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Original Paper

Effect of Nano-Silica on The Thermo-Physical Properties of the Thermal Eutectic $(Na_{0.6}K_{0.4})NO_3$ System

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Abstract

Here, we investigate the effect of adding nano-silica particles on the thermo-physical properties of the $(Na_{0.6}K_{0.4})NO_3$ based thermal energy storage systems. Five different systems tagged as M_{00}, M_{01}, M_{02}, M_{03} and M_{04}, with different nano-silica percentage of 0, 1, 2, 3, and 4 wt%, respectively, were prepared. Various experimental techniques were employed to study the thermo-physical properties of the systems during (solid-solid) phase P_1, (solid-liquid) phase P_2 and (liquid-solid) phase P_3, and to clarify the effect of nano-silica on the thermal energy storage efficiency during both charging and discharging processes. According to the Differential Scanning Calorimeter (DSC) thermal analysis, it was found that the system M_{02} whose nano-silica addition rate of 2 wt%, has the most favorable thermal characteristics (i.e., highest specific heat and lowest enthalpy change). Moreover, the addition of 2 wt% represents the optimum distribution of nano-silica inside the principal base system M_{00}. This leads to an improvement in the porosity of the system due to the degree of homogeneity caused by the thermophoresis effect distribution, the high surface area of the nano-silica with the activity of the M_{00} matrix alongside the degree of the alkalinity of nano-silica. Besides, the electric conductivity measurements showed that the 2wt% percentage is the optimum one for thermal energy storage systems.

Keywords

phase change material, thermal storage, nano silica, calorimetry

1. Introduction

Thermal energy storage systems can be classified into sensible heat storage, latent heat storage and thermo-chemical heat storage. Latent heat storage systems use the Phase Change Materials (PCMs) as thermal energy storage media, where the thermal energy is stored or released during the material phase change transition processes. Phase Change Materials (PCM) have been widely used for the thermal storage systems due to their capability of storing and releasing large amounts of energy within a small PCM volume, a moderate temperature variation and prolong the charging and discharging period. Additionally, significant attention has been given to using salts as a phase change storage media (using encapsulation and otherwise) (Goswami et al., 1990, pp. 257-262; Xu et al., 2015, pp. 286-307; Gaosheng et al., 2018, pp. 1771-1786; Hassan et al., 2019, pp. 491-523). Moreover, several mixtures of alkali nitrates and nitrites have been used as a heat transfer medium because of its low cost and good compatibility with common structural materials (Borul et al., 1954, pp. 233-238). The $NaNO_3$-KNO_3 system is one of the most extensively investigated binary inorganic salt systems (Voskresenskaya et al., 2017, pp. 431-437; Silverman et al., 1977, pp. 1-26; Kamimoto et al., 1981, pp. 319-331; Kearney et al., 2003, pp. 170-176; Zhang et al., 2003, pp. 441-446; Berg et al., 2004, pp. 2224-2229; Villada1 et al., 2014, pp. 622-625; Lin et al., 2018, pp. 685-708). The PCM's low thermal energy storage efficiency remains, however, a big challenge for researchers. The PCM's thermal performance is positively correlated with three different parameters, the thermal conductivity coefficient, area for heat transfer, and the heat transfer temperature difference. Accordingly, the thermal performance can be enhanced by; enhancing the thermal conductivity, extending the heat transfer area, and improving the uniformity of heat transfer processes (Tao et al., 2018, pp. 245-259). The thermal conductivity can be enhanced by using additives with high thermal conductivity coefficient. The high thermal conductivity carbon-based, metal- fillers, porous materials, and nano-particles are commonly used as additives to enhance the thermal conductivity of the PCM (Lin et al., 2018, pp. 2730-2742). Using of the metal-based porous material, such as metal foam enhances heat transfer by reducing the cell size leading to the large contact surface area. In this case, the scattered air within the pores expands significantly to cause the ejection restriction of the phase transformation for the PCM during the actual operation at elevated temperatures (Wu et al., 2011, pp. 1371-1380). Using metal fillers led to a reduced discharging time and significant weight and cost to the thermal storage systems as well (Farid et al., 2004, pp. 1597-1615). In addition, corrosion could appear when using salts as PCM (Joel, 2008; Dorete et al., 2012, pp. 13-25; Grant, 2002, pp. 1-34). Also the addition of graphite to the binary thermal storage system leads to enhance the thermal conductivity coefficient and reduced the total latent heat (Xiao et al., 2015, pp. 272-284; Berg et al., 2004, pp. 2224-2229; Xiao et al., 2014, pp. 52-58; Zhao et al., 2014, pp. 272-277; Lopez et al., 2010, pp. 1586-1593). For nano-enhanced PCM material, the thermal conductivity depends not only upon the nano particle's concentration, the particle size and shape, but also on the base PCM material (Chieruzzi et al., 2013, pp. 448-456; Dudda et al., 2013, pp. 37-42; Leong et al., 2019, pp. 18-31; Jeyaseelan et al., 2019, pp. 235-242). In contrast to previous studies,

which addressed the impact of nano-particle on the thermal performance of PCM thermal storage material, the current study is devoted to investigate the effect of nano silica on both the thermal and the physical properties of the binary molten salt $0.6NaNO_3$-$0.4KNO_3$. Phase Change Materials (PCMs) based on latent heat energy storage techniques over a nearly isothermal temperature range using Paraffin Wax Nano composite Based on Carbon-Coated Aluminum Nano particles have been regarded (Chen et al., 2017, pp. 12603-12609). The thermal stability of paraffin wax was improved by the shape stabilization with 10 wt% of carbon nano tubes (Fredi et al., 2017, pp. 405-420). They mentioned that the modified paraffin wax is a promising strategy to meet the highly efficient thermal management system for electric vehicles.

2. Method

The binary salt was prepared by mixing 60% of $NaNO_3$ with 40% of KNO_3 by weight, in its solid form; these salts nitrates are ultra-pure from Aldrich Company. The mixture heated up to 350℃ to achieve a complete melting for this mixture; the system was then cooled at room temperature. This system represents the eutectic system $(Na_{0.6}K_{0.4})NO_3$, and denoted in this work as M_{00} system. The solid binary salt was then milled to powder, and the nano-silica was dispersed into four concentrations: 1, 2, 3 and 4 wt% in the solid binary nitrate $(Na_{0.6}K_{0.4})NO_3$ system separately to get M_{0x} (x=1, 2, 3, and 4%wt.) systems. The binary system and the nano-silica particles were dispersed in 20 ml of distilled water by ultrasonic mixing for 2 hours using MXBAOHENG Ultrasonic Homogenizer FS-T Series with nominal frequency of 20 kHz. The solutions were stirred by the strong ultrasonic homogeneous instrument for 2 hours, afterwards, the water solutions were heated at 150℃ on a hot plate to fully remove the water for at least 1 hour (Shin et al., 2011, pp. 1064-1070).

By grinding the dried composites, samples were obtained, after the operation process for all samples, they were immediately used for thermal, electrical, structure and electron macroscopic analysis, to identify the effect of the nano-silica on the thermo-physical properties for the $(Na_{0.6}K_{0.4})NO_3$, which is representing the thermal storage media.

3. Result

3.1 DSC Measurements

The DSC thermo grams measurements for M_{00} and M_{0x} (x=1, 2, 3, 4 wt%) systems have been carried out during heating and cooling. The DSC measurements were performed by using SHIMADZU DSC-60 plus series equipment. Figure 1 shows the thermo-grams for the base matrix (M_{00}) as representative example. The figure indicates to the existence of three peaks. The first broad peak located at $\approx 125\,^{o}C$, is mainly due to the solid-solid phase transition (P_1). This phase is related to the change in the specific heat (sensible heat storage) and the transition from the displacive type modified by orientation switching (Bauer et al., 2010, pp. 272-278; Al Sharhani, 2016; Hatakeyama et al., 1989, pp. 327-335).

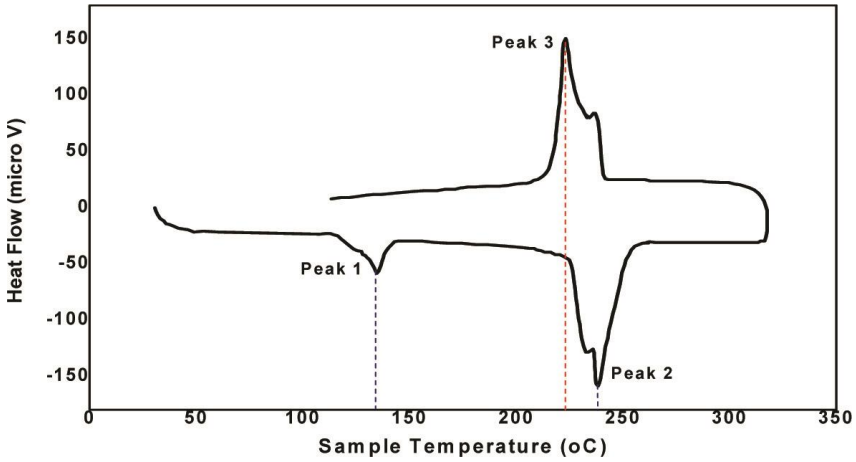

Figure 1. The DSC Thermo-Grams for M_{00} System

While the second endothermic peak located at ≈234°C, is related to the melting point of the M_0 system, i.e., the phase change from solid-liquid phase (P_2). The third exothermic peak at ≈223°C represents the phase change from liquid-solid phase (P_3), i.e., the solidification process. The same three peaks appeared with the thermograms measurements of the samples M_{0x} (x=1, 2, 3, 4 %wt.). The variations in the thermal parameters, such as the enthalpy, transition point, and peak position have been studied for all samples. For example, the specific heat of the sample scan be determined from the relation (Hatakeyama et al., 1989, pp. 327-335):

$$Cpx = \left(\frac{I_x}{I_s}\right)\left(\frac{M_s}{M_x}\right) C_{ps} \quad (1)$$

Where I_x is the peak height of the sample, I_s is the height of the standard material from the zero line of the starting of the equipment (DSC), M_s is the mass of the standard material (Al_2O_3), M_x is the mass of the sample and C_{ps} is the specific heat of the standard material.

Also, the activation energy for all phases (P_1, P_2 and P_3) at any system by using the modified Kissinger equation (Rysava, 1987, pp. 1015-1021):

$$\ln(\Delta Q) = G - \frac{Eg}{kT} \quad (2)$$

Where different heights corresponding to different temperatures for each peak have been obtained. The extracted data were used to plot as ln(ΔQ) and1/T according to the equation and hence to get the activation energy.

All the thermal kinetic parameters for the M_0 system are shown in Figure2 (a and b) as representative example. It can be easily seen that the transition temperature does not nearly change in the all phases (P_1, P_2 and P_3) with the increasing the concentration of the nano-silica in the M_{0x} system. These results suggest that the nano-silica inside the M_{0x} system having a uniform distribution and a homogeneous dispersion. This leads the SiO_2 (nano-silica) takes part in the network structure as a network former (Chieruzzi et al., 2013, pp. 448-456).

The variations in entropy (ΔH), the peak height, the transient temperature (ΔT) and the transient time (Δt) with the concentration of the nano-silica for all phases (P_1, P_2 and P_3) are mainly related to the distribution effect on the interaction potential of Na^+ and K^+ ions around the $(NO_3)^-$ group in the M_{0x} system (Taha et al., 1994, pp. 217-226). For the entropy (ΔH) and the peak height, it is clear from the figure that there is a minimum value corresponding to concentration value x≈2% of nano-silica. This means that the M_0 system at that percentage become more stable than that at any other concentration of nano-silica, due to the stability of the thermodynamics function (Thirriwg, 2006, pp. 113-121).

The minimum value of (ΔH) at this concentration (x≈2% of nano-silica) indicates that the system has a higher ordered and mechanical stability than other any concentration.

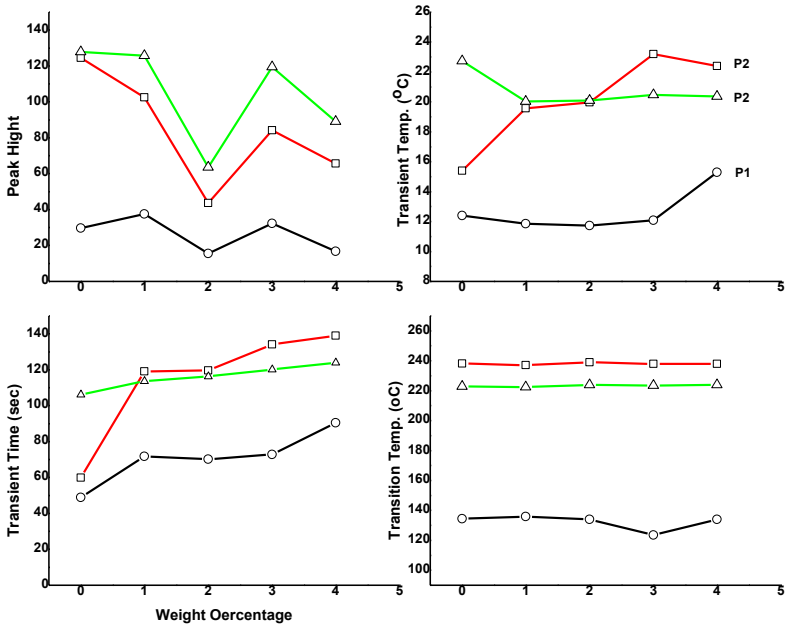

Figure 2. The Thermal Kinetic Parameters (Peak Height, Transient Temperature, Transient Time and Transition Temperature) for M_{0x} System with Different Concentration of Nano Silica

This is supported by the variation of the transient temperature (ΔT) and the transient time (Δt), where (ΔT) and (Δt) which does not nearly change in the concentration range 1%≤ x≤ 2% for each phase (P_1, P_2 and P_3). These results are mainly related to the introduction of the incompatible second components, like K^+ ion in the $NaNO_3$ structure or Na^+ ion in the KNO_3. The introduction of ions influenced the order kinetics in a significant way which is related to the equilibrium kinetics in the M_0 system (Ping et al., 2009, pp. 27-36).

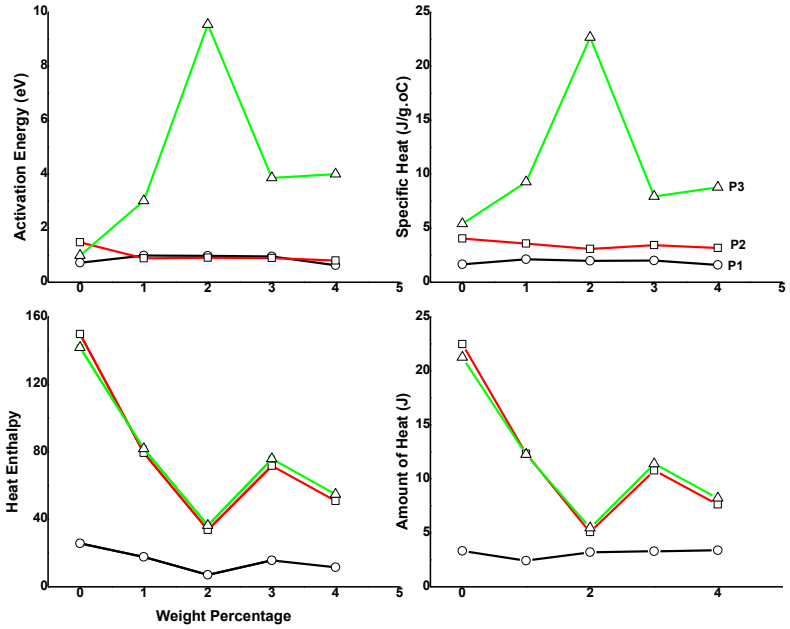

Figure 3. The Thermal Kinetic Parameters (Activation Energy, Specific Heat, Heat Enthalpy and Amount of Heat) for M_{0x} System with Different Concentration of Nano Silica

The changes in the activation energy (E_g), the specific heat (C_p) and the latent heat (ΔQ) for the different phases (P_1, P_2 and P_3) in the M_{01} systems are mainly related to the thermal activation process in this system. These parameters are affected by the concentration percentage of nano-silica and the variation in the strength of Na^+ and K^+ ions bonds in the $(Na_{0.6}k_{0.4})NO_3$ (M_0) system. This variation in the bonds strength plays an important role in the delocalization of charge carried inside the M_{0x} system. The changes in the latent heat (ΔQ) and (C_p) for the phase (P_1) are very small, because this phase has a rather low heat for the transformation process. However, in the two phases P_2 and P_3, the changes in ΔQ and C_p are greater than the phase P_1, which is mainly related to the large volume variations during the transformation process.

The value of the activation energy in phase (P_3) is higher than the values obtained for the phase P_2 and phase P_1. This is because the ordered parameters in the phase P_3 increase with decreasing the temperature of transformation (liquid-solid). However, the ordered parameters decrease with increasing the temperature in phase (P_2) (solid-liquid) phase, i.e., higher disorder, so that the E_g in phase P_3 is higher than P_2 and P_1 phases (Papon et al., 2002).

The effect of the nano-silica on the thermal properties for the thermal storage M_0 system could be potentially due to the large distribution of the nano-silica per unit volume. This is because the nano-particl has a small diameter and could be more effective dispersed into the salt $(Na_{0.6}K_{0.4})NO_3$ and give better pores system and thermal characteristic, that is mainly related to the high specific surface energy in the M_0 system associated with the high surface area of the nano- silica inside the M_0 matrix (Chieruzzi et al., 2013, pp. 448-456).

The obtained results confirmed that the rates of changes in the kinetic and thermo-physical parameters are mainly dependent on the concentration rate of nano-silica inside this system. The results confirmed that the optimum concentration for the thermal storage $(Na_{0.6}K_{0.4})NO_3$ system is x≈2% of nano-silica.

3.2 Electrical and Thermal Conductivity Measurements

One of the most popular of the nano-silica is mainly related to its good resistance of heat and electricity, so that it has tendency to agglomerate or cluster due to the dominant intermolecular Van der-Waals interaction between the particles. So that the electrical and thermal conductivity of the mixed samples with nano-silica particles mainly depend on the characterization of these nanoparticles and the uniform of dispersion of the nanoparticles in the matrix $[Na_{0.6}K_{0.4}]NO_3$ (Ning et al., 2009, pp. 518-523).

Figure 3 shows the variation of the electrical conductivity for the system M_{01} as a function of the temperature. The inset shows the variation of electrical conductivity with the concentration of nano silica at certain temperature (≈125^{o}C). From this figure, we can see that the values of electrical conductivity increase with increase the nano-silica up to x=2%, and then it decreases with the increase of the nano-silica. This modification enhanced the electrical conduction mechanism inside the M_{01} system (Chieruzzi et al., 2013, pp. 448-456). The increase in the electrical conductivity up to x=2%, may be related the mono dispersion of spherical nano-silica in the matrix M_0 system. Besides that, the increase in the rate of the reorientation process inside the M_0 matrix for the K^+ and Na^+ ion surrounding the NO_3^- ion group by the effect of temperature on the M_{01} matrix. However, the decreasing in the electrical conductivity with the increasing of nano-silica after (x=2% wt), could be attributed to the reduction in the bond of mobility ions released by the distribution of nano-silica inside the M_0 matrix. It could be also attributed to the effect of the alkalinity degree of nano-silica ratio for the M_{01} system. Also, the nano-silica has a lower relative density than M_0 system, therefore for given mass replacement from nano-silica into the M_0 system consequently leads to a lower pore volume, due to the size of the nano-silica particles. Beside that the nano-silica is not a good conductor for the electrical properties (Kumar, 2008, pp. 684-687).

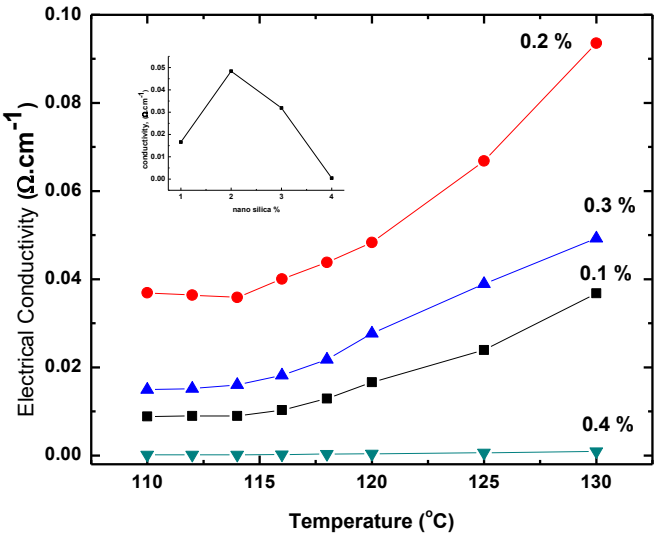

Figure 4. The Variation of Electrical Conductivity with Temperature for Different Nano-Silica Concentrations in the Solid-Solid Phase

The activation energies of the M_{0x} crystal systems are calculated according to the well-known exponential relation (Rysava, 1987, pp. 1015-1021).

The dependence of activation energy on the concentration of nano-silica is shown in Figure 4. It is clear from the figure that there is a minimum value at x=2% nano silica. The variation of activation energy is mainly related to the lattice thermal vibration and the formation of polarizabillity arising from the cationic Na^+ and K^+ ions around the $(NO_3)^-$ group (Taha, 1989, pp. 341-354).

This process is mainly affected by the temperature of the system and the rate of concentration of nano-silica inside the M_0 matrix system. The modification of activation energy (Eg) by the presence of nano silica can be attributed to the appearance of different polaronic and defect levels in the structure of the M_{01} system (Papon et al., 2002).

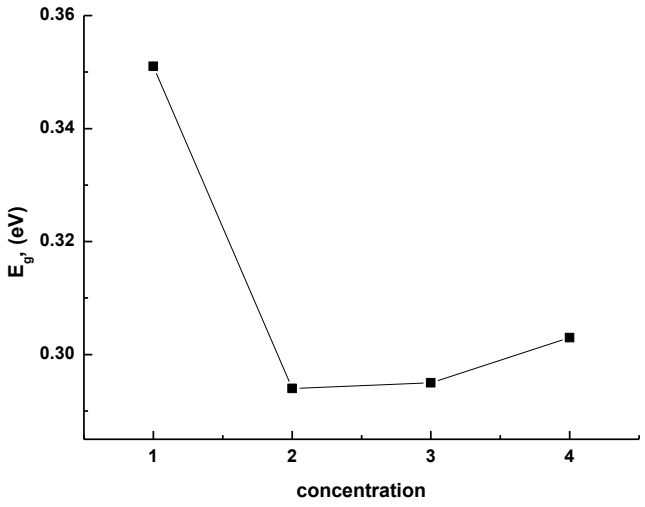

Figure 5. The Variation of Activation Energy Eg with Different Concentrations of Nano Silica in the Solid-Solid Phase

The thermal conductivity (k) for theM_{0x} systems was calculated from the analysis of the DSC thermo-gram curve for the phase P_1 and during heating by using the following relation:

$$k = \frac{qL}{A(T_h - T_l)} \quad (3)$$

Where q is the heat flow, L is the thickness, A is the area, (T_h-T_l) is the difference between high and low temperature.

The variation of the thermal conductivity k of the M_0 and M_{01} systems with the concentration of the nano-silica is shown in Figure 5. It is clear from the figure that thermal the conductivity decreases with the increasing of concentration of the nano-silica and then it reaches a nearly constant value starting at x=2% of nano silica.

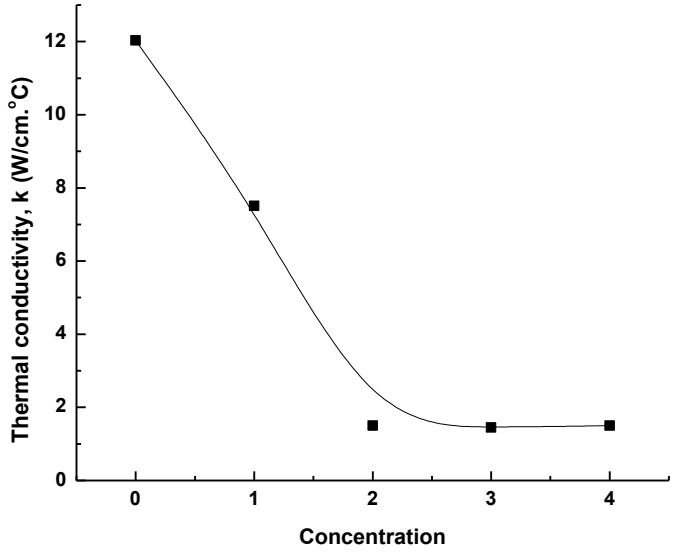

Figure 6. The Variation of Thermal Conductivity with Different Concentration of Nano-Silica for M_{01} System in the Solid-Solid Phase

This indicates that the presence of nano silica increases the thermal resistance to the thermal fluctuations process (Kumar, 2008, pp. 684-687).

It can be said also that the stability of thermal conductivity starting at x=2%. This is because the decreasing for the thermal fluctuations leads to decrease in the free energy, i.e., the system become thermally stable (Kumar, 2008, pp. 684-687).

4. Conclusion

The additive nano-silica to the eutectic $(Na_{0.6}K_{0.4})NO_3$ system bring a new and good additional physical properties to the thermal storage materials, which reasonable to improve the thermal charge and discharge heat energy during the phase changes transformation process. It has been found that the optimum conditions for this additive are satisfied at 2% wt for nano-silica Nano-silicais characterizes by high mechanically stability and act as insulator for heat and electricity. The variation in the thermo-physical properties (C_p, ΔH, ΔQ, and peak height) for each phase (P_1, P_2 and P_3) are mainly related to the effect of the nano-silica. It causes also an enhancement in the thermal properties, which is the aim from this work. The thermal analysis measurements indicated that nano-silica has no effect on the transition temperature (T_r), which is mainly related to the high stability of solid-solid phase (P_1), due to the kinetic hindrance of the disphasic region (Na K) around the (NO_3) group in the M_0 system. The effect of the nano-silica on the thermal storage media (M_0) matrix is mainly related to the reflected modification of the electronic structure of this material. This considerable variation can be attributed to the appearance of different polaronic and defect levels. It has been found that the system M_{02} whose

nano-silica addition rate of 2 wt%, has the most favorable thermal characteristics. This leads to an improvement in the porosity of the system due to the degree of homogeneity caused by the thermophoresis effect distribution. The distribution of the nano-silica in the M_0 system (thermophoresis effect) makes changes in the porous ratio, due to the high specific area of the nano-silica. This change in the porous system leading to effect on the performance of heating and cooling cycle, beside the rate of melting and freezing for this system.

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