

Table 1 Composition quaternary molten salt

Types of molten salt	Composition (wt%)	Mass (wt%)
KNO ₃	54.55	54.55
NaNO ₃	9.09	9.09
LiNO ₃	18.18	18.18
Ca(NO ₃) ₂	18.18	18.18

The first quaternary heat transfer fluid was created by combining primary molten salt mixes with the composition range shown in Table 1. The mass ratio for producing quaternary molten salt is 6:1:2:2 [6]. The mixing of quaternary molten salt were stored in a furnace to eliminate any water and moisture from the mixture for 4 hours to dry at 150°C. After the drying process is completed, the dried salt mixture is placed in a tube furnace for melted at temperature of 400°C for 8 hours. Then the mixture is taken and cooled for several hours until it reaches a temperature of 115°C. One the cooling process are done the quaternary molten salt were crushed into powder in preparation for following process. Next, the process for adding SiO₂ nanoparticles in quaternary molten salt. Three samples of silicon dioxide (SiO₂), each with a different composition, were added after the quaternary molten salt combination was created. SiO₂ mass and composition with quaternary molten salt are displayed in Table 2. To identify the best compositions among these three distinct compositions, 0.5 wt%, 1.0 wt%, and 1.5 wt% SiO₂ compositions were chosen [7].

Table 2 The mass and composition of quaternary molten salt with SiO₂

Sample	SiO ₂ composition (wt%)	SiO ₂ mass (gram)
A	0.5	0.1
B	1.0	0.2
C	1.5	0.3

Following the completion of the quaternary molten salt, the mixture was separated into 3 samples in accordance with Table 2. SiO₂ and quaternary molten salt were mixed according to Table 2. The mixture was heated at 250°C for 90 minutes in a furnace to combine it thoroughly. Then, the nanocomposite is dried in an 80°C drying box until it is ready to be tested. The samples were crushed into tiny particles once the chilling process was complete to conduct material testing [8].

To characterize the physical and thermal properties of the salt mixture, four different types of testing must be carried out, including the measurement of the melting point using differential thermal analysis (DTA), the measurement of the thermal stability using thermal gravimetric analysis (TGA), the measurement of heat

capacities using differential scanning calorimetry (DSC) and the element analysis using X-ray diffraction (X-RD) [9].

3. Result and Discussion

The data analysis procedure is essential and necessitates thorough research and careful evaluation in order to reach the expected results and meet all objectives and scopes. In this study, a molten salt mixture that consists of quaternary properties is analyzed to meet the criteria for a heat transfer fluid with a low melting point, thermal stability, and heat capacity.

3.1 Melting Point

One of the properties of molten salt as a heat transfer fluid is the melting point, where the mixture starts to melt and turns into liquid. Differential Scanning Calorimetry (DSC) was used to determine the melting point of the molten salt. According to Table 3, there are 3 kinds of samples with relatively lower melting points. Sample B reached a melting point of 87.3°C, sample A obtained 115.3°C and sample C obtained 101.1°C. Sample B shows that the melting point temperature of the best composition of the quaternary molten salt then Sample A and C. By comparison to Ren et al., 2014 [10], samples A and C have a higher melting point, most likely because potassium nitrate has the highest melting point among the components. Thus, based on the research conducted, sample B reached the lowest melting temperature (refer Fig. 1).

Table 3 The melting point of nanoparticle quaternary molten salt

Sample	Composition of SiO ₂	Sample testing weight (wt%)	Melting point (T _m) °C
A	0.5	25.7	115.3
B	1.0	24.9	87.3
C	1.5	25.6	101.1

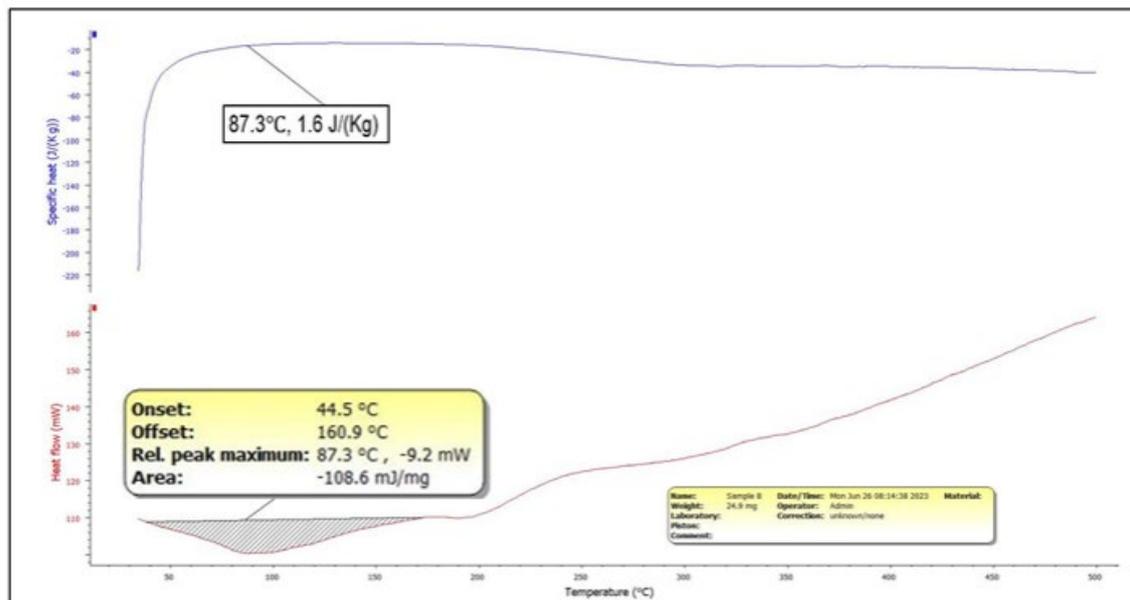


Fig. 1 DSC curve of sample B (54.55 wt% KNO₃, 9.09 wt% NaNO₃, 18.18 wt% LiNO₃, 18.18 wt% Ca(NO₃)₂, 1.0 wt% SiO₂)

3.2 Heat Capacity

From Table 4, sample A accomplished a heat capacity of 1.3 J/K.g while sample B achieved 1.6 J/K.g and sample C attained 1.2 J/K.g. Sample B has a high heat capacity and low melting point. Compared to Song et al., 2018 [7], all samples' specific heat in this study is slightly low because the manual mixing technique is not good enough compared to the thermostatic salt bath as in research. When the mixing time exceeds the critical mixing time, the heat capacity of the nanofluids rises by varying amounts depending on the preparation parameters.

Table 4 The heat capacity of nanoparticle of quaternary molten salt

Sample	Composition of SiO ₂ (wt%)	Heat Capacity (J/K.g)
A	0.5	1.3
B	1.0	1.6
C	1.5	1.2

3.3 Thermal Stability

The thermal stability of the graph is determined through the total mass change from the test (as shown in Table 5 and Fig 2). The mass change of the sample is decreased over time because the sample’s mass degrades when the heat is applied. The mass change is thus negative, indicating that the end sample’s mass is smaller and reduced as compared to the mass before testing. As a result, the sample with the lowest mass change might be designated as the best sample. The maximum temperature or stability limit is often defined as the temperature at which the sample has lost 3% of its starting weight. So, it can be said that sample C has the best mass change when compared to sample A and B (refer Fig. 2). The high weight loss is due to evaporation-absorbed water.

Table 5 The thermal stability of nanoparticle quaternary molten salt

Sample	Composition of SiO ₂ (wt%)	Mass Changes (mg)
A	0.5	-0.185413
B	1.0	-0.186064
C	1.5	-0.538917

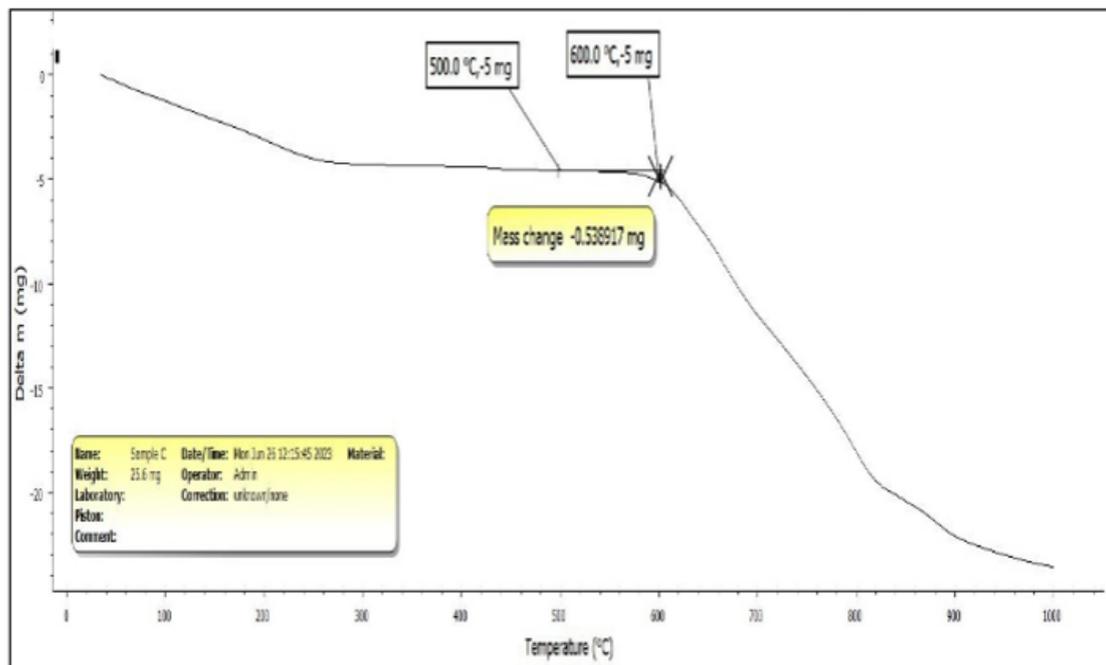


Fig. 2 TGA curve of sample C (54.55 wt% KNO₃, 9.09 wt% NaNO₃, 18.18 wt% LiNO₃, 18.18 wt% Ca(NO₃)₂, 0.5 wt% SiO₂)

3.4 Element Analysis

The sample primarily consists of potassium nitrate, sodium nitrate, lithium nitrate, calcium nitrate and silicon dioxide (refer Fig. 3). However, in practical applications, molten salt cannot meet air, so calcium nitrate does not form. Apart from the absence of calcium nitrate, the other components of the sample remain relatively unchanged, although there are slight variations in the position and intensity of their peaks. The transformation of a portion of calcium nitrate resulted in a slight deviation in melting point, initial crystallization points and thermal decomposition temperature during the experiment. In summary, during the experiment, some of the calcium

nitrate dissolved into the lattice of other compounds, forming a new solution. However, this does not affect the performance testing of the new low melting point salts, which demonstrate high-temperature tolerance and good thermal stability [11].

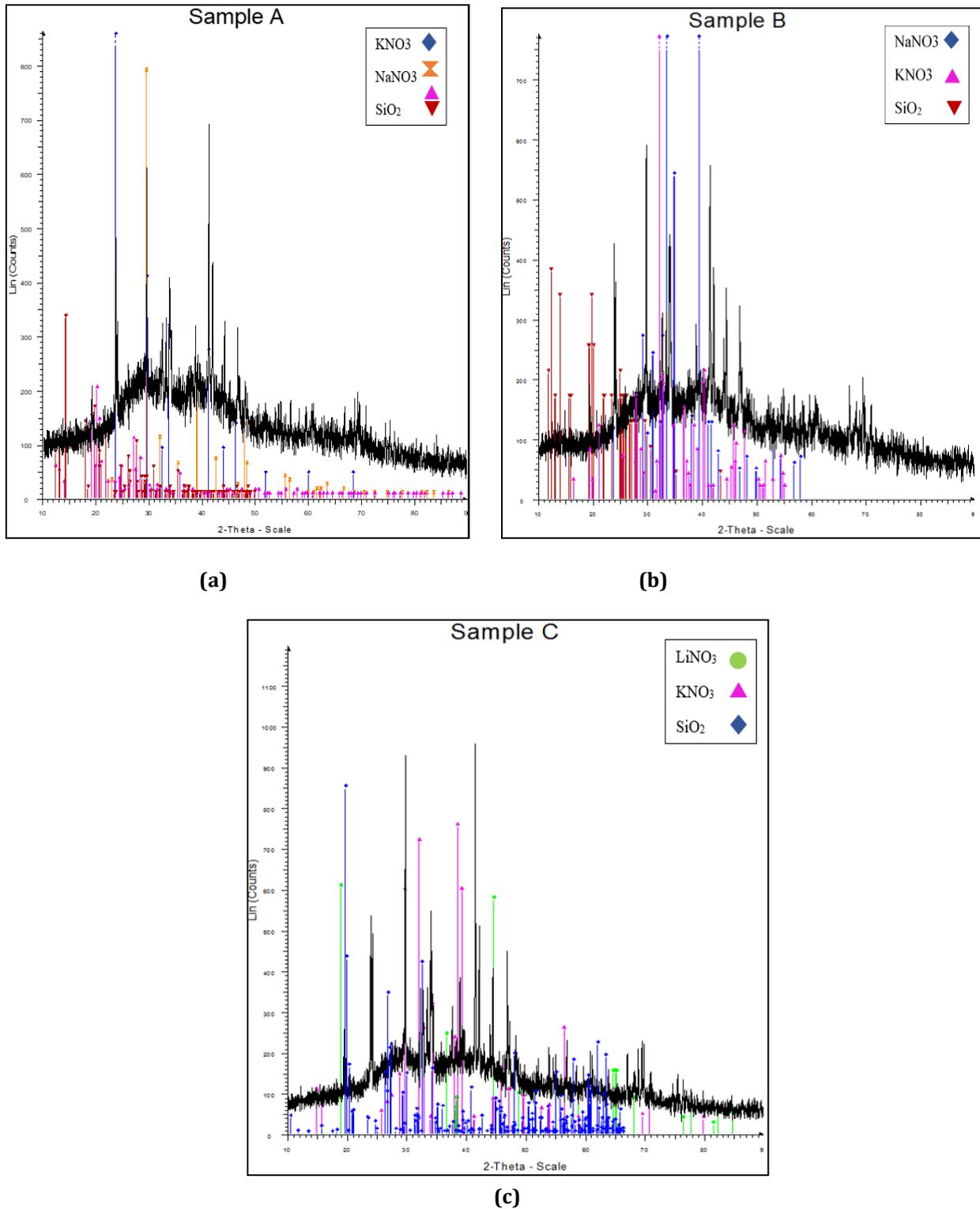


Fig. 3 X-RD graph of nanoparticles of SiO₂ of (a) Sample A; (b) Sample B; (c) Sample C

4. Conclusion

The experiments successfully achieved the desired objectives of the study. The main objective was to prepare a nanoparticle quaternary molten salt composition based on nitrate salts. The composition consisted of four salt components: KNO_3 , NaNO_3 , LiNO_3 , and $\text{Ca}(\text{NO}_3)_2$. All three samples with varying concentrations of Silicon dioxide (SiO_2) nanoparticles (0.5wt%, 1.0wt%, and 1.5wt%) were prepared for analysis using TGA, DSC, and X-RD tests. The selection of salts for the mixture was based on the physical and thermal properties of the individual salts, including melting point, thermal stability, heat capacity, and element analysis of the nanoparticle quaternary molten salt, achieving the second objective. Based on the results and data discussion, the best composition of SiO_2 nanoparticles in the quaternary molten salt for heat transfer fluid and heat storage was determined. Sample B exhibited the lowest melting point of 87.3°C, sample B had the highest heat capacity of 1.6 J/K.g, and sample C demonstrated the best thermal stability with the lowest mass change of -0.538917mg. Therefore, it can be concluded that Sample B had the optimal composition of SiO_2 in the quaternary molten salt, providing a low melting point and high heat capacity.

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Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of the paper.

Author Contribution

The authors are responsible for the study conception, research design, data collection, data analysis, result interpretation and manuscript drafting.

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