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Thermal properties and thermal stability of the binary Na_2CO_3-K_2CO_3 system for high temperature thermal energy storage

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Concentrated solar power (CSP) plants have become an attractive technology due to the benefit of producing emissions-free power, especially in regions where the sun is abundant. However, one of the major barriers of CSP is the intermittent nature of solar radiation, which can make this technology less competitive with conventional power generation. Therefore, the integration of thermal energy storage (TES) to the CSP plant offers a means to potentially increase the economic viability of this technology. Phase change materials (PCMs) are considered to be an effective alternative to the traditional two tank molten nitrate salt sensible TES systems due to their higher energy density and potentially lower cost. Furthermore, high-temperature PCMs, which enable storage of energy at higher tempeartures (700-750 °C) than that of the established two tanks sensible TES, are of particular interest . This is mainly due to further increases in the system efficiency leading to a reduction in cost of energy. To this end, the current investigation reports on the characterisation of a Na_2CO_3-K_2CO_3 system as a potential low cost PCM for high tempearture TES. The phase diagram of the Na_2CO_3-K_2CO_3 system has been previously studied and a range of salt ratios with a minimum melting point of approximately 710°C were reported.[1] The primary objective of this study is to determine the thermodynamic properties of the PCM at different ratios using differential scanning calorimetry (DSC) . This allows the evaluation of a composition and/or a range of compositions in which the maximum latent heat of fusion is acheived. Group one carbonate salts have been found to be decomposed to metal oxide and CO_2 under specific conditions.[2] Therefore, the thermal and chemical stability of the PCM using simultaneous thermal analysis (STA) has also been investigated.

The phase change temeprature and latent heat of fusion (given in Tables 1 and 2) were measured by DSC based on two cycles of heating and cooling at the rate of 10 K/min under nitrogen atmosphere. It can be seen from Table1, the PCM ratios of Na_2CO_3 at 55,60 and 65 mol% gives a subcooling of less than 2.0°C which makes the PCM an effective candiate for TES. The results (Table 2) also show that the enthalpy of fusion is inceased by 19% from 55 to 65 mol%.However, for 45 mol%, despite its high latent heat, the composition does not allow isothermal operation as the freezing and melting points are significantly different, causing operational issues. The thermal stability of the uncycled PCM for the composition between 55 mol% and 65 mol% of Na_2CO_3 were also analysed by STA under nitrogen atmosphere. The results show that the PCM for the ratios analysed is extremely stable between 500°C and 800°C.

Table 1. Summary of melting/freezing temperatures of the binary Na_2CO_3-K_2CO_3 system at various compositions.

Na_2CO_3 (mol%)	Heating	Cooling	Difference	Heating	Cooling	Difference
	1st cycle			2nd cycle		
	T_{onset} (°C)	T_{end} (°C)	$\Delta T_{Subcooling}$ (°C)	T_{onset}(°C)	T_{end}(°C)	$\Delta T_{Subcooling}$ (°C)
45	716.6	724.1	7.5	713.4	723.9	10.5
55	706.2	704.2	-2.0	706.9	704.6	-2.3
60	707	704.7	-2.3	706.2	704.8	-1.4
65	710.2	709.5	-0.7	707.4	710.5	3.1

Table 2. Summary of latent heat of the binary Na_2CO_3-K_2CO_3 system at various compositions.

Na_2CO_3 (mol%)	Heating	Cooling	Difference	Heating	Cooling	Difference
	ΔH_{fus}(J/g) 1st cycle			ΔH_{fus}(J/g) 2nd cycle		
45	133.3	145.3	12.0	148.1	143.3	-4.8
55	136.6	123.8	-12.8	129.7	124.2	-5.5
60	141.4	135.1	-6.3	143.8	130.4	-13.4
65	151	154.5	3.5	149.9	154.9	5

References

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2. Stern, K. H.; Weise, E. *High Temperature Properties and Decomposition of Inorganic Salts. Part 2. Carbonates*; NATIONAL STANDARD REFERENCE DATA SYSTEM: 1969.