Effect of solvent on specific heat capacity enhancement of binary molten salt-based carbon nanotube nanomaterials for thermal energy storage

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Abstract

The specific heat capacity of a binary molten salt-based carbon nanotube nanomaterial was experimentally measured in both solid and liquid phases. The effect of the solvent on the specific heat capacity was examined for a wide range of chemical compositions for a binary carbonate salt mixture. The binary salt mixture consisted of lithium carbonate and potassium carbonate. Multi-walled carbon nanotubes were dispersed in the solvent to synthesize the nanomaterials. A surfactant, gum arabic, at 1% mass concentration with respect to the solvent was added to disperse the carbon nanotubes homogeneously in the salt mixture. The results indicated that the specific heat capacity of the carbonate salt mixtures was significantly enhanced by adding the carbon nanotubes in the solid and liquid phases. Moreover, the enhanced specific heat capacity was affected by the chemical composition of the salt mixtures. Furthermore, molecular dynamics simulations were used to examine the effects of different chemical compositions of the binary salt mixtures with nanotubes on the specific heat capacities of the nanomaterials.

Keywords: Nanomaterial, Specific heat capacity, Carbon nanotubes, Molten salt, Molecular dynamics simulation

1. Introduction

Since nanofluids have been firstly shown to significantly increase the thermal conductivity of solvents [1], the thermal conductivity of the nanofluids has been extensively studied for a variety of nanoparticles (as summarized in [2, 3]). Additionally the drastically increased critical heat flux in pool boiling was also observed by You et al. [4]. These exceptional features of nanofluids have spurred research into diverse heat transfer applications and have promoted the use of nanofluids as working fluids. A number of experimental and numerical studies utilizing nanofluids in diverse fields have been reported in the past two decades [5-12]. Initially, conventional liquids, such as water, alcohol, and ethylene glycol, were used as nanofluid solvents. Over time, other solvent materials, such as alkali molten salts, have been utilized in unique nanofluid applications, such as thermal energy storage. Molten salts and their eutectics have been considered to be thermal energy storage media for concentrating solar thermal power plants and heat transfer fluids in heat exchangers.

Recently, studies have shown that the specific heat capacity of the molten salt-based nanofluids or nanomaterials were significantly enhanced in the solid and liquid phases by the dispersion of nanoparticles in salts [13-20]. However, contradictory observations have been made on the specific heat capacity of the nanofluids and nanomaterials (summarized in [21]). In 2009, Nelson et al. [22], reported that the specific heat capacity of polyalphaolefin-graphite nanofluids was enhanced up to 50% compared with that of the solvent and further increased with temperature. Following that study, other reports observed increased specific heat capacities of other nanofluids and nanomaterials. However, the mechanism responsible for the increased specific heat capacity

remained unknown. A previous study suggested several enhanced specific heat capacity models between nanoparticles and solvent molecules [14] and reported the existence of dense liquid layering adjacent to nanoparticles. This phenomenon was confirmed experimentally and numerically [22-24]. However, there remains insufficient experimental evidence to support a definitive conclusion. Therefore, additional work is required to examine the effects of different experimental conditions on the specific heat capacity of different solvent materials.

The aim of this study is to investigate the effect of solvent composition on the specific heat capacity enhancement for binary carbonate salt-based nanomaterials mixed with multi-walled carbon nanotubes. As performed in a previous study [17], which tested two chemical compositions, the effects of the chemical composition of two constituent salts for the solvent phase on the specific heat capacity were examined for a wide range of compositions. To verify the effects of the solvent phase composition on the specific heat capacity, measurements of the specific heat capacity were carried out for a variety of carbonate salt chemical compositions. These measurements help determine how the thermal and chemical properties of pure solvents influence the specific heat capacity of nanomaterials formulated from nanoparticles mixed with solvent.

In the present study, the specific heat capacity of the nanomaterials was measured in the solid and liquid phases, which have different solvent chemical compositions. The chemical composition of each nanomaterial was obtained using inductively coupled plasma-mass spectrometry (ICP-MS) after specific heat capacity measurements were performed using a differential scanning calorimeter. Based on the results for the specific heat capacity and the chemical composition, the effect of the chemical composition on the thermal properties of the solvent was resolved.

Finally, molecular dynamics simulations were also conducted to numerically investigate the characteristics of the compressed layers, which have been implicated in enhancing specific heat capacity, as a function of the chemical composition of the solvent material.

2. Nanomaterial Synthesis

Binary carbonate salt mixtures were used as solvents for the molten salt nanomaterials. The salt mixture was composed of lithium carbonate (Li_2CO_3 , Sigma Aldrich, St. Louis, MO) and potassium carbonate (K_2CO_3 , Sigma Aldrich, St. Louis, MO). Multi-walled carbon nanotubes (MWCNTs, Meliorum Technologies, Rochester, NY) were dispersed in the carbonate salt mixtures ($\text{Li}_2\text{CO}_3 + \text{K}_2\text{CO}_3$). The diameter and length of the MWCNTs were 10-30 nm and 1.5 μm , respectively. All chemicals were used as received. Figure 1 shows images of the MWCNT taken by a transmission electron microscope (TEM, JEOL JEM-2010). Figure 2 shows the nanomaterial synthesis procedure. First, the MWCNTs were dispersed in distilled water with 0.1 wt.% gum arabic (Sigma Aldrich, St. Louis, MO). The concentration of the MWCNTs was fixed at 1% mass ratio with respect to the base salt mixture. Gum arabic was used as a surfactant because it was reported that the gum arabic is appropriate to prevent the agglomeration of the MWCNTs during the dehydration step shown in Fig. 2 [19]. A water-MWCNT suspension was sonicated in an ultrasonic bath for 2 hours (Step 1). Afterward, the carbonate salt mixture was added to the aqueous MWCNT suspension (nanofluid), and the resultant aqueous salt-MWCNT nanofluid was subjected to sonication again for 3

hours (Step 2). Finally, the aqueous salt-MWCNT nanofluid was evaporated on a large petri dish on a hot plate set at 100 °C to recover the dehydrated powder of the molten salt-based MWCNT nanomaterials (Step 3).

Fig. 1. Transmission electron microscope images of multi-walled carbon nanotubes.

Fig. 2. Schematic of the synthesis of molten salt nanomaterials.

3. Specific Heat Capacity Measurements

A differential scanning calorimeter (DSC, TA Instruments-Q20) was used to measure the specific heat capacity of the pure salt mixtures and nanomaterials. Based on the heat flow measured by the DSC instrument, the specific heat capacity was determined by following a standard method, American Standard Test Method (ASTM E1269)

[26]. The heat flow difference between an empty pan (Tzero aluminum pan, TA Instruments) and a reference sapphire disk was recorded over the temperature. The measurements were repeated for all samples (pure salt mixture or nanomaterials) under the same thermal cycling conditions. Because this study only focused on the specific heat capacity of the molten salt-based MWCNT nanomaterials, during the heating process, the temperature was rapidly ramped at 20 °C/min. This ramp rate is fast in comparison with those used in other DSC studies [27-29], but increased the measurement accuracy of the specific heat capacity [30], because the measured heat flow was proportional to the sample mass, specific heat capacity, and heating rate, as shown in Eq. (1). A slower heating rate would have been considered if phase change-related thermal properties, such as transition temperature or latent heat, were of the primary focus.

$$\frac{dQ}{dt} = m \cdot c_p \cdot \beta \quad (1)$$

where dQ/dt is the heat flow, m is the sample mass, c_p is the sample specific heat capacity, and β is the heating rate.

The thermal cycle of the DSC was conducted between 150 °C and 560 °C. Due to thermal equilibrium issues, the first heat flow curves in all measurements for the empty pan, the sapphire disk, and the samples (pure salt mixtures and nanomaterials) were excluded in the calculation of the specific heat capacity. For the samples, the thermal cycles in the DSC were repeated 5 times to determine the reproducibility of the measurements and the variations (i.e., degradation) in the specific heat capacity. The enhancement of the specific heat capacity was examined for both solid (at 400 °C) and liquid (average from 525 to 555 °C) phases.

As shown in Fig. 3, after the evaporation step (Step 3), two different patterns (a fine salt region and a coarse salt region) formed on the petri dish. It was expected that, in the fine salt region, lithium carbonate was more concentrated, and in the coarse salt region, potassium carbonate was more concentrated. Because the specific heat capacity of the carbonate salt mixture used in this study is strongly dependent on the overall chemical composition, we next determined the exact compositions of the base salt mixtures. Jo and Banerjee reported that the specific heat capacity of the carbonate salt mixture in the liquid phase varied from 1.29 to 2.75 J/g·K as the concentration of lithium carbonate increased from 25 to 83% [31]. The chemical composition of the base salt mixtures for the nanomaterial samples was examined using ICP-MS. The dehydrated nanomaterial samples on the petri-dish were divided into the two regions and were subsequently subjected to DSC and ICP-MS measurements. Five samples of the solvent (at different lithium carbonate and the potassium carbonate concentrations) were obtained from the ICP-MS measurements and correlated with the specific heat capacity measurements. To determine the enhancement of the specific heat capacity for the five nanomaterial samples, the specific heat capacity values of the pure salt mixtures at the same composition as those of the nanomaterials were estimated by interpolating the measured values for the pure salt mixtures in our previous study [31]. Figure 4 exhibits the specific heat capacity of the pure carbonate salt mixture in the liquid phase as a function of the lithium carbonate composition. The specific heat capacity values of the carbonate salt mixtures under the same compositions of the nanomaterials (indicated by arrows) were interpolated from previously reported results or extrapolated from reference data. For example, the specific heat capacity of the pure carbonate salt mixture for Case 3 (the $\text{Li}_2\text{CO}_3\text{:K}_2\text{CO}_3$ molar ratio is 64.3:35.7) was determined by a linear interpolation of two adjacent data points at

61.9 mol. % and 66 mol. % of lithium carbonate. The specific heat capacity values in both liquid and solid phases for the five carbonate salt mixture compositions are reported in the Results section.

Fig. 3. Photo image of the nanomaterial obtained on a petri dish after dehydration process.

Fig. 4. Specific heat capacity of pure carbonate salt mixtures as a function of the composition [31].

Fig. 5. Compressed liquid layer in a molecular dynamics simulation domain.

4. Molecular Dynamics Simulation

In previous studies, a dense layer of solvent liquid (compressed liquid layer) was experimentally and numerically observed in various types of nanomaterials [17, 23-25, 32]. Figure 5 shows an example of a configuration (a carbon nanotube and surrounding salt molecules) used in the molecular dynamics (MD) simulations in this study. The compressed liquid layer is indicated as a shaded area adjacent to the carbon nanotube. As shown in the cumulative density curve of the salt mixture in Fig. 5, the compressed liquid layer had higher density values compared with the average density. As hypothesized in previous studies, the compressed liquid layer is a unique characteristic of

nanomaterials and may be responsible for enhancing the specific heat capacity. Furthermore, as reported in an earlier study, the enhancement of the specific heat capacity of the same carbonate salt mixture as that used in this study was influenced by different features of the compressed solvent liquid layer near the nanoparticles [17].

For these reasons, MD simulations were performed to examine the construction of the compressed liquid layer and the characteristics of the salt molecules near the MWCNTs. The Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS; Sandia National Laboratory) was used to calculate the interactions. The construction of the carbon nanotube, the salt molecules, and a simulation domain was accomplished using Material Studio (Accelrys, Inc. 2008). Instead of using MWCNTs, a (6, 6) armchair single-walled carbon nanotube (SWNT) was modeled in the MD simulations, and the total number of salt molecules was fixed at 1500 molecules. The simulation domain was a 50 Å-sized cube. Initially, the SWNT was placed at the centroid of the simulation box, and the molecules of the salt mixture were randomly situated in the box. A periodic boundary condition was applied to the simulation domain.

The interactions between two atoms were determined by a Lennard-Jones (LJ) potential with the Coulomb force for non-bonded atoms, as shown in Eq. (2). The LJ potential parameters for the SWNT were obtained from the literature [24], and the parameters for the solvent salt mixture were obtained from Material Studio based on a cvff force field. As for the interaction of unlike atoms, the LJ potential parameters were calculated by using the arithmetic mean of Eq. (3). A cutoff radius of 12 Å was used for calculating the LJ interactions. Additionally, as

shown in Eq. (4), bond-stretching, bending, and torsion were considered in simulating the bonded-interactions. All parameters of each atom for the non-bonded and bonded interactions are listed in Table 1.

The same simulation procedures as previous studies were used to explore the interactions between the carbonate salt mixture and the nanoparticles [17, 32]. As mentioned earlier, because of the arbitrary placement of the solvent molecules, there was a high probability for the intermolecular spacing to acquire non-physical values, i.e., some of the molecules may overlap within the simulation domain. This initial state (non-physical situation) is not appropriate for the simulation of the interaction between the SWNT and the solvent molecules. Hence, an energy minimization step was enforced to separate the solvent molecules, thereby enabling a more realistic numerical simulation. In the minimization step, the solvent atoms adjacent to the SWNT were moved and the temperature of the system was decreased to 0 K. After carrying out the minimization, an equilibrium procedure was implemented in two steps. First, a relaxation step was performed using a micro-canonical ensemble (NVE integration). Subsequently, the temperature of the system was increased to a certain starting temperature by the isobaric-isothermal (NPT) ensemble. In the present study, 800 K was used as the starting temperature, i.e., greater than the melting temperature of the salt mixture (761 K). Following the equilibration process at 800 K, the temperature of the SWNT was instantaneously increased to 1400 K and the final simulation (NVE ensemble) was carried out. In this process, the energy transfer between the SWNT and the surrounding solvent was examined.

$$E(r) = \frac{q_i \cdot q_j}{r} + 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (2)$$

$$\varepsilon_{i,j} = \sqrt{\varepsilon_i \cdot \varepsilon_j}, \quad \sigma_{i,j} = \frac{(\sigma_i + \sigma_j)}{2} \quad (3)$$

$$E = K_s \cdot (r - r_0)^2 + K_b \cdot (\theta - \theta_0) + K_t \cdot (1 + d \cdot \cos(n\phi)) \quad (4)$$

Table 1 System parameters for molecular dynamics simulations

Lennard-Jones constants					Stretching		Bending		Torsion		
Material	Interaction	ε [kcal/mol]	σ [Å]	charge	K_s	r_0	K_b	θ_0	K_t	d	n
SWNT	C - C	0.105	3.851	0	480.0	1.340	90.000	120.0	12.370	-1.00	2
Eutectic	C - C	0.148	3.617	+1.54	4612.0	1.290	107.4354	120.0	1.1392	-1.00	0
	O - O	0.228	2.880	-1.18							
	Li - Li	4.735	2.839	+1							
	K - K	5.451	3.197	+1							

5. Measurement Uncertainty

According to ASTM method employed in this study, the specific heat capacity was determined by the following

equation [26]:

$$c_{p,s} = c_{p,st} \frac{\Delta q_s \cdot m_{st}}{\Delta q_{st} \cdot m_s} \quad (5)$$

where c_p , Δq , m are the specific heat capacity, the heat flow difference between the specimen and the empty pan, and

the mass, respectively. Subscripts s and st represent the samples and sapphire reference material, respectively.

Because the heat flow differences in Eq. (5) were obtained by subtracting the baseline heat flow (empty pan, subscript b) from the heat flow of the sapphire and the sample, the measurement uncertainty is given by Eq. (6) [33]:

$$\frac{U_{c_{p,s}}}{c_{p,s}} = \sqrt{\left(\frac{U(c_{st})}{c_{st}}\right)^2 + \left(\frac{U(\Delta q_b)}{\Delta q_b}\right)^2 + \left(\frac{U(\Delta q_{st})}{\Delta q_{st}}\right)^2 + \left(\frac{U(\Delta q_s)}{\Delta q_s}\right)^2 + \left(\frac{U(m_{st})}{m_{st}}\right)^2 + \left(\frac{U(m_s)}{m_s}\right)^2} \quad (6)$$

As shown in Eq. (6), the measurement uncertainty results from the reference sapphire and sample specific heat capacities, masses and heat flows. The heat flow is the most dominant uncertainty at $\pm 2\%$. The maximum measurement uncertainty of the specific heat capacity was estimated to be $\pm 3.5\%$.

6. Results

Figure 6 compares the specific heat capacities of the nanomaterials in the liquid phase with those of the pure carbonate salt mixtures as a function of the chemical composition (molar ratio of the carbonates). The specific heat capacities of the pure carbonate salt mixtures and the nanomaterials drastically increased at around 65% molar concentration of the lithium carbonate. It was recently reported by Jo and Banerjee that the specific heat capacity of the pure carbonate salt mixture in the liquid phase abnormally behaves as the composition of two salts. However, no clear explanation was provided for the drastic increase of the specific heat capacity of the pure carbonate salt mixture with 66 to 68 mol. % lithium carbonate [31]. The authors indicated that the heat flow in liquid phase fluctuated with

the temperature within the narrow composition range. It is expected that abundant lithium carbonate more than the eutectic composition (62 mol. % lithium carbonate) may stay as slurry-like solid, and it would affect the specific heat capacity of the liquid phase pure carbonate salt mixture.

As shown in Fig. 6, the specific heat capacity of the nanomaterial was significantly enhanced for all samples. However, the increment in the specific heat capacity was not identical in the nanomaterial samples. The results show that the enhanced specific heat capacity of the nanomaterials was influenced by the solvent or chemical composition.

Fig. 6. Specific heat capacity of pure carbonate salt mixtures and nanomaterials in liquid phase for five different chemical compositions.

The ICP-MS-measured carbonate salt mixture chemical composition of the solvent for the nanomaterial samples varied from 36.6 mol. % to 79.2 mol. % lithium carbonate. As mentioned earlier, the specific heat capacity of the pure salt mixtures for the same compositions as those of the nanomaterials were estimated from the measured data from a

previous study [31]. The specific heat capacity of the pure solvent varied from 1.35 J/g·K to 2.53 J/g·K, increasing with the lithium carbonate composition. For the nanomaterials, the specific heat capacity varied from 1.71 J/g·K to 3.27 J/g·K. The specific heat capacity measurements and the chemical compositions are summarized in Table 2. As shown in Fig. 6, the level of enhancement in the specific heat capacity of the nanomaterial samples (red circle), compared with those of the pure salt mixtures (black triangle), increased as the chemical composition of the neat solvent increasingly deviated from the eutectic composition (i.e., $\text{Li}_2\text{CO}_3\text{:K}_2\text{CO}_3$ at a molar ratio of 62:38). While the enhancement of the specific heat capacity for Case 3 in Table 2 (64.3:35.7) was limited to 6.0%, the specific heat capacity enhancements for Case 1 (79.2:20.8) and Case 5 (36.6:63.4) were 29.3% and 26.7%, respectively.

Table 2 Chemical compositions and specific heat capacity of pure salt mixtures and nanomaterials

Cases	Molar composition ($\text{Li}_2\text{CO}_3\text{:K}_2\text{CO}_3$)	Pure salt mixtures [J/g·K]		Nanomaterials [J/g·K]	
		Solid (400 °C)	Liquid (525-555 °C)	Solid (400 °C)	Liquid (525-555 °C)
1	79.2:20.8	1.284	2.526	1.612	3.266
2	68.0:32.0	1.239	2.501	1.359	3.015
3	64.3:35.7	1.218	1.676	1.312	1.777
4	42.5:57.5	1.126	1.410	1.161	1.700
5	36.6:63.4	1.070	1.348	1.219	1.707

Fig. 7. Specific heat capacity of nanomaterials and pure salt mixtures in solid phase (400 °C) for five chemical compositions of solvent.

A similar feature was observed in the solid phase at 400 °C, as shown in Fig. 7. The level of enhancement in the specific heat capacity of the nanomaterial samples (blue square) compared with those of the pure salt mixture (black triangle) increased as the chemical composition of the neat solvent increasingly deviated from the eutectic composition. The plot of the specific heat capacity for the pure carbonate mixture monotonically increased and was a fairly linear function of the lithium carbonate concentration. However, the plot for the nanomaterial shows an upwardly concave shape. Although the composition in the solid phase at a minimum level of enhancement did not correspond with that in the liquid phase, it was observed that the increase in the specific heat capacity of the nanomaterials in the solid phase was also higher at both ends.

The enhancements in the specific heat capacity of the nanomaterials were plotted for both liquid and solid phases in Fig. 8. The enhancement plots are V-shaped as the mole fraction of lithium carbonate in the mixture increased. As

mentioned earlier, the level of enhancement in the specific heat capacity was affected by the chemical composition of the solvent. The minimum level of the enhancements in the specific heat capacity for the samples tested in this study was obtained for a chemical composition of 64.3:35.7, which is closest to the eutectic composition (62:38) of lithium carbonate and potassium carbonate. The enhancements at both ends of the concentration range (36.6 mol. % and 79.2 mol. % of Li_2CO_3) were usually the highest, which were 26.7% and 29.3% in the liquid phase and 13.9% and 25.6% in the solid phase, respectively.

Fig. 8. Enhancements of specific heat capacity of MWCNT nanomaterials in liquid and solid phase for five different chemical compositions of solvent.

7. Discussion

The specific heat capacity measurements were performed for nanomaterials obtained by mixing carbonate salts mixtures with MWCNTs, wherein the chemical composition of the solvent (salt mixture) was parametrically varied.

The nanomaterials showed wide range of enhanced specific heat capacities. In a previous study [17], the presence of a compressed liquid layer in the vicinity of nanoparticles was hypothesized; this layer was believed to affect the thermal property of the overall system. Additionally, molecular dynamics (MD) simulations showed that the molar concentration ratio of the solvent salt mixture (i.e., mole fraction of potassium carbonates to lithium carbonates) was different from that of the solvent bulk (i.e., the carbonate salt mixture). The resultant material properties of the compressed liquid layer due to the molar concentration ratio of the constituent salts within the compressed layer (compared with that in the solvent bulk) could affect the enhancement of the specific heat capacity of the overall nanomaterial. To estimate the specific heat capacity of these nanomaterials, MD simulations were performed for the same nanomaterials observed by DSC; however, SWNTs were modeled instead of the experimentally used MWCNTs. The mole fraction of lithium carbonate was varied from 34.0% to 85.7%. This range encompassed the range of molar ratios used in the DSC measurements (i.e., 36.6% to 79.2%).

Fig. 9. Density variations of solvent material as a function of chemical composition.

Figure 9 shows the cumulative density variation of the solvent (carbonate salt mixtures) adjacent to a SWNT for six solvent chemical compositions. The results show that the compressed layer was formed in the vicinity of the nanotube. Among the six cases, two solvents with mole fractions 85.7:14.3 and 74.6:25.4 had relatively weak intensities in the first density peak of the density plots, whereas the other four cases had significantly higher values for the first peaks. In particular, the magnitude of the first peak of the density plot increased as the molar ratio of lithium

carbonate in the salt mixture decreased. These trends and results were consistent with previously reported results for graphite nanomaterials [17], in which a higher magnitude density peak was observed in the simulation of nanomaterial samples containing lower mole fractions of lithium carbonate. Based on these results, it can be concluded that the magnitude of the density peak decreased as the mole fraction of the lithium carbonate salt increased. Therefore, at a certain mole fraction of the salt mixture, the formation of the compressed phase may be hindered due to the inherent nature of inter-molecular interactions.

Nevertheless, the nanomaterials explored in this study demonstrated significant levels of enhanced specific heat capacity values. These enhancements were affected by several parameters and features. One notable feature was the spatial concentration variation of the carbonate fractions (salts) within the compressed layer (compared with that of the bulk composition). Figure 10 shows the concentration plots and demonstrates the significant spatial concentration variation of the constituent salts within the compressed layer. More potassium molecules per unit volume were contained within the compressed layer than in the solvent bulk for all numerical simulations. Thus, the compressed layer definitely has different thermo-physical properties compared with those of the solvent bulk (i.e., the pure salt mixture). It should be pointed out that the pure salt mixture having the same composition as that of the compressed layer is likely to have different physical and chemical properties. This phenomenon is attributed to anisotropic properties of the compressed layer wherein a semi-crystalline ordering of the molecules is induced by the nanoparticles. This ordering is influenced by the underlying lattice structure of the nanoparticles. For example, the lattice-induced ordering of the semi-crystalline compressed layer can be different for SWNT compared with other

nanoparticles [32]. Additionally, local fluctuations in the transport mechanisms, such as heat and mass (species) transfer, due to spatial concentration gradients (i.e., thermophoresis) may be responsible for the effective specific heat capacity enhancement of the nanomaterials as well as modification of the effective values of other material properties, such as density, viscosity and thermal conductivity.

The effect of the chemical composition on the specific heat capacity enhancement was also explored by constructing concentration plots, as shown in Fig. 10. Four plots, (A), (B), (E), and (F), show relatively wide potassium carbonate-dominant regions where the concentrations of potassium carbonates are higher than those in the solvent bulk composition. The other two plots, (C) and (D), have narrower regions, wherein the potassium carbonate concentrations are higher than those of the solvent bulk composition. The four nanomaterials (A, B, E, and F) showed significantly enhanced specific heat capacities, whereas the other two nanomaterial compositions (C and D) showed lower enhanced values. In other words, the nanomaterials (A, B, E, and F) that displayed wider regions of concentration variation showed dramatically higher levels of enhancement in the specific heat capacity, whereas the nanomaterials (C and D) that displayed narrow regions of concentration variation showed lower levels of enhancements. Therefore, the imbalance between the molar concentrations of the two salts (lithium carbonate and potassium carbonate) in the compressed layer can have significant influence on the overall nanomaterial specific heat capacity.

Fig. 10. Molar ratio of potassium carbonate to lithium carbonate along relative position as function of chemical composition.

The solvent composition can influence the specific heat capacity of the nanomaterials through different transport mechanisms. Several tested nanomaterials were comprised of salt mixtures with molar ratios that were significantly different from the eutectic composition. For these samples, a portion of the constituent salts remained as non-liquids over the range of temperatures used in the DSC measurements. Hence, these samples behaved as a slurry for temperatures exceeding the eutectic temperature. In DSC measurements, the specific heat capacity enhancement

increased as the composition of the salt mixture increasingly deviated from the eutectic point. Therefore, as the proportion of the solid salt phase (i.e., the mass fraction of the non-liquid material) increased, the degree of enhancement of the specific heat capacity also increased. Hence, the state of the solvent material (completely melted or slurry) is an important factor in determining the enhancement level of the specific heat capacity. However, additional studies are required to verify the formation of the slurry and its effect on the resultant properties of the nanomaterial samples in the solid and liquid states.

8. Conclusions

The specific heat capacity values of nanomaterials comprising carbonate salt mixtures with MWCNTs were measured using DSC. The effect of the solvent salt mixture chemical composition was examined by measuring the mole fractions of the two constituent salts (lithium carbonate and potassium carbonate). The concentrations of the two salts were measured using ICP-MS technique. MD simulations were also performed for a wider range of chemical compositions. The results indicated that the chemical composition of the solvent strongly affected the specific heat capacity. The knowledge gained from the experiments and numerical simulations are summarized as follows:

(a) The specific heat capacities of the carbonate salt mixtures in both solid and liquid phases were significantly enhanced by doping with multi-walled carbon nanotubes. The enhancements varied from 6.0% to 29.3% in the liquid phase and from 3.1% to 25.6% in the solid phase (at 400 °C).

(b) The chemical composition of the solvent (carbonate salt mixture) affected the specific heat capacity enhancement of the nanomaterials. As the solvent chemical composition of the solvent increasingly deviated from the eutectic composition, the enhancement of the specific heat capacity increased.

(c) The MD simulations showed that the compressed liquid layer formed in the solvent in the vicinity of the nanoparticles had different (and spatial variations) mass densities and molar ratios of the constituent salts compared with those of the solvent bulk phase. These differences were expected to affect the properties of the nanomaterials. The results from the MD simulations showed the formation of density peaks in the compressed layer. The magnitude of the first density peak in the compressed layer increased in magnitude as the molar ratio of lithium carbonate decreased. Hence, the molar ratio of the solvent material (salt mixtures) may have a significant influence on the formation of the compressed layer and thereby, the properties of the resulting nanomaterial.

(d) Based on the experimental results, the composition of the solvent phase can significantly influence the resulting specific heat capacity of the nanomaterials. A portion of the salt mixture in the nanomaterials can exist in a solid phase even after the melting point was exceeded in the DSC experiments. This results in the formation of a slurry in the testing pans used in the experimental measurements. The nanomaterials that were likely to form a slurry exhibited higher levels of enhancement in the specific heat capacity. Additionally, the magnitude of the enhancements was higher for the samples with chemical compositions that increasingly deviated from the eutectic composition.

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Acknowledgments

The authors acknowledge the support of the Department of Energy (DOE) Solar Energy Program (Golden, CO) under Grant No. DE-FG36-08GO18154; Amd. M001 (Title: “Molten Salt-Carbon Nanotube Thermal Energy Storage For Concentrating Solar Power Systems”).

Figure captions

Figure 1: Transmission electron microscope images of multi-walled carbon nanotubes.

Figure 2: Schematic of the synthesis for molten salt nanomaterials.

Figure 3: Photo of the nanomaterial obtained on a petri dish after dehydration process.

Figure 4: Specific heat capacity of pure carbonate salt mixtures as a function of composition [31].

Figure 5: Compressed liquid layer in a molecular dynamics simulation domain.

Figure 6: Specific heat capacity of pure carbonate salt mixtures and nanomaterials in liquid phase for five different chemical compositions.

Figure 7: Specific heat capacity of pure salt mixtures and nanomaterials in solid phase (400 °C) for five chemical compositions.

Figure 8: Enhancements of specific heat capacity of nanomaterials in liquid and solid phase for five different chemical compositions.

Figure 9: Density variations of solvent material as a function of chemical composition.

Figure 10: Molar ratio of potassium carbonate to lithium carbonate along relative position as function of chemical composition.

Table 1 System parameters for molecular dynamics simulations

Lennard-Jones constants					Stretching		Bending		Torsion		
Material	Interaction	ϵ [kcal/mol]	σ [Å]	charge	K_s	r_0	K_b	θ_0	K_t	d	n
SWNT	C - C	0.105	3.851	0	480.0	1.340	90.000	120.0	12.370	-1.00	2
Eutectic	C - C	0.148	3.617	+1.54	4612.0	1.290	107.4354	120.0	1.1392	-1.00	0
	O - O	0.228	2.880	-1.18							
	Li - Li	4.735	2.839	+1							
	K - K	5.451	3.197	+1							

Table 2 Chemical compositions and specific heat capacity of pure salt mixtures and nanomaterials

Cases	Molar composition (Li ₂ CO ₃ :K ₂ CO ₃)	Pure salt mixtures [J/g·K]		Nanomaterials [J/g·K]	
		Solid (400 °C)	Liquid (525-555 °C)	Solid (400 °C)	Liquid (525-555 °C)
1	79.2:20.8	1.284	2.526	1.612	3.266
2	68.0:32.0	1.239	2.501	1.359	3.015
3	64.3:35.7	1.218	1.676	1.312	1.777
4	42.5:57.5	1.126	1.410	1.161	1.700
5	36.6:63.4	1.070	1.348	1.219	1.707