Effect of Static Magnetic Field on Nucleation of Cobalt Nitrate Hexahydrate

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Freezing of cobalt nitrate hexahydrate (CoNHH) under a static magnetic field was studied at three different magnetic field intensities. The results show that the magnetic field has a significant effect when the sample enters the solid phase and reduces the stochastic behaviour of the nucleation. Thermal properties investigated using thermogravimetric and differential thermal analysis revealed the shift to a lower temperature for the onset of decomposition and melting temperature after the freeze-thaw in a magnetic field. Besides that, we observed a significant change in the FT-IR peaks that might indicate the emergence of cobalt nitrate with a lower hydrate number, a phase separation effect, and the evaporation of NO_3^- ions. Refinement of the XRD spectra shows a single phase of CoNHH with a slight lattice parameter change after the freezing-thawing in a magnetic field. The freezing behaviour of CoNHH was compared to that observed previously for water, a salt solution, and an ethylene glycol solution. We investigated the relationship of the freezing behaviour with hydrogen bonding and magnetic properties and its impact on the change in the Gibbs free energy. The results of this study are important to optimise the performance of CoNHH as latent thermal energy storage.

Keywords: Cobalt Nitrate Hexahydrate $Co(NO_3)_2$ ·6H₂O, Nucleation, Supercooling Degree, Static Magnetic Field.

1. Introduction

The diminishing availability of fossil resources, in addition to negative impacts on the environment, has accelerated the shift towards sustainable energy resources¹. The utilisation of natural resources such as solar radiation, ocean waves, wind, and biogas has contributed significantly to the process of restoring natural balance while also fulfilling the demand for energy. However, due to the energy crisis, an optimal method to store renewable energy is crucial. These circumstances encourage the development of a method to ensure efficient and sustainable energy storage¹.

Energy storage plays an important role in energy conservation and utilisation of renewable energy. One of the technologies for storing energy that has undergone rapid development in the last 20 years is thermal energy storage (TES). TES stores thermal energy in the form of latent or sensible heat through heating (melting, evaporation) or cooling (freezing, condensation) of the storage medium. The stored energy will be ready for utilisation later when the process is reversed. TES technology, which has developed since 1970s, can be one of the solutions for overcoming the imbalance between energy supply and demand and can make significant contributions to meet the need for energy in a more efficient and environmentally friendly manner².

Latent TES using a phase change material (PCM) is considered more efficient than sensible TES because it offers greater energy density (per unit mass or volume), with a small temperature difference (even almost zero) between the charging and discharging processes^{3,4}. Organic or inorganic PCMs, however, have their advantages and disadvantages⁵. In particular, a relatively high supercooling degree and phase separation effect are the main considerations for inorganic salt hydrate PCMs, besides the possibility of a change in the stoichiometric composition during heating and cooling^{6,7}.

Several active methods have been used to reduce the supercooling degree of salt hydrate PCMs, including water and salt solutions, by applying an electric field, magnetic field, ultrasound, or high pressure (Refs.⁸⁻¹⁰). To date, freezing under pulsed, static, or oscillating magnetic fields was limited to water, salt solution, or ethylene glycol^{11-15,} and several contradicting results have been obtained from the experimental reports, so its effectiveness is still under debate¹⁶. Meanwhile, many inventions have been patented¹⁶ and technologies have been developed with either purely magnetic effects or combinations of electric fields, and freezing has attracted attention for food and biological product storage^{14,16-19}.

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The cells alive system (CAS)²⁰ and proton freezers²¹ are among the leading technological products that offer many advantages compared with the conventional freezing method. These technologies are promising because freezing under magnetic fields has resulted in smaller ice crystals and more homogeneously distribution, thus minimising the damage and maintaining the quality of the preserved samples^{16,20,21}.

In this paper, we report an experimental study of the effect of a static magnetic field on the nucleation process of the salt hydrate cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, referred to as CoNHH). The molecular structure of CoNHH comprises Co²⁺ ions bonded with NO₃⁻ ions, surrounded by six water molecules to form a hexagonal configuration²². The red crystal of CoNHH has a monoclinic structure with the space group C2/c²³.

The study was based on an analysis of the temperature–time graph during nucleation under the influence of a static magnetic field with three different intensities from a permanent magnet. The examination parameters consist of the temperature and time characteristics of nucleation and freezing, supercooling degree, and total crystallisation period. The thermophysical properties of CoNHH from previous studies related to its performance as latent TES are summarised in Table 1.

To date, not many studies have investigated this magnetic PCM, possibly due to the complex thermal properties^{24,28,29} and the fact that it is even more expensive than other salt hydrate PCMs that are commonly based on alkaline or alkaline earth metals, such as CaCl₂·6H₂O.

A recent study based on differential scanning calorimetry (DSC) measurements by Honcová et al.²⁴ showed that the supercooling degree of CoNHH is dependent sensitively on the freezing-thawing cycle, being 14 °C for the first cycle and 25 °C for the fourth cycle. Furthermore, an additional 1 mass% of CaO as a nucleating agent to CoNHH reduces the supercooling degree to 8.1 °C and becomes higher for faster heating/cooling rates. The smallest supercooling degree of (7.9 ± 2.5) °C was obtained for 1 mass% of nucleating agent mixture with a ratio of 1:1, consisting of graphite and Ba(OH)₂·8H₂O to CoNHH. The results of this study aimed to study the magnetic field effect to nucleation of CoNHH and to optimize its performance as latent TES.

2. Methods

Sample CoNHH (molecular weight 291.04 g/mol) with a purity of 98% was purchased from Sigma Aldrich. Samples with a mass of 3 g were placed in a test tube with an outer diameter of 1.34 cm and length of 15 cm. The temperature sensor is a T-type thermocouple with a diameter of approximately 1 mm and an accuracy of 0.2% + 1 °C. For data recording, eight channel thermocouples are connected to an Applent data logger³⁰. The magnetic field intensity was measured using a digital magnetic meter (Mg 3002).

The experimental system for nucleation under a magnetic field is shown in Figure 1. An adiabatic bath

T_m (°C)	ΔT_{s} (°C)	$\Delta H_{fus} (J g^{-1})$	$c_{p,l} (J g^{-1} K^{-1})$	$c_{p,s} (J g^{-1} K^{-1})$	$\rho_s (g m L^{-1})$	Reference
56	14	140		1.682	2.04 ± 0.05	24
46.9 ± 1.76 *)	13	131 ± 15	3.45 ± 0.74	2.22 ± 0.05	-	25
51.5 ± 0.5 *)	-	-	-	-	-	26
57	-	128	-	-	-	27

Table 1. Thermophysical properties of CoNHH from previous studies.

*) Freezing temperature



Figure 1. Schematic experiment for freezing of CoNHH in magnetic field.

can be set to a minimum temperature of approximately 12 °C. The experiment was performed simultaneously for four samples in a test tube, each of them exposed to magnetic fields of different intensities, and a sample without a magnetic field (H_0) was measured as a reference. Each sample in the test tube was equipped with a temperature sensor positioned at the centre. Three different magnetic field intensities were produced by neodymium magnets with a diameter of 25 mm and height of 3 mm, which were placed in an attractive arrangement. One, two, and three pairs of magnets were fixed to a metal zinc sheet to produce magnetic field intensities of $H_1 = 74 \text{ mT}$, $H_2 = 142 \text{ mT}$, and $H_3 = 215$ mT, respectively. The nucleation experiment was initiated by immersing the sample in warm water just above the melting point for some minutes to homogenise the temperature inside the sample. When all the samples had melted and reached the same temperature of 60 °C, they were suddenly exposed to a magnetic field and cool temperature environment inside the adiabatic bath, in conjunction with the temperature data recording until all the samples solidified. The experiment was repeated 20 times with a new sample for each measurement, which was used to evaluate each set of parameters due to the complex thermal properties of CoNHH and the possibility of the phase separation effect, which commonly occurs during the freezing-thawing cycle for salt hydrate PCMs^{4-7,10}.

The statistical analysis of the freezing parameters was performed using the JMP 16 software program with the significance level set at 5%. The Shapiro-Wilk test was employed to check the normal distribution of the data. If the data fulfilled a normal distribution (*p*-value > 0.05), a one-way analysis of variance (ANOVA) was performed to determine whether the magnetic field had a significant effect. On the other hand, when the assumption of normality was not fulfilled (*p*-value < 0.05), the non-parametric Kruskal-Wallis test was employed to compare the characteristic parameters of freezing under different magnetic fields³¹.

Simultaneous thermogravimetric (TG) and differential thermal analyses (DTA) were performed using an STA PT1600 Platinum Series analyser (LINSEIS, USA) under a N_2 atmosphere. Samples with amounts in the range 5–15 mg were heated from room temperature to 375 °C at a constant heating rate of 5 K min⁻¹. The data were further analysed to obtain DSC thermograms.

The Fourier transform infrared spectroscopy (FT-IR) spectra of the samples were recorded using an IRPrestige21 (Shimadzu, Japan) spectrometer at 30 scans using the KBr sampling method.

Hysteresis magnetic measurement was carried out using vibrating sample magnetometry with a maximum applied field of 2 T to measure the initial sample's magnetisation at room temperature (22 °C).

X-ray diffraction (XRD) patterns of the granular sample were measured at room temperature (22 °C) using a D8 Advance (Bruker) diffractometer, Bragg-Bentano Diffraction and CuK α radiation ($\lambda = 1.54060$ Å) for the initial sample of CoNHH and the CoNHH sample after thawing–freezing in H₂. The refinement analysis of the XRD patterns was carried out according to the Rietveld method³².

3. Results and Discussion

Typical freezing curves of CoNHH at different applied magnetic fields are shown in Figure 2a, while Figure 2b shows the analysis method used to determine the temperature and time characteristics; the effect of the magnetic field on the nucleation of CoNHH is obvious. The nucleation temperature, T_n , that occur at nucleation time, t_n , is the lowest (supercooling temperature) at the first crystal nucleus formation with the critical radius of the crystal, before it increases abruptly due to the release of latent heat to reach a freezing temperature, T_{α} and thereafter, it decreases monotonously. The supercooling degree, ΔT_{e} , is defined as the difference between T_{e} and T_{u} . The transition at T_n and T_f is accompanied by a peak in the time-derivative curve (dT/dt-t). A closer look at the freezing curve shows that two curvatures are evident during the monotonous decrease in temperature after T_c owing to the different time-dependent temperature profiles of the latent heat and sensible heat release³³. Additionally, the border between them is indicated by an inflection in the dT/dt-tcurve, with coordinate $(t_i, T_i)^{34}$. These time and temperature characteristics limit the growth of crystal dendrites from the nucleus following latent heat release prior to the solid sensible heat release. The crystallisation period (Δt_{\perp}) is defined as the difference between t_i and t_i .

Prior to the analysis of the magnetic field effect on the freezing behaviour of CoNHH, each temperature and time characteristic data was checked for its normality distribution.



Figure 2. (a) Temperature profile during solidification under different magnetic field intensities. (b) Temperature vs time (black curve) and temperature derivative curve (red line) of CoNHH during solidification.

The results of the normality test are summarised in Table 2 along with the variance test that shows the corresponding *p*-values. From this table, it may be observed that the magnetic field has a significant effect (*p*-value < 0.05) on the t_n , T_f and t_f , as well as on T_i and t_i . On the other hand, no variance was observed for T_n , ΔT_c , and Δt_c .

The results of the freezing analysis of CoNHH under three different applied fields (sample without a field was used as the reference) are shown for the temperature (Figure 3) and time characteristic parameters (Figure 4). Included are the statistical analyses that comprise the means and standard deviation values as well as the quantiles for 20 freeze–thaw cycles.

From Figure 3 one can see that there is no notable trend for T_n , T_f , T_i and ΔT_s with changing magnetic field. The result of the variance test shows that the magnetic field effect is clear when the CoNHH sample enters the solid phase. It is worth mentioning that T_f was the temperature when a large fraction of the solid phase was formed, and T_i indicates the end temperature of the liquid to solid phase change that occurs at t_i . The significant effect of the magnetic field on the time characteristic parameters of t_n , t_p , and t_i is also shown by the decrease of its average values and its smaller variation with the increase in the magnetic field intensity, thus thereby reducing the stochastic behaviour of the nucleation³⁵. On the other hand, the supercooling degree and crystallisation period do not show significant variance with change in the magnetic field; that is, it might resemble an extrinsic property of the material, as they affected by the amount of the sample³⁶. In the case of supercooling degree, it is also influenced by the cooling rate^{24,37}.

We note that the experimental results presented in this study are dissimilar to previous studies for the freezing of

Table 2. *p*-values obtained after applying the Shapiro-Wilk test to check the normality of the data and the Kruskal-Wallis and ANOVA tests to study the significance of the magnetic field on the freezing of CoNHH. Figures in bold indicate the parameter that has a significant effect on the magnetic field.

Temperature parameters	Shapiro-Wilk normality test					
	H_0	H ₁	H_2	H ₃	- ANOVA	Kruskal-Wallis
T_n	0.0357	0.2659	0.0318	0.2641	-	0.1956
T_{f}	0.0089	0.6779	0.0097	0.3088	-	< 0.0001
T_i	0.0009	0.5075	0.2892	0.0266	-	< 0.0001
ΔT_s	0.0139	0.3768	0.4938	0.7538	-	0.3265
			Time parameters			
t_n	0.6651	0.1249	0.2691	0.2901	0.0012	-
t_{f}	0.9736	0.1259	0.2544	0.2785	0.0003	-
t_i	0.7539	0.6419	0.9975	0.1685	< 0.0001	-
Δt_c	0.0066	0.1165	0.3249	0.5001	-	0.6233



Figure 3. Individual data and statistical analysis of the temperature parameters for freezing of CoNHH as a function of magnetic field intensities: (a) nucleation temperature (T_v) , (b) freezing temperature (T_v) , (c) inflection temperature (T_v) , and (d) supercooling degree (ΔT_v) .



Figure 4. Individual data and statistical analysis of the time parameters for freezing of CoNHH as a function of the magnetic field intensities: (a) nucleation time (t_p) , (b) freezing time (t_p) , (c) inflection time (t_p) , and (d) crystallisation period (Δt_p) .

pure water^{11,12,15}, 0.9% NaCl solutions^{11,12,18}, and 5% ethylene glycol solution¹². For example, Aleksandrov et al.¹⁵ reported a continuous decrease in the supercooling degree of a 0.5 g water sample with a magnetic field of up to 0.5 T and a negligible change thereafter. Otero et al.11 did not find any static magnetic field effect on either the supercooling or freezing kinetics of both 10 mL pure water samples and 0.9% NaCl solutions, although the experiments had been performed intensively for the attractive (107–359 mT) and repulsive poles (0-241 mT). Zhao et al.12 showed that although no significant magnetic effect was found for deionised water, clear differences existed for a 0.9% NaCl solution and 5% ethylene glycol solution for a maximum applied field of 43.5 mT (5 mL sample). In particular, the nucleation temperature of the 0.9% NaCl decreased in the magnetic field, while its phase transition time was shorter than that in the absence of a magnetic field. On the other hand, the nucleation temperature of 5% ethylene glycol increased in the magnetic field, while its phase transition time was unaffected by the magnetic field. Mok et al.18 showed that ice crystals of 2 mL of 0.9% sodium chloride solution treated by the static magnetic field formed irregular shapes with different patterns for both the attractive (480 mT) and repulsive magnetic fields (50 mT), and the phase transition time was highly dependent on the magnetic field configuration.

The thermal properties of CoNHH before and after nucleation experiment are shown in Figure 5, which shows the TGA/DTA and DSC thermograms. The TGA curve of initial sample indicates that CoNHH decomposes via three weight-loss processes occurring in the temperature ranges of 73–180 °C, 180–198 °C, and 198–263 °C, in agreement with previous studies^{24,28}, particularly for a slow heating rate of 2 K min⁻¹ for pronounced phenomena²⁸. Moreover, the DTA curve exhibits more than three overlapping endothermic peaks corresponding to the weight-loss phenomena. The results obtained exhibit that dehydration of CoNHH into tetrahydrate

starts at a temperature of approximately 35 °C, which is well below the melting temperature due to incongruent melting²⁹. This process mostly occurs at 75 °C and continuously goes through the dihydrate phase up to 180 °C, with cobalt nitrate monohydrate as an intermediate at 150 °C²⁸ and formation of cobalt (III) oxonitrate (for partial reaction of the water leaving in the third step)²⁹. Further heating of the sample to higher temperatures caused thermal decomposition and the formation of anhydrous cobalt nitrate as a major component and cobalt oxides (CoO, Co₂O₂, and Co₂O₄), instantaneously in an inert atmosphere^{28,29}. These intermediate products easily decompose to Co₃O₄ as a stable phase²⁸. We note that the thermal behaviour of CoNHH depends sensitively on the experimental conditions at a particular heating rate, as rapid heating causes a hydrate melt which changes the system drastically with side reactions and evaporation of HNO, and other species, resulting in a more contour-less TG curve²⁸. From DSC thermogram, the melting temperature is 56 °C, and this result is in good agreement with previous studies (Table 1).

Thawing-freezing in magnetic fields gives rise to some changes in the TG and DTA curves. A shift to a lower temperature for the onset of the TG curve signifies the beginning of the decomposition followed by a more step transition. Overlapping DTA peaks at a temperature just above the first decomposition step above 75 °C followed by a new DTA signal at a high temperature between 200–263 °C. The DSC thermogram also indicates the decrease of the melting temperature and melting enthalpy. However, indirect measurement has a hindering effect on the accuracy of melting enthalpy from the DSC data.

The FT-IR spectra shown in Figure 6 show broad peaks at approximately 3640 cm⁻¹ and 1687 cm⁻¹ due to OH stretching and bending of water $(H_2O)^{38}$, which are indicative of an ionic unperturbed nitrate³⁹. The spectra show some characteristic bands due to nitrate ions (NO₃⁻),



Figure 5. Left: TGA/DTA curves, and right: DSC thermogram, of (a) initial sample of CoNHH, and (b)-(e) CoNHH after thawing-freezing in different magnetic fields of: H_0 , H_1 , H_2 , and H_3 .

in addition to Co-N vibration at 1172 cm^{-1 28}. Moreover, the characteristic bands for anhydrous cobalt nitrate^{29,39,40}, dihydrate, and hexahydrate^{29,39} were also observed with relatively small intensity.

FT-IR spectroscopy performed after the nucleation experiment showed prominent changes in the fingerprint

region (500–1500 cm⁻¹). In general, the peak's position due to H_2O did not change, but its intensity increased after the freezing–thawing cycle in the different magnetic fields, namely, H_0 , H_1 , H_2 , and H_3 . This result signified the possibility of a phase separation effect. On the other hand, the peak intensity due to the formation of cobalt nitrate



Figure 6. FT-IR spectra of CoNHH in the range of 400–4000 cm⁻¹ for the initial sample, and for the samples after thawing-freezing in different magnetic fields of: H_0 , H_1 , H_2 , and H_3 .

dihydrate at approximately 2355 cm⁻¹ increased. Crucially, the peaks due to the nitrate ions shifted significantly from 1485 cm⁻¹ for the initial sample to 1454 cm⁻¹ for H₀ (marked with an asterisk in Figure 6). These peaks disappeared for the samples that experienced freezing at different magnetic field intensities, with the simultaneous appearance of a new peak at approximately 1530 cm⁻¹. Similar phenomena occurred for the peaks at 830 cm⁻¹ and might be due to the evaporation of nitrate ions from the sample. The emergence of a broad peak at approximately 3000 cm⁻¹ and a weak shoulder at approximately 2700 cm⁻¹ while freezing the CoNHH in the absence and in the presence of a magnetic field conditions (cross in Figure 6) that became more pronounced with the increase in magnetic field intensity was presumably due to the formation of cobalt nitrate with a lower hydrate number.

Figure 7 shows the results of the structural analysis of CoNHH that displays the refinement of the XRD spectrum of the initial sample and the CoNHH sample after thawing–freezing in H_2 . Both samples show the pure phase of CoNHH without any sign of the impurity phases. The results of the XRD refinement are summarised in Table 3, which shows the lattice parameters of CoNHH in comparison to a previous study²².

It is tempting at this point to correlate the freezing behaviour of CoNHH in a static magnetic field to its magnetisation and compare it with previous studies for the nucleation of water



Figure 7. XRD patterns of (a) initial sample of CoNHH and (b) CoNHH after thawing-freezing in a magnetic field of H_2 presented as the observed (crosses) and calculated (full lines) results as well as their differences (bottom trace).

Table 3. Lattice parameters of initial sample of CoNHH and CoNHH after thawing-freezing in a magnetic field of H_2 , and the corresponding data from reference²².

Sample						
Col	CoNHH after					
Initial sample (present work)	Prelesnik et al. ²²	thawing-freezing in a magnetic field of H ₂				
<i>a</i> = 14.96 Å	<i>a</i> = 14.96 Å	<i>a</i> = 14.94 Å				
<i>b</i> = 6.136 Å	<i>b</i> = 6.112 Å	<i>b</i> = 6.135 Å				
<i>c</i> = 12.662 Å	<i>c</i> = 12.632 Å	<i>c</i> = 12.659 Å				
$\beta = 118.44$ °	$\beta = 118.45$ °	$\beta = 118.44$ °				

or salt solution. In this case, the magnetisation M is related to the material's response to the applied magnetic field H^{41} .

$$M = \chi H \tag{1}$$

where χ is the magnetic susceptibility. In contrast to the diamagnetic response of water⁴², the *M*–*H* curve taken at room temperature (*T* = 22 °C), as seen in Figure 8, shows that CoNHH is weakly ferromagnetic. The hysteresis behaviour is clearly seen at applied fields below 500 mT, and the coercive field is approximately 40 mT.

It has been experimentally demonstrated that the static magnetic field changes the structure and physicochemical properties of water⁴³. In particular, water becomes more stable by magnetic treatment with less molecular energy and more activation energy, thus indicating that the average size of water clusters becomes larger with magnetic treatments, resulting in the formation of more hydrogen bonds and enhancement of its strength^{13,43}. This is in agreement with the results of an intensive simulation study that predicted that the structure of the water is more stable and the ability of the water molecules to form hydrogen bonds is enhanced when a magnetic field is applied⁴⁴. In other words, the magnetic field constrains the movement of the water molecules, thus inhibiting the vibration and rotation of molecules to promote nucleation at higher freezing temperatures with the enhancement of the magnetic field⁴⁵. We note that in the case of water, the breakup of the hydrogen bond leads to an increase in diamagnetism⁴⁶⁻⁴⁸. In the case of an aqueous NaCl electrolyte solution, the effect of the magnetic field on hydrogen bonding very sensitively depends on the concentration of the solution. In a low-concentration solution, the structural behaviour is dominated by the properties of the water molecules, and hence the hydrogen bonding ability is enhanced as the magnetic field is increased, just as in the case of pure water. Conversely, the enhanced mobility of the ions under a magnetic field causes serious damage to the hydrogen bond network in a high-concentration solution⁴⁹.

Application of an external electric field and a magnetic field is expected to exert opposite effects on the number of hydrogen bonds, that is, an electric field breaks the hydrogen bond network, while a magnetic field enhances the hydrogen bonding⁴⁴. However, for an appropriate condition, the thermodynamic formulation might be presumed similar, as both methods have resulted in a smaller crystal size^{8,9}.



Figure 8. Magnetisation curve of CoNHH at 22 °C.

The energy due to the magnetic field is presumed to be much lower than the electrical or mechanical energy and highly depends on the sample's amount. Hence, we propose that the effect of the application of a magnetic field on nucleation can be described by the change in the Gibbs free-energy (ΔG) of the system. A new *MH* term might be added to the volume contribution of $\Delta G^{50,51}$,

$$\Delta G_H = \Delta G_0 + MH,\tag{2}$$

where *M* is the magnetisation, *H* is the intensity of the magnetic field, and ΔG_0 is the Gibbs free-energy in the absence of magnetic field. Thus, the effect of the magnetic field on the nucleation of water and water-based materials is dependent very sensitively on the hydrogen bonding, in addition to magnetisation and temperature, as an increase in temperature generally leads to the randomising effect of thermal agitation. The appropriate mechanism for water and CoNHH might be different, as the increase in temperature might hamper the ferromagnetic ordering of CoNHH.

4. Conclusions

The nucleation of magnetic PCM CoNHH at different static magnetic fields shows that the magnetic field has a significant effect on the nucleation time, freezing time and temperature, and inflection time and temperature. In this case, the decrease in average values of t_i , t_o and t_i with the increase in the magnetic field intensity is accompanied by a smaller variation for the 20 freeze-thaw cycles data. On the other hand, the results also reveal no magnetic field effect on the supercooling degree and crystallisation period. The thermal properties of CoNHH reveal the stepwise formation of distinct hydrates, including hexa-, tetra- and di-hydrate of cobalt nitrate, anhydrous cobalt(II)nitrate, as well as cobalt oxides. The melting temperature from the DSC thermogram is 56 °C. Thawing-freezing in magnetic fields gives rise to changes in the TG and DTA curves, namely a shift to a lower decomposition temperature and overlapping and the growth of new DTA peaks. The DSC thermogram

also indicates the decrease of the melting temperature and melting enthalpy. FT-IR spectra show the characteristic band structures of H₂O, nitrate ion, and Co-N vibrations, in addition to anhydrous, dihydrate, hexahydrate, and cobalt nitrate. FT-IR spectra showed significant change for the sample after the freeze-thaw cycle at zero or in a magnetic field. This result signifies the occurrence of cobalt nitrate with a lower hydrate number, phase separation effect, and evaporation of NO,⁻ ions. The result of the XRD refinement data of the initial sample revealed the lattice parameters, which closely resembled those of the reference. The freezing-thawing in a magnetic field gives the effect to the slight lattice parameter change. The magnetisation measured at room temperature (22 °C) showed that CoNHH is a weak ferromagnetic with hysteresis behaviour below 500 mT and the coercive field is approximately 40 mT. The results were compared with previous studies for the nucleation of water, a salt solution, and an ethylene glycol solution, and discussed in terms of hydrogen bonding and the measured magnetic properties. The observed magnetic field effect of CoNHH nucleation when the sample enters the solid phase might be related to the alignment of the magnetic moments of cobalt ions in the periodic structure of the solid phase. Due to the relatively small energy of the magnetic field, its effect on nucleation might be highly dependent on the sample quantity and the material's magnetic properties, in addition to its interplay with hydrogen bonding.

The results of this study might provide an understanding of the static magnetic field effect on the nucleation of materials. Minimising the phase separation effect with a suitable nucleator agent or thickening agent is an important task to optimise the performance of CoNHH as latent TES. A challenge is to expand this experimental study using a pulsed or oscillating magnetic field with varying frequencies to fully understand the mechanism behind it. It would also be interesting to study the importance of the magnetic field effect for the nucleation of any PCM using an additional nanoparticle magnetic dopant with various types and concentrations in response to the applied magnetic field.

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