Effect of Expanded Graphite on Nitrate-Based Phase Change Materials being used in Thermal Energy Storage Systems

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Abstract. This research is focused on the preparation and characterization of new graphite-based phase change material (PCM) for energy storage application. Characterization like microstructure and chemical composition were discussed using XRD and SEM with EDX. Added to the above thermal conductivity of the prepared samples were studied. This PCM is based on nitrate fillers with expanded graphite (EG). Samples were synthesized with EG concentration of 3%, 5%, 7% and 9 wt%. This composite PCM consists of salts and graphite or eutectic. The SEM images shown the uniform distribution of EG into the nitrate based PCM. Thermal conductivity measurement shows the thermal conductivity is increased with EG concentration. The obtained results suggest that the graphite-based nitrate PCM is a promising element to use in high-thermal energy storage applications.

Keywords: Expanded graphite; Sodium nitrate (NaNO₃); Potassium nitrate (KNO₃); XRD; SEM

1. Introduction
According to the recent studies, the lack in commercial suitability of solar energy-based electricity generation is due to variability of solar energy source, which reduces the overall plant efficiency. In commercially available photovoltaic technologies, the dynamic variations of solar radiation were induced by passing clouds, which is relevant in case of concentrated solar technology. Smoothing these natural phenomena is seen as an appealing option with the aid of effective thermal storage device instead of a mixture of fossil fuels. During the day, solar radiations are available it will be considered to be more during the mid-day. The necessary excess power well be gathered, stored and eventually released early in the morning, at night and also during peak times. Three major thermal storage methods currently considered are sensitive heat, latent heat and thermo chemical heat. At present, this sort of storage is referred to medium-term storage. In case of sensitive heat storage, thermal energy is retained by changing the temperature of the storage system. The amount of energy stored depends on its particular temperature and the difference in temperature. It can also be used for medium-term storage, primarily dedicated to short-term storage (adapted to handle complex variations such as cloud effects) with water vapour buffer storage (up to 6 hrs). As that of the simplest technology, the use of molten salt as a storage medium has been well developed and found to be implemented in the development of solar electricity with thermo cline [1] or two tank systems [2]. Higher energy storage densities [3] are considered to provide latent heat storage (LHS) methods. Heat is stored by solid to solid and liquid to solid or gas to liquid storage phase change storage. In fact, around the same time span, the solid-liquid phase transition is poor due to volume variation and significant variation in enthalpy. Thermal chemical reactions are the foundation of the last approach to thermal storage [4]. Corresponding performance could require long-term storage, but combined with excessive costs, its technological complexity is found to be not easy to integrate with higher solar power generation. This study was based on a latent approach for heat energy storage and more precisely, on a solid-liquid phase-change transition materials according to the results of literature studies. The first phase
relates to the choice of PCMs based on maximum storage capability, minimum cost, less impact on the environment, stability, thermal conductivity and industrial availability. According to the literature the majority of PCMs are available at working temperature and concerned with present thermal conductivity in the range of 1 Wm⁻¹K⁻¹[5, 6]. This contributes to a decrease in the heating system and controlled release during the solid-liquid phase transition [7]. Various approaches have been developed for the successful improvement of thermal transfer by the increase of the heat transfer area [8], inclusion of conductive fins [9], metal dispersion [10], and brushes of oriented or random carbon fibres [11], carbon nano fibres dispersion [12] and expanded natural graphite (ENG) impregnation [13]. Recently, the use of nano-particles is often used to overcome such problems [14, 15]. Recent studies to incorporate expanded graphite with PCMs have shown a remarkable improvement in thermal conductivity of PCMs [16]. In addition, graphite was incorporated with flammable polymers as a fire-retardant agent [15, 17, 18]. The purpose of this work is to investigate the thermal and physical property of EG incorporated with nitrate- based PCM materials [19]. EG by nature is a porous material possessing high thermal conductivity and high specific surface area [20, 21].

2. Experimentation:

2.1 Materials used
Commercial potassium and sodium nitrate with a melting point 330°C and 310°C, bulk density 2100Kg/m³ and 2260Kg/m³ respectively are utilized. Commercial EG with a density of 25-470 kg/m³ and thermal conductivity of 1.4 W/mk is used.

2.2 Sample Preparation
The figure 1 shows, synthesis flow routes of samples. The weighed amount of individual salts were loaded into crucibles and heated in box furnace. The temperature was initially maintained at 150°C for four hours, then the temperature was increased up to 400°C. The mixture was stirred periodically and the same temperature was maintained for 8-10 hrs in order to obtain the homogenized mixture. After melting, the samples were needed to retain at temperature of 115°C for one hour before removing the sample from the furnace. The prepared composite samples were taken out of furnace, cooled at room temperature and the prepared composites are labeled corresponding to the amount of graphite.

![Figure 1. Synthesis steps for molten salts and graphite composition](image-url)
2.3 Characterization Methods
SEM was carried out in an EOL JCM 6000Plus from 5x to 60kx at a resolution of 10 nm and EDX elemental analysis were carried from Boron to Uranium elements. X-ray diffraction was carried in Rigako by using mono chromatized Cu Kα radiation with Ni filter in the 2θ range of 10-20. The thermal conductivity of pure KNO₃ and NaNO₃ and their mixture with different EG quantities was evaluated using a laser thermal conductivity analyzer (LFA).

3. Result and discussions
3.1 Analysis of morphology
Figure 2 shows the SEM image of EG added molten salts with different weight percentages. The loose and porous structure of the EG with appropriate mixing and absorption of KNO₃/NaNO₃ were observed. Thermal composite appears to have achieved a uniform and homogeneous crystal structure of KNO₃/NaNO₃ into pores of expanded graphite.

![SEM images](image1.png)

Figure 2. Microstructure of molten salts and graphite composition

3.2 Chemical Compositions Analysis
The chemical composition of the materials observed by EDX is used to identify the specimen elementary composition. The EDX spectrum displays peaks corresponding to the energy level, each of these peaks are found to be unique to an atom and corresponds to a single element. A higher peak in the spectrum represents the more concentrated element in the specimen. Figures 3 and 4 shows the EDX of molten salts with EG. The graphite is a crystallized form of the carbon element. The higher
peaks in EDX analysis reveal the presence of higher concentration of carbon. Comparing the EDX of KNO$_3$ and NaNO$_3$, KNO$_3$ has a higher spectrum peak because its crystal aggregation is higher than that of NaNO$_3$ and the particle size is also larger. When the mass percentage of KNO$_3$ is increased, the carbon count is reduced. It is because of the overlap of KNO$_3$ crystal collected along the path of crystal growth.

![Figure 3. Chemical composition graph of KNO$_3$ (57%)/NaNO$_3$ (40%) /graphite (3%)](image)

![Figure 4. Chemical composition graph of KNO$_3$ (62%)/NaNO$_3$ (28%) /graphite (9%)](image)

3.3 XRD

XRD patterns of EG porous material and its composites with KNO$_3$ and NaNO$_3$ salts are shown in Figure 5(a-d). It is found to represent a wide asymmetrical angle of asymmetrical peak dispersion at 2θ angle between 5-90\(^\circ\), the respective climax covers a broad peak observed around 27.5\(^\circ\). The two distinct peaks of the polymeric mixture are found between 27.5\(^\circ\) and 28.9\(^\circ\) which are the characteristic peaks of the polymeric mixture of KNO$_3$/NaNO$_3$/EG. Decrease in the width of the corresponding peaks shall be found in case of KNO$_3$/NaNO$_3$/EG 5 wt %. This could be due to the disruption, but EG
in the crystalline structure of KNO$_3$/NaNO$_3$. KNO$_3$/NaNO$_3$/EG 7 wt % composite shows further decrease in may due to higher ionic potassium size (K$^+$), which was found to reduce further in crystalline structure due to dispersion of KNO$_3$-NaNO$_3$ chain in the composite. The ionic radius of Na$^+$ is much smaller than K$^+$ which may not interrupt the interaction between KNO$_3$ & NaNO$_3$ chains.

![XRD pattern of KNO$_3$/NaNO$_3$ with 3wt% of graphite](image1.png)

**Figure. 5(a)** XRD pattern of KNO$_3$/NaNO$_3$ with 3wt% of graphite

![XRD pattern of KNO$_3$/NaNO$_3$ with 5wt% of graphite](image2.png)

**Figure. 5(b)** XRD pattern of KNO$_3$/NaNO$_3$ with 5wt% of graphite
Thermal conductivity

The results of measurements of thermal conductivity at room temperature as a function of the graphite in the composite are shown in the figure 6. Graphite is an allotropic form of carbon in its crystal structure, acts as a thermal conductivity enhancer as it possesses the free electron in a valence shell. EG has improved its loose and porous structure that can absorb more nitrate salts per unit volume. In present investigation, four samples with 3 wt%, 5 wt%, 7 wt% and 9 wt% of EG have been evaluated by laser flash method at room temperature. As shown in Fig.6, findings showed that pure KNO₃/NaNO₃ thermal conductivity increased from 0.5 W/mK to 1.52 W/mK with an addition of 3 wt% to EG, 1.98 W/mK with an addition of 5 wt% to EG, 2.1 W/mK with an addition of 7 wt% to EG and 2.3 W/mK with an addition of 9 wt% to EG preferring a uniform heat distribution.
Figure 6. Thermal conductivity of the molten salts with graphite

The thermal conductivity of all composition is shown to increase with increase in the quantity of EG. Evolution of nitrate or eutectic chloride is observed equivalent and similar findings are found in industrial PCMs with high purity. It is generally seen that the composite material has a considerably higher thermal conductivity than the pure PCM.

Thermal conductivity of the pure KNO$_3$/NaNO$_3$ was found to be 0.5 W/m.K, which is very low and limits the applicability in thermal energy storage material. In fact Materials with low thermal conductivity cannot achieve a uniform distribution of heat between their composites. This aspect was observed to cause the creation of heat spots which were actually detrimental to any practical system. This is the key reason why nitrate salts have been incorporated into thermal conductivity enhancers (TCE’s) in order to improve their thermal transport properties.

4. Economic impact

Apparently the added graphite material is going to occupy some of space inside nitrate salts and reduce the heat storage capacity of thermal energy storage device. Still a small percentage (< 7%) of heat storage losses is acceptable compared to a large increase in heat transfer in the solid boundary. The cost of EG is found to be cheap for large applications in industrial products, so there is a very small rise in the heat storage systems cost. A survey shows that price of EG is 11-15% lower than that of PCM salts. In the indirect molten salt system, the oil-salt heat exchanger and molten salts were responsible for 15-30% of the total cost. With the same thermal energy storage capacity, an additional 3-9% of expanded graphite can only be produced at less than 1-5% extra cost. Added to this, the output power is determined by the heat transfer of the thermal energy storage system. Though the heat transfer can be increased with the inclusion of porous graphite by 2-3 times, other aspects like the mixing phase, overall cost of the TES system which can be measured by using EG as a small change or even a reduction of up to 10 %.

5. Conclusions

The new composite material such as EG added in-organic PCMs was found to increase the efficiency of thermal storage system. This material is particularly for medium-concentration thermal storage system in the temperature range of 200 to 300oC. Microstructural and Chemical composition study of prepared samples conformed that the physical integration of the KNO3/NaNO3 with graphite. The graphite as a supporting material, it appears to be an efficient element to improve the efficiency of molten salts. The thermal conductivity of the synthesized material is found to increase with an increase in the graphite content. From above study the new prepared composite can be used for medium temperature energy storage system applications.
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