# Solidification of Salt Hydrate Eutectics Using Multiple Nucleation Agents

**Sophia Ahmed, Robert Mach, Haley Jones, Fabiola Alamo, and Patrick J. Shamberger**

**Abstract** Salt hydrates are a class of phase-change materials (PCMs) capable of storing thermal energy at a high volumetric energy density for a low cost (<\$10/kWh$_{th}$), making them of interest for improving the energy efficiency of buildings and displacing peak load associated with environmental control systems. However, select salt hydrates are susceptible to irreversible degradation associated with phase segregation, and to undercooling—the occurrence of a metastable liquid below the melting point due to a lack of nucleation sites for the crystalline solid. Here, we present a study of phase-specific epitaxial nucleation agents which mitigate undercooling in eutectic nitrate salt hydrate systems. While eutectics can depress melting temperatures into favorable ranges, metastable eutectics experience undercooling. We demonstrate that the nucleation of multiple phases in systems which are susceptible to undercooling can increase the potential for phase segregation and chemical stratification to occur. Furthermore, we illustrate the utility of multiple nucleation agents in these systems to co-crystallize multiple crystalline phases.

**Keywords** Salt hydrates · Solidification · Thermal energy storage · Eutectic · Phase segregation · Thermophysical properties

## Introduction

Phase-change materials (PCMs) are a class of materials that absorb and release a large amount of heat during reversible phase transformations and are great for thermal energy storage (TES) applications. Thus, PCMs offer an approach to (1) buffer transient temperature rises in pulsed power electronics [1], automotive [2], and aerospace systems [3], with minimal additional mass and volume to a system, or (2) to displace load on environmental control systems for buildings, allowing for shifting of load demand on the power grid, and ultimately, improving the penetration or intermittent renewable power sources. Salt hydrates are a class of inorganic PCMs

---

S. Ahmed (✉) · R. Mach · H. Jones · F. Alamo · P. J. Shamberger
Texas A&M University, 3003 TAMU, College Station, TX 77843, USA
e-mail: ahmed.sophia97@tamu.edu

F. Tesfaye et al. (eds.), *REWAS 2022: Energy Technologies and $CO_2$ Management (Volume II)*, The Minerals, Metals & Materials Series,
https://doi.org/10.1007/978-3-030-92559-8_14

of particular interest due to their high volumetric energy density, moderate thermal conductivity, and low cost [4]. Furthermore, stoichiometric salt hydrate and anhydrous salt endmembers can be combined to form a large number of eutectic systems, allowing for fine control of the melting temperature of the material, and affording an approach to develop customized PCMs for particular applications. Despite this potential, salt hydrates are subject to two principal limitations: (1) phase segregation can potentially result in irreversible changes to the melting behavior with cycling and (2) nucleation limitations in salt hydrate systems can require additional undercooling prior to the onset of solidification on cooling. The confounding effects of phase segregation and undercooling on the stability of salt hydrate eutectics is poorly understood.

Phase segregation refers to the physical separation of liquid and solid phases due to buoyancy-driven processes and tends to occur during periods in which both solid and liquid phases coexist (i.e., during solidification and melting processes). Thus, phase segregation is associated with repeated cycling of a PCM between solid and liquid states. Phase segregation is problematic, in that it has the potential to result in chemical stratification, or compositional inhomogeneity within the system, *when the phases that segregate have dissimilar compositions*. Compositional inhomogeneity can cause the overall melting behavior of a volume to change, as thermal equilibrium is achieved at different temperatures within different portions of the volume. This situation occurs in some salt hydrate systems, most notably sodium sulfate decahydrate (Glauber's salt) [5], but is not an intrinsic property of all salt hydrates. Several approaches have been taken to avoid issues associated with phase segregation, most notably including the use of additives which increase the viscosity of a PCM, or form a viscoelastic gel, thereby limiting the separation of phases in the phase segregation process [6]. Despite these attempts, in systems that are thermodynamically predisposed to phase segregate, degradation of properties with cycling can be delayed, but generally not entirely avoided [7].

In addition, salt hydrates are susceptible to undercooling, which refers to a phenomenon where a material does not solidify at the equilibrium melting temperature, but rather requires additional cooling before a solid phase nucleates. Undercooling results from a nucleation-limited process, in which substantial energetic barriers to nucleation limit the initiation of solidification. To overcome undercooling, additional solid phases may be introduced into a system, which are selected due to their tendency to nucleate the solid phase of interest [8]. One of the principal approaches to identify active nucleation agents is the use of materials with epitaxial relationships with the PCM phase that is solidifying; this approach affords a convenient approach to identifying candidate phases and has shown broad utility across multiple classes of materials. Nucleation agents with epitaxial relationships have been demonstrated in different classes of PCMs (e.g., the addition of borax to sodium sulfate decahydrate [5]), as well as in the processing of polymers (e.g., the addition of talc to PET [9]) and metals (e.g., seeding during casting of metals [10]).

In this publication we assess the potential impact of phase segregation, together in concert with metastable solidification, to result in changes in the melting behavior of eutectic systems. It has previously been noted that eutectics, due to their tendency to solidify multiple solid phases simultaneously and often in an inseparable interpenetrating manner, are robust to issues associated with phase segregation. However, this claim neglects the potential impact of metastable solidification. Here, we assess the issue from a rigorous consideration of solidification behavior and phase relationships and illustrate with examples from different salt hydrate eutectic systems. We demonstrate that metastable solidification can result in chemical segregation and degradation of melting properties and assess the use of multiple nucleation agents to help mitigate this issue.

## Solidification in Multi-component Salt Hydrate Systems

As a salt hydrate solidifies or melts, different solidification reactions can occur depending on the composition of the system and the characteristics of the phase diagram (Table 1). In all cases, coexistence of a liquid phase and one or more solid phases can potentially result in phase segregation, as solid phases generally have dissimilar densities from the liquid brine phase. However, the primary mechanism which results in degradation of the thermophysical properties of a PCM is not the phase segregation process itself, but rather the tendency for phase segregation to result in chemical stratification. Furthermore, this chemical stratification can be exacerbated by the formation of additional metastable phases which are very weakly soluble in water (e.g., lower hydrates of the salt), but which do not undergo the desired phase transition process at the invariant reaction temperature. Thus, the tendency for phase segregation to result in irreversible changes to the melting and solidification behavior in a PCM depends on (1) the tendency for phase segregation to result in compositional stratification and (2) the potential for additional metastable phases to form that don't readily revert to stable phases above or below the transition temperature. Three main types of melting/solidification reactions have been considered for potential use as PCMs, and are discussed here: congruent melting, eutectic melting, and incongruent melting (Fig. 2). The relative behavior of these three systems is described below.

**Table 1** Comparison of various types of melting reactions that can occur in salt hydrate systems

| Type of melting reaction | Example (Fig. 2) | Reaction | Type of Eutectic composition | Phase Segr. possible? | Compositional strat. possible? |
|---|---|---|---|---|---|
| Congruent | C | $L \leftrightarrow \beta$ | | Yes | No. $X_\beta = X_{Liq}$ |
| Eutectic | $E_1$ | $L \leftrightarrow \beta + \gamma$ | Equilibrium | Yes | No. $X_{eutsol.} = X_{\beta+\gamma} = X_{Liq}$ |
| | $E_2$ | $L \leftrightarrow \beta(+\gamma)$ | Metastable | Yes | Yes. $X_{sol.} = X_\beta \neq X_{Liq}$ |
| Incongruent (peritectic) | I | $L + \delta \leftrightarrow \gamma$ | | Yes | Yes. $X_\gamma \neq X_\delta \neq X_{Liq}$ |

***Congruent solidification*** occurs when the liquid phase transforms into a single solid phase at an invariant temperature, where the solid phase and the liquid have the same compositions (e.g., $L \leftrightarrow \beta$, Fig. 2, point C) [7]. In this case, during melting or during solidifying, phase segregation may occur, due to buoyancy differences between the two coexisting phases ($L$, $\beta$). However, as these two phases have the same chemical composition, phase segregation cannot result in compositional stratification (Fig. 2). Furthermore, in a congruent reaction, there is no tendency for additional metastable phases to form. Thus, materials which exhibit congruent melting reactions are robust over large numbers of cycles and exhibit no change in melting/solidification behavior as a result of phase segregation. It is worth stressing that, while phase segregation still occurs in these cases, it does not generally impact the reversibility of the system. One example of a congruently melting PCM, lithium nitrate trihydrate ($LiNO_3 \cdot 3(H_2O)$) melts congruently at 30.1 °C [11]. While solid $LiNO_3 \cdot 3(H_2O)$ has a greater density than the liquid phase, and therefore phase segregation may occur, chemical stratification will not result. Thus, this reaction is stable over hundreds of cycles with no measurable change in melting behavior [12]. Other examples of phases of interest in salt hydrates which exhibit congruent melting include zinc nitrate hexahydrate, $Zn(NO_3)_2 \cdot 6(H_2O)$ [13], and magnesium nitrate hexahydrate, $Mg(NO_3)_2 \cdot 6(H_2O)$ [14].

***Incongruent solidification*** occurs when a solid phase melts, producing a compositionally different liquid than the original solid. This occurs at a peritectic point, where the liquid phase and one solid phase together transforms to form a solid phase at an invariant temperature (e.g., $L + \delta \leftrightarrow \gamma$, Fig. 2, point I). Importantly, the liquid and the solid (δ) have different compositions in the region of phase coexistence above the peritectic point. Phase separation can occur with this reaction due to buoyancy differences between phases, and compositional inhomogeneity would result. This results in melting over a broader range of temperature, and in extreme cases will cause some portions of the volume to no longer melt. Additionally, if the solid (δ) is weakly soluble in water, its dissolution above the liquidus can be kinetically limited, resulting in some volume not participating in transformations during future cycles. One example of a salt hydrate that experiences incongruent solidification if brought to temperatures above its melting point of 31.9 °C is sodium sulfate decahydrate, $Na_2SO_4 \cdot 10(H_2O)$ [15]. It undergoes a peritectic reaction as it incongruently solidifies, making it unstable for use throughout many cycles.

***Eutectic solidification*** occurs when a liquid phase transforms to two or more solid phases at an invariant temperature and composition (e.g., $L \leftrightarrow \beta + \gamma$, Fig. 2, point $E_2$). In the case of a eutectic, the composition of the liquid is the same as the composition of the aggregate solid mass. Phase segregation may occur due to buoyancy differences as well as how the eutectic solidifies. In the case of equilibrium solidification, both solid phases crystallize simultaneously, often in an intimately interpenetrating fashion. In this case, the aggregate composition of the solid mass is the same as the composition of the liquid, and chemical inhomogeneities do not result (Fig. 1a). In the case of metastable solidification, one phase nucleates and begins solidifying, while the second phase is kinetically limited. This results in a liquid line of descent that moves away from the eutectic composition (Fig. 2, dashed

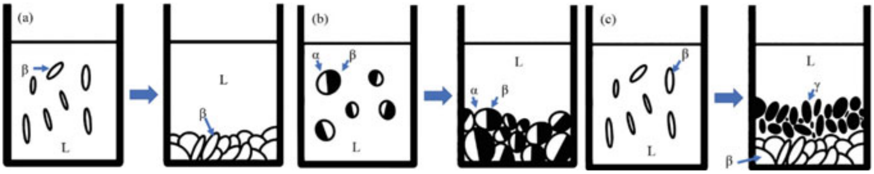
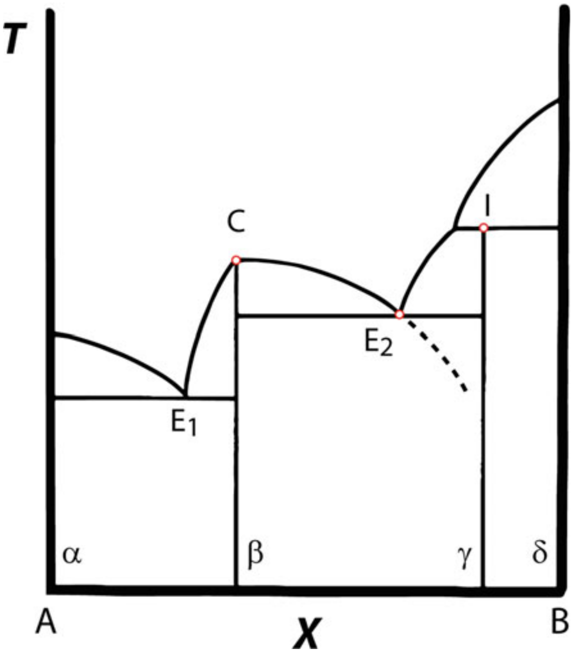


**Fig. 1** α and β phases segregating from the liquid brine phase due to differences in density. Composition will be uniform as there is a lack of compositional stratification occurring. **a** Represents solidification, **b** eutectic solidification under equilibrium conditions, and **c** eutectic solidification with metastable solidification at one phase

line), and can result in compositional heterogeneities (Fig. 1c). Unlike incongruent melting, additional solid phases are not introduced at the eutectic reaction, and thus eutectics do not tend to be susceptible to formation of weakly soluble phases which no longer transform. An example of an equilibrium eutectic is the $LiNO_3$–$LiClO_4$–$H_2O$ pseudobinary eutectic where it melts at a local minimum of 27 °C [16]. A metastable eutectic is studied with the $LiNO_3·3(H_2O)$–$LiNO_3$–$NaNO_3$ system described below, which experiences a high degree of undercooling without the aid of nucleation agents.

**Fig. 2** Example phase diagram demonstrating congruent (C), eutectic ($E_1$, $E_2$), and incongruent melting (I) at a peritectic. The dashed line near $E_2$ represents the metastable extension for the liquidus of phase β below $E_2$. In the case where solidification of phase γ is kinetically limited at $E_2$, this line represents the change in the liquid composition with cooling. This is an original figure made for this publication by the authors



## Case Study: $LiNO_3$–$NaNO_3$–$H_2O$ Eutectic

$LiNO_3·3(H_2O)$ has been identified as a salt hydrate of interest for near room-temperature heating and cooling applications because of its melting temperature of 30.1 °C and also its relatively large specific heat of fusion of 287 J/g [11]. The eutectic composition of binary and ternary systems based on $LiNO_3·3(H_2O)$ has been predicted using a modified BET method [17, 18]. Based on these predictions, we synthesized the ternary eutectic in the system $LiNO_3$–$NaNO_3$–$H_2O$ that corresponds with equilibrium solidification of the phases: $LiNO_3·3(H_2O)$–$LiNO_3$–$NaNO_3$ (henceforth referred to as the LiNaW eutectic). Solidification behavior in this system was investigated through both DSC (Fig. 3), and by tracking the internal temperature of a 3 mL volume cooled and heated continuously (at 0.1–1 ºC/min) in a recirculating water bath (Fig. 4).

Nucleation agents were added to the solution to decrease the undercooling observed in the solidification of the LiNaW eutectic. Nucleation agents are materials which introduce low interfacial energy between the solid particle and the solidifying material, which serve as nucleation sites and therefore, reduce undercooling. The nucleation agents, zinc hydroxy nitrate hydrate, $Zn(OH)(NO_3)·H_2O$, and $Cu_3(NO_3)(OH)_5·2(H_2O)$, otherwise known as the mineral likasite, have been demonstrated to reduce undercooling in $LiNO_3·3(H_2O)$ systems down to 6.3 °C [19]. Here, we illustrate the solidification behavior of both the pure LiNaW eutectic and in the presence of the nucleation agent likasite, which reduces undercooling specifically in the solidification of $LiNO_3·3(H_2O)$. In both cases, solidification is observed to occur in two distinct pulses, each associated with distinct exothermic peaks (Fig. 3). Addition of likasite decreases the primary undercooling, $\Delta T_1$, which is defined as the temperature difference between the equilibrium melting temperature

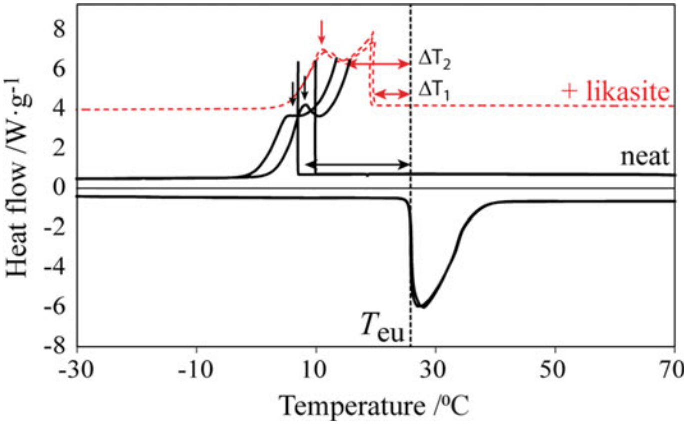


**Fig. 3** DSC Curves of two cycles of neat $LiNO_3·3(H_2O)$–$LiNO_3$–$NaNO_3$ and two cycles of the same neat $LiNO_3·3(H_2O)$–$LiNO_3$–$NaNO_3$ including the nucleation agent likasite. In both cases, two distinct peaks are observed on cooling, suggesting that solidification occurs

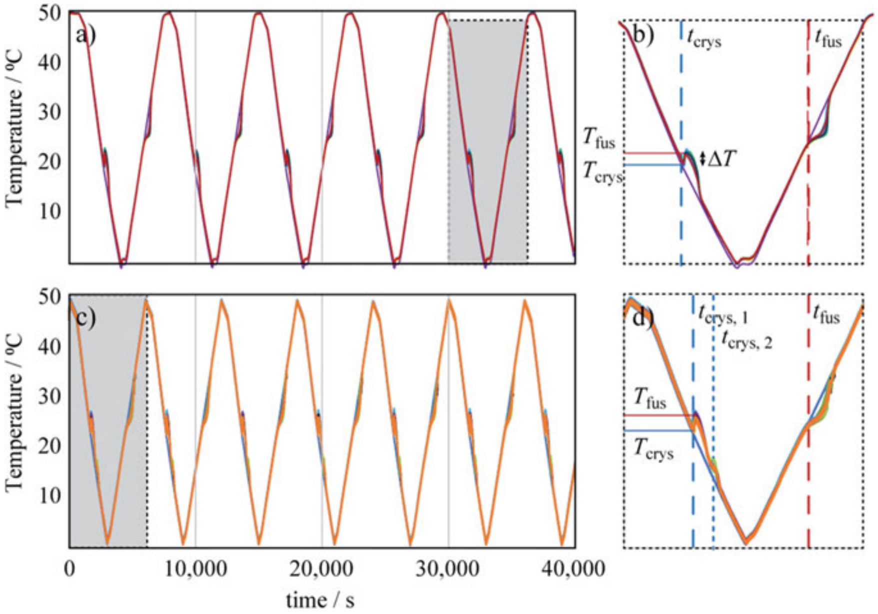


**Fig. 4** Cycling of $LiNO_3{\cdot}3(H_2O)$–$LiNO_3$–$NaNO_3$ eutectic with likasite and $BaCO_3$, $CaCO_3$, and $SrSO_3$. **a** Features a more stressed system with cycling occurring at a higher temperature than (**c**). **b** and **d** are individual cycles of (**a**) and (**c**), respectively

and the onset of solidification. However, the impact of likasite on the temperature of the secondary solidification peak is relatively minor. This observation supports the observations that in systems which are subject to metastable nucleation-limited solidification, solidification of a eutectic does not necessarily result in simultaneous solidification of all equilibrium phases.

To determine the impact of metastability on the cycling behavior of the LiNaW eutectic, a larger volume (3 mL) was sealed in a stainless-steel tube and cycled for hundreds of cycles. Importantly, the system was intentionally stressed by cooling to progressively higher and higher minimum temperatures, to attempt to induce solidification of just one phase at the eutectic point, and therefore, push the system into a regime in which phase segregation can induce compositional heterogeneities (Fig. 4). Over a sufficiently large number of cycles under stressing conditions, melting is observed to occur over a larger range in temperature, and solidification is observed to occur at two distinct temperatures, suggesting that compositional heterogeneities have been induced within the solidifying volume, resulting in degradation of cycling behavior.

## Conclusion

Degradation in thermal properties in PCMs due to phase segregation is a known challenge in incongruently melting systems. It is generally assumed that eutectic systems are robust to this issue, due to the tendency for all phases to co-solidify at equilibrium in a eutectic system. However, in the case where one or more phases are kinetically delayed, relative to other phase(s) solidifying at the eutectic, the opportunity exists for phase segregation to result in composition inhomogeneities within a volume, and for this to result in unstable behavior with cycling. We demonstrate these potential challenges in one candidate ternary eutectic system: $LiNO_3{\cdot}3(H_2O)$–$LiNO_3$–$NaNO_3$. Despite the inclusion of nucleation agents included expressly to decrease the magnitude of undercooling, the system illustrates solidification of different phases at different temperatures on cooling, and furthermore, after cycles which are intentionally designed to push the system into a metastable solidification regime, melting behavior changes with progressive cycling, and the system no longer exhibits a single well-defined solidification or melting temperature. Thus, phase segregation can still represent a technical limitation in at least some eutectic systems. Further exploration of this phenomena is required to assess how general or specific of a case the illustrated case represents, as well as approaches to best mitigate the issue for technological applications.

## References

1. de Bock HP et al (2020) A system to package perspective on transient thermal management of electronics. J Electr Pack 142(4). https://doi.org/10.1115/1.4047474
2. Kim K-B, Choi K-W, Kim Y-J, Lee K-H, Lee K-S (2010) Feasibility study on a novel cooling technique using a phase change material in an automotive engine. Energy 35(1):478–484, 2010/01/01/. https://doi.org/10.1016/j.energy.2009.10.015
3. Mulligan JC, Colvin DP, Bryant YG (1996) Microencapsulated phase-change material suspensions for heat transfer in spacecraft thermal systems. J Spacecr Rocket 33(2):278–284. https://doi.org/10.2514/3.26753
4. Lorsch HG, Kauffman KW, Denton JC (1975) Thermal energy storage for solar heating and off-peak air conditioning. Energy Conv 15(1–2):1–8
5. García-Romero A, Diarce G, Ibarretxe J, Urresti A, Sala JM (2012) Influence of the experimental conditions on the subcooling of Glauber's salt when used as PCM. Solar Energy Mater Solar Cells 102:189–195. 2012/07/01/ 2012. https://doi.org/10.1016/j.solmat.2012.03.003
6. Royon L, Karim L, Bontemps A (2013) Thermal energy storage and release of a new component with PCM for integration in floors for thermal management of buildings. Energy Build 63:29–35, 2013/08/01/ 2013. https://doi.org/10.1016/j.enbuild.2013.03.042
7. Lane GA, Shamsundar N (1983) Solar heat storage: Latent heat materials, vol. I: background and Scientific Principles. J SolEnergy Eng 105(4):467–467. https://doi.org/10.1115/1.3266412
8. Vonnegut B (1947) The Nucleation of ICE formation by Silver Iodide. J Appl Phys 18(7):593–595. https://doi.org/10.1063/1.1697813
9. Haubruge HG, Daussin R, Jonas AM, Legras R, Wittmann JC, Lotz B (2003) Epitaxial Nucleation of Poly(ethylene terephthalate) by Talc: Structure at the Lattice and Lamellar Scales. Macromolecules 36(12):4452–4456, 2003/06/01. https://doi.org/10.1021/ma0341723

10. Xing LQ, Chen B (1995) Phase-seeded solidification of undercooled Ni-B-Si alloy. J Mater Sci Lett 14(7): 480–482, 1995/01/01. https://doi.org/10.1007/BF00665908
11. Shamberger PJ, Reid T (2012) Thermophysical properties of Lithium Nitrate Trihydrate from (253 to 353) K. J Chem Eng Data 57(5): 1404–1411, 2012/05/10 2012. https://doi.org/10.1021/je3000469
12. Tamraparni A, Shamberger PJ, Felts JR (2020) Cyclic stability of lithium nitrate trihydrate in plate fin heat exchangers. Appl Therm Eng 179:115476, 2020/10/01/ 2020. https://doi.org/10.1016/j.applthermaleng.2020.115476
13. Sieverts A, Petzold W (1933) Binäre Systeme: Nitrate von Metallen der zweiten Gruppe des periodischen Systems und Wasser. II. $Be(NO_3)_2$–$H_2O$, $Zn(NO_3)_2$–$H_2O$ und $Cd(NO_3)_2$–$H_2O$. Z Anorg Allg Chem 212(1):49–60. https://doi.org/10.1002/zaac.19332120108
14. Sieverts A, Petzold W (1932) Binäre Systeme: Nitrate von Metallen der zweiten Gruppe des periodischen Systems und Wasser. I. $Mg(NO_3)_2$–$H_2O$. Z Anorg Allg Chem 205(1–2):113–126. https://doi.org/10.1002/zaac.19322050110
15. Carlsson B, Stymne H, Wettermark G (1979) An incongruent heat-of-fusion system—$CaCl_2 \cdot 6H_2O$—Made congruent through modification of the chemical composition of the system. Solar Energy 23(4), 343–350, 1979/01/01/ 1979. https://doi.org/10.1016/0038-092X(79)90129-4
16. Lovera-Copa JA, Ushak S, Reinaga N, Villalobos I, Martínez FR (2020) Design of phase change materials based on salt hydrates for thermal energy storage in a range of 4–40 °C. J Thermal Anal Calorim 139(6):3701–3710, 2020/03/01 2020. https://doi.org/10.1007/s10973-019-08655-1
17. Zeng D, Voigt W (2003) Phase diagram calculation of molten salt hydrates using the modified BET equation. Calphad-Comput Coupl Phase Diag Thermochem 27:243–251
18. Stokes RH, Robinson RA (1948) Ionic hydration and activity in electrolyte solutions. J Am Chem Soc 70(5):1870–1878
19. Shamberger PJ, O'Malley MJ (2015) Heterogeneous nucleation of thermal storage material $LiNO_3 \cdot 3H_2O$ from stable lattice-matched nucleation catalysts. Acta Mater 84: 265–274, 2015/02/01/ 2015. https://doi.org/10.1016/j.actamat.2014.10.051