



# Simulation-Assisted Determination of the Minimum Melting Temperature Composition of $MgCl_2$ -KCl-NaCl Salt Mixture for Next-Generation Molten Salt Thermal Energy Storage

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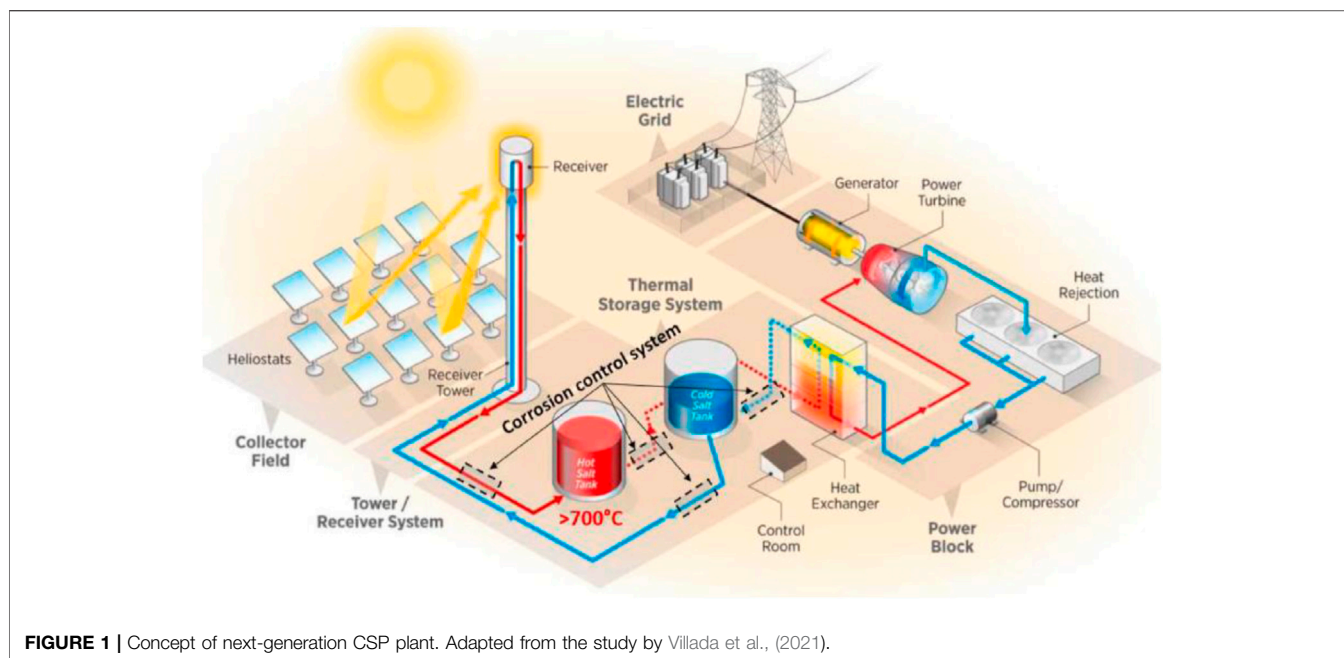
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Molten chloride mixtures such as  $MgCl_2$ -KCl-NaCl are potential thermal energy storage (TES) materials and heat transfer fluids (HTFs) for next-generation concentrating solar power (CSP) systems due to their high operation temperatures ( $>700^\circ\text{C}$ ) and low costs. This ternary  $MgCl_2$ -KCl-NaCl salt mixture with a low material cost ( $<0.35$  \$/kg) is a promising salt for high-temperature TES/HTF applications, for example, it could enable next-generation CSP plants to have significant power cycle efficiency and lower levelized cost of electricity (LCOE). In this study, the minimum melting temperature composition for the  $MgCl_2$ -KCl-NaCl mixture was estimated by FactSage simulation, while the binary and ternary phase diagrams of the  $MgCl_2$ -KCl-NaCl salt system, including their phase transitions, were studied. Five different eutectic compositions of the  $MgCl_2$ -KCl-NaCl mixture from literature and simulations were selected to determine the minimum melting temperature composition by the differential scanning calorimetry technique. Results show agreement between experiments and simulations of the melting temperature and its composition. Hence, values of the exact and reliable minimum melting temperature and salt composition in mol% and wt% are given. Based on the determined melting temperature, the minimum operating temperature of  $MgCl_2$ -KCl-NaCl is recommended according to the safety margin for CSP applications.

**Keywords:** concentrating solar power, eutectic composition, heat transfer fluid, thermal energy storage, phase diagram

## INTRODUCTION

Concentrating solar power (CSP) has been extensively investigated as a key technology for green electricity generation. A dispatchable form of CSP is the possibility to incorporate thermal energy storage (TES) using molten salts. In addition, for large-scale applications, this technology integrated with TES presents an economic advantage regarding manageability which implies lower demand-oriented levelized cost of electricity (LCOE) than volatile photovoltaic technology (Liu et al., 2016). Molten nitrate salts, especially the so-called solar salt ( $\text{NaNO}_3$ - $\text{KNO}_3$  60–40 wt%), have been studied extensively for TES and heat transfer applications in the temperature range of  $290$ – $565^\circ\text{C}$  (Bonk et al., 2018). However, their thermal stability is limited by the decomposition above  $565^\circ\text{C}$ . Thus, the



research programs on next-generation CSP, for example, the SunShot Initiative of United States Department of Energy (DOE) focus on higher operation temperature for better power cycle efficiency and major cost reduction using chloride salt mixtures comprising  $\text{CaCl}_2$ ,  $\text{KCl}$ ,  $\text{MgCl}_2$ ,  $\text{NaCl}$ , and  $\text{ZnCl}_2$  among others (Du et al., 2017; Murphy et al., 2019; Vidal and Klammer, 2019).

Low-cost molten chloride salts are some of the most promising high-temperature TES and heat transfer fluid (HTF) materials in next-generation CSP plants and other energy applications (e.g., nuclear molten salt reactor) due to, for example, their high thermal stability ( $>800^\circ\text{C}$ ) and low prices ( $<0.35$  \$/kg) (Murphy et al., 2019; Vidal and Klammer, 2019; Ding and Bauer, 2021; Villada et al., 2021). In next-generation CSP plants (see Figure 1), the  $\text{MgCl}_2$ - $\text{KCl}$ - $\text{NaCl}$  mixture can achieve higher power cycle efficiencies by using, for example,  $\text{sCO}_2$  Brayton power cycle. In its potential high-temperature TES/HTF applications, this ternary salt presents different challenges which require a study from their initial composition and preparation to the final system integration.

The exact and reliable data of the salt properties, such as melting temperature, are vital and essential for the design, construction, and operation of a TES system based on molten salts. However, due to the corrosivity and volatility of molten alkali chlorides at high temperatures and forming of salt hydrates (e.g.,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ), the experimental determination of thermodynamic properties, particularly at high temperatures, is complex. Thermodynamic simulation provides a practical way to assist the study on the thermophysical properties of molten chlorides. The salt properties, as well as the corrosion control, of molten chloride salts have been intensively studied in these years for TES/HTF applications. Two recent review articles from our group (Ding and Bauer, 2021; Villada et al., 2021) are suggested for more details on thermophysical properties and

corrosion control of  $\text{MgCl}_2$ -containing molten chlorides. The initial studies on chloride salt properties were performed by DOE as molten salt coolants in nuclear reactors using experiments and thermodynamic simulation (Manohar et al., 2010). In the early 1990s, experimental results of binary  $\text{KCl}$ - $\text{MgCl}_2$ ,  $\text{KCl}$ - $\text{NaCl}$ , and  $\text{MgCl}_2$ - $\text{NaCl}$  were reviewed and published by Janz et al. (Rowe et al., 1972; Janz et al., 1975). In the 1920s, the experimental  $\text{MgCl}_2$ - $\text{KCl}$ - $\text{NaCl}$  ternary diagram has been presented by Scholich with a reported minimum melting temperature below  $400^\circ\text{C}$  for the composition 32.5 mol%  $\text{NaCl}$ , 18.5 mol%  $\text{KCl}$ , and 49 mol%  $\text{MgCl}_2$  (Scholich, 1920). However, due to the experimental limitations at that time, the reported old minimum melting temperature and eutectic composition of  $\text{MgCl}_2$ - $\text{KCl}$ - $\text{NaCl}$  need to be validated. Some research groups have carried out such validation *via* experiments and simulations, but discrepancies of minimum melting temperature compositions available in the literature (Scholich, 1920; Jänecke, 1950; Podlesnyak et al., 1987; Mohan et al., 2018a; Vidal and Klammer, 2019) are relatively high (about 2 mol%). This may be due to different water contents in the salt mixture used in the experiment, particularly in hygroscopic  $\text{MgCl}_2$ . Currently, our group published a review paper (Villada et al., 2021) to recommend the most relevant salt properties besides minimum melting temperature for the design, construction, and operation of a TES/HTF system based on  $\text{MgCl}_2$ - $\text{KCl}$ - $\text{NaCl}$ . The properties include vapor pressure, heat capacity, density, thermal conductivity, and dynamic viscosity.

Since about 2015, there has been a strong renewed interest in the ternary  $\text{MgCl}_2$ - $\text{KCl}$ - $\text{NaCl}$  mixture as one of the most promising TES materials in next-generation CSP due to the abundance and low price of the single salts and relatively low melting temperature (Mohan et al., 2018a; Ding et al., 2018). The DLR started research with the  $\text{MgCl}_2$ - $\text{KCl}$ - $\text{NaCl}$  ternary mixture in 2015 (Maksoud and Bauer, 2015; Ding et al., 2018), and the

National Renewable Energy Laboratory (NREL) considered the binary mixture  $\text{MgCl}_2\text{-KCl}$  in 2016 (Mehos et al., 2017). Several researchers from Savannah River National Lab (SRNL), Oak Ridge National Laboratory (ORNL), Argonne National Lab, and Australian National University (ANU) have also been exploring the ternary mixture for sensible and latent TES applications (Tian and Zhao, 2013; Mohan et al., 2019). A new molten chloride salt test facility with the high-temperature molten chloride test loop is being designed by the Oak Ridge National Laboratory (ORNL) to demonstrate the viability of molten chlorides for power generation. In their most recent report (Robb et al., 2019), the loop has a designed operating temperature of  $725^\circ\text{C}$  with 20 kg of salt mixture with an approximate composition of 21–23 mol% NaCl, 42–43 mol% KCl, and 34–36 mol% of  $\text{MgCl}_2$ . The system considers the alloys Ha C-276/In 600 as the main structural materials, including corrosion monitoring and control. With the most recent advances in the area of molten chlorides, it can be demonstrated that this technology has a lot of application potential in next-generation CSP systems and nuclear molten salt reactors (MSRs) to generate electricity more efficiently and cost-effectively.

Melting temperature is a key parameter in the selection of a sensible TES or heat transfer fluid (HTF) since it determines the minimum operation temperature (partly the storage capacity) and system design to avoid salt freezing (Bonk et al., 2018; Vidal and Klammer, 2019). For this reason, this study covers a relevant topic as it is the selection of the appropriate composition of the mixture which is one of the challenges associated with improving the properties of TES materials. The minimum melting temperature and eutectic composition of the  $\text{MgCl}_2\text{-KCl-NaCl}$  ternary mixture were studied *via* FactSage thermodynamic simulation. Comparison with previous results and experimental validation with a differential scanning calorimeter (DSC) is presented after the study on the binary mixtures and their eutectic compositions as well as comparison with previous eutectic compositions reported in the literature. The current study will provide a reliable eutectic composition and minimum melting temperature of the  $\text{MgCl}_2\text{-KCl-NaCl}$  system as an important step of developing it for applications in the CSP industry and other energy industries. This composition can be used for the commercially used salt mixture, and the important properties such as heat capacity, viscosity, and thermal conductivity, can be better determined for engineering the salt for TES/HTF applications.

## MATERIALS AND EXPERIMENTAL METHODS

### Molten Salt Preparation

Five kinds of mixed chlorides were prepared by mixing KCl, NaCl, and  $\text{MgCl}_2$  at different mixed ratios according to the literature and FactSage prediction. The purities of the chloride salts were >99.9% for NaCl purchased from VWR BDH

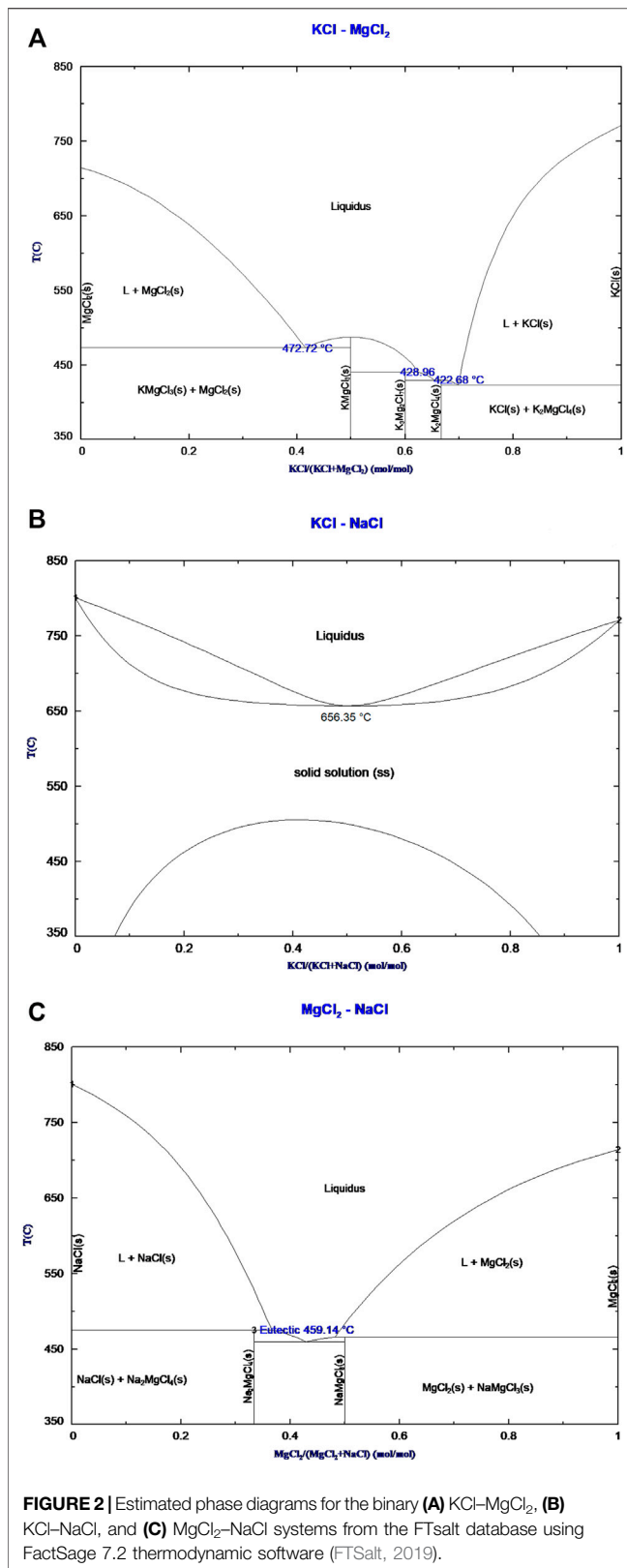
Chemicals, the purities of KCl and anhydrous  $\text{MgCl}_2$  were both 99%, purchased from Acros Organics and Alfa Aesar, respectively. Since  $\text{MgCl}_2$  may absorb  $\text{H}_2\text{O}$  from the moisture under air, all salt mixtures were prepared inside a glove box under argon atmosphere (argon 5.0, 99.999%,  $\text{O}_2 < 0.5$  ppm,  $\text{H}_2\text{O} < 10$  ppm). In addition,  $\text{MgCl}_2$  was held at  $150^\circ\text{C}$  for 18 h to remove the most hydrated water and avoid hydration. Subsequently, around 5.0 g of each salt mixture was prepared from stoichiometric weighing of each single chloride salt, followed by mixing and grinding for at least 20 min manually to ensure homogenization. For the DSC analysis, around 10–20 mg sample was transferred into aluminum crucibles, a pierced lid was placed on top of the crucible, and then hermetically sealed with a sealing press from Netzsch. Then, the samples were carefully transported in a desiccator from the glovebox to the DSC apparatus to avoid atmospheric exposure and salt hydration.

### Differential Scanning Calorimetry Measurements

Thermal analysis was carried out with a differential scanning calorimeter DSC 404 from Netzsch using aluminum crucibles under argon atmosphere (Argon 5.0), which was temperature-calibrated using Netzsch standard materials (In, Bi, Zn) in a temperature range of  $100\text{--}480^\circ\text{C}$ . Three heating and cooling runs from room temperature up to  $480^\circ\text{C}$  were performed in total to avoid discrepancies in the melting temperature produced by the traces of hydrated  $\text{MgCl}_2$ . The same heating and cooling rates ( $10^\circ\text{C}/\text{min}$ ) were applied for all samples to allow qualitative comparison of the melting point between the samples and using an empty pan as a reference. The first cycle was used for the removal of traces of absorbed water followed by pre-melting and homogenization of the mixture. For the phase diagrams, the onset of the melting peak during heating was extracted since it represents the melting temperature of the salt mixture.

### Thermodynamic Simulation With FactSage

FactSage is a commercial thermochemical databank system running in a Windows environment with the modules of Information, Database, Calculation, and manipulation (<https://www.factsage.com/>). This study utilizes version 7.2 of this software. Calculation is the main module of FactSage, which is based on the minimum Gibbs-free energy and CalPhaD (calculation of phase diagrams) theory to predict the equilibrium conditions of a system (Bale et al., 2016). It includes the submodules such as Reaction, Predom, EpH, Equilib, Phase Diagram, and Optisage. FactSage gives access to databases of thermodynamic data for thousands of compounds, including hundreds of liquid and solid metals, liquid and solid oxides, molten and solid salts, and aqueous solutions. In this study, the submodule Phase Diagram was used to simulate the binary and ternary phase diagrams of the  $\text{MgCl}_2\text{-KCl-NaCl}$  salt system to support the experimental determination of the minimum melting temperature composition and melting temperature *via* DSC.



**FIGURE 2** | Estimated phase diagrams for the binary (A) KCl–MgCl<sub>2</sub>, (B) KCl–NaCl, and (C) MgCl<sub>2</sub>–NaCl systems from the FTsalt database using FactSage 7.2 thermodynamic software (FTSalt, 2019).

## RESULT AND DISCUSSION OF BINARY SYSTEMS: KCl–MgCl<sub>2</sub>, KCl–NaCl, MgCl<sub>2</sub>–NaCl

### Literature Review

There have been numerous studies to investigate the binary KCl–MgCl<sub>2</sub>, KCl–NaCl, and MgCl<sub>2</sub>–NaCl mixtures and their compositions as candidate materials for thermal energy storage. The phase diagrams of the KCl–MgCl<sub>2</sub> and MgCl<sub>2</sub>–NaCl binary systems were experimentally studied by Menge (1911) (Menge, 1911) as well as the binary NaCl–KCl by Kurnakow (1907) (Kurnakow and Zhemchuzhnyi, 1907). Later, Janz, Scholich, and Jänecke (Scholich, 1920; Jänecke, 1950; Janz et al., 1975; Janz and Tomkins, 1981) confirmed those results and discussed their thermophysical properties.

In the review of the literature published by Rowe et al. (Rowe et al., 1972), three eutectic compositions, namely, E<sub>1</sub>, E<sub>2</sub>, and E<sub>3</sub> are reported for the KCl–MgCl<sub>2</sub> system. The compositions are 58 mol % MgCl<sub>2</sub> for E<sub>1</sub> with a eutectic temperature of 470°C, 36 mol% MgCl<sub>2</sub> for E<sub>2</sub>, and 30 mol% MgCl<sub>2</sub> for E<sub>3</sub> with a eutectic temperature of 431 and 430°C, respectively. Polimeni et al. (Polimeni et al., 2018) as well as Xu et al. (Xu et al., 2018a) evaluated the KCl–MgCl<sub>2</sub> binary mixture as the HTF in CSP solar tower configuration. In 2016, The National Renewable Energy Laboratory (NREL) considered the eutectic binary mixture MgCl<sub>2</sub>–KCl (37.5–62.5 wt%, 32.0–68.0 mol %, melting temperature of 426°C) as the TES/HTF in the next-generation CSP system.

For the KCl–NaCl binary mixture, Kurnakow (Kurnakow and Zhemchuzhnyi, 1907) found that this system forms a complete solid solution which unmixes at lower temperatures. The minimum temperature of 664°C is located between 50–51 mol% KCl.

The MgCl<sub>2</sub>–NaCl system was experimentally studied by Menge (Menge, 1911) with a eutectic temperature of 430°C for a composition of 56 mol% NaCl and later, Rowe et al. (Rowe et al., 1972) summarized previous results with a eutectic temperature of 450°C for 62 mol% NaCl.

### FactSage Thermodynamic Simulation

The binary phase diagrams of KCl–MgCl<sub>2</sub>, KCl–NaCl, and MgCl<sub>2</sub>–NaCl have been estimated using the Phase Diagram module as well as the FTsalt database which contains data of the species Mg, K, and Na chloride, and the temperature range was chosen between 350–850°C. The binary phase diagrams of the KCl–MgCl<sub>2</sub>, KCl–NaCl, and MgCl<sub>2</sub>–NaCl estimated with FactSage are shown in Figure 2. The compositions mentioned here are all based on mole fractions.

According to FactSage 7.2, the KCl–MgCl<sub>2</sub> system presents three eutectic temperatures at 472.72°C, 428.96 °C, and 422.68°C with the intermetallic KMgCl<sub>3</sub>, K<sub>3</sub>Mg<sub>2</sub>Cl<sub>7</sub>, and K<sub>2</sub>MgCl<sub>4</sub> respectively, which are in good agreement with the literature data for E<sub>1</sub> and E<sub>2</sub> (Rowe et al., 1972). Discrepancies in the eutectic temperature for E<sub>3</sub> are 8°C lower than the previous reported temperature.



**TABLE 1** | Invariant reactions of KCl–MgCl<sub>2</sub>, KCl–NaCl, and MgCl<sub>2</sub>–NaCl using FactSage thermodynamic simulation (L: Salt liquid).

System KCl–MgCl <sub>2</sub>	Phase transition	T (°C)	Composition (X <sub>mole</sub> )
L <=> MgCl <sub>2</sub> +KMgCl <sub>3</sub>	Eutectic (E <sub>1</sub> )	472.72	0.4158 KCl–0.5842 MgCl <sub>2</sub>
L + KMgCl <sub>3</sub> <=> K <sub>3</sub> Mg <sub>2</sub> Cl <sub>7</sub>	Peritectic (P <sub>1</sub> )	440.09	0.6253 KCl–0.3747 MgCl <sub>2</sub>
L <=> K <sub>3</sub> Mg <sub>2</sub> Cl <sub>7</sub> +K <sub>2</sub> MgCl <sub>4</sub>	Eutectic (E <sub>2</sub> )	428.96	0.6541 KCl–0.3459 MgCl <sub>2</sub>
L <=> K <sub>2</sub> MgCl <sub>4</sub> +KCl	Eutectic (E <sub>3</sub> )	422.68	0.6987 KCl–0.3013 MgCl <sub>2</sub>
System KCl–NaCl	Phase transition	T (°C)	Composition (X <sub>mole</sub> )
L <=> NaCl + KCl (ss)	Solid solution (ss)	656.35	0.4977 KCl–0.5023 NaCl
System MgCl <sub>2</sub> –NaCl	Phase transition	T (°C)	Composition (X <sub>mole</sub> )
L + NaCl <=> Na <sub>2</sub> MgCl <sub>4</sub>	Peritectic (P <sub>1</sub> )	474.95	0.3662 MgCl <sub>2</sub> –0.6338 NaCl
L + MgCl <sub>2</sub> <=> NaMgCl <sub>3</sub>	Peritectic (P <sub>2</sub> )	465.67	0.4818 MgCl <sub>2</sub> –0.5182 NaCl
L <=> Na <sub>2</sub> MgCl <sub>4</sub> +NaMgCl <sub>3</sub>	Eutectic (E <sub>1</sub> )	459.14	0.4296 MgCl <sub>2</sub> –0.5704 NaCl

For the KCl–NaCl binary mixture, the formation of the solid solution can be confirmed with a minimum temperature of 656.35°C and a composition of 50.23 mol% NaCl which is good agreement with the previous reported data from Rowe and Kurnakow (Rowe et al., 1972; Kurnakow and Zhemchuzhnyi, 1907).

The MgCl<sub>2</sub>–NaCl system exhibits eutectic temperature at 459.14°C with a composition of 57 mol% NaCl followed by the formation of the compounds NaMgCl<sub>3</sub> and Na<sub>2</sub>MgCl<sub>4</sub> that leads to a peritectic transformation at 465 and 474°C, respectively.

Compared to the KCl–NaCl and MgCl<sub>2</sub>–NaCl phase diagrams, the KCl–MgCl<sub>2</sub> has the lowest melting temperature of 422.68°C. These three binary phase diagrams are important as the starting point of the evaluation of the ternary phase diagram.

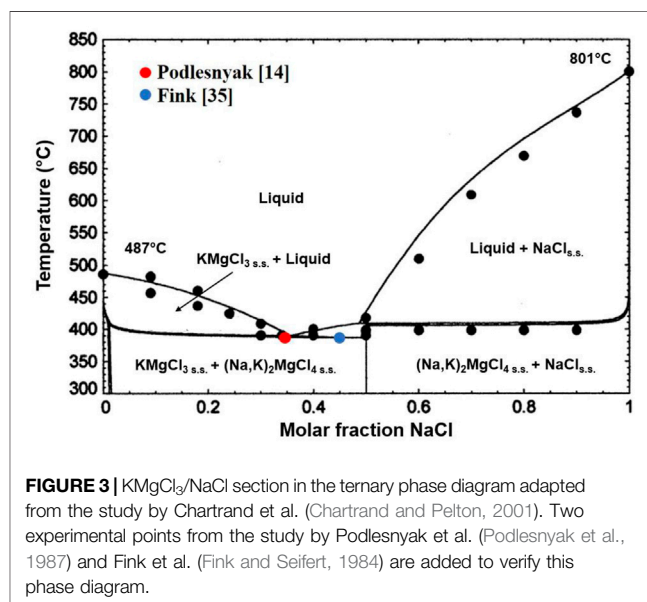
These results of the binary chloride salt simulation include different eutectic, peritectic, and solid-solution compositions. Those invariant points are summarized in Table 1 at 1 atm in the temperature range 350–850°C.

## RESULT AND DISCUSSION OF THE TERNARY SYSTEM MgCl<sub>2</sub>–KCl–NaCl

### Literature Review

In the first MgCl<sub>2</sub>–KCl–NaCl ternary diagram presented by Scholich in 1920 (Scholich, 1920), no ternary compounds but incongruently melting binary compounds, such as Na<sub>2</sub>MgCl<sub>4</sub>, and the congruently melting binary KMgCl<sub>3</sub> were reported. Below 480°C, MgCl<sub>2</sub> is insoluble in the (NaCl + KCl) solid solution. This was confirmed by Chartrand and Pelton (Chartrand and Pelton, 2001) who reported evidence of the solid solubility between Na<sub>2</sub>MgCl<sub>4</sub>–K<sub>2</sub>MgCl<sub>4</sub> and NaMgCl<sub>3</sub>–KMgCl<sub>3</sub>.

Further studies by Bradwell et al. (Bradwell et al., 2012) have used the composition 30 mol% NaCl, 20 mol% KCl, and 50 mol% MgCl<sub>2</sub> as the molten electrolyte with a melting temperature of 396°C. In a recent work, Li et al. (Li et al., 2017) investigated a variety of compositions with a minimum temperature between 383–396°C. Xu et al. (Xu et al., 2018b) experimentally studied different compositions of the ternary mixture in the range of 40–50 mol% MgCl<sub>2</sub>, in which the minimum temperature at 405°C was found for a composition of 27.5 mol% NaCl, 32.5 mol% KCl,



**FIGURE 3** | KMgCl<sub>2</sub>/NaCl section in the ternary phase diagram adapted from the study by Chartrand et al. (Chartrand and Pelton, 2001). Two experimental points from the study by Podlesnyak et al. (Podlesnyak et al., 1987) and Fink et al. (Fink and Seifert, 1984) are added to verify this phase diagram.

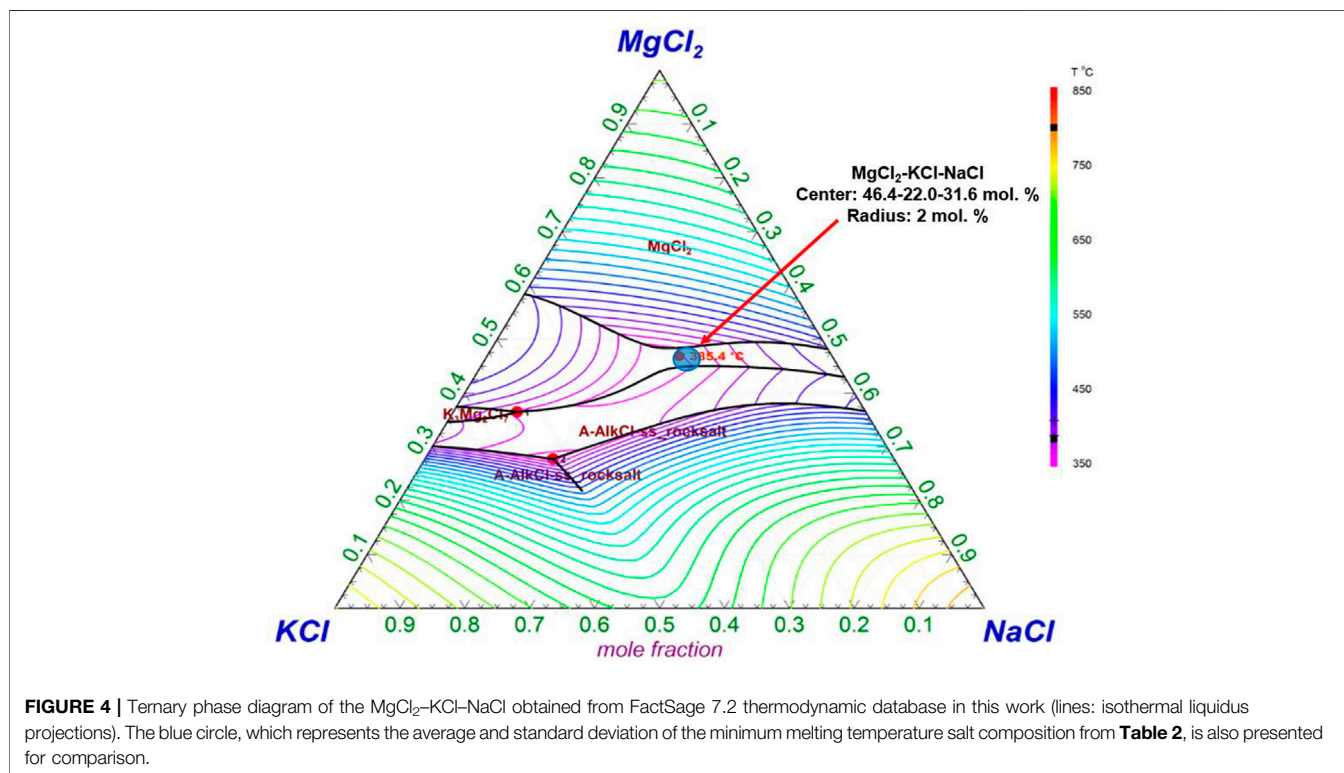
and 40 mol% MgCl<sub>2</sub>. Mohan et al. (Mohan et al., 2018a; Mohan et al., 2018b) experimentally validated the ternary mixture by DSC with a melting temperature of 387°C for the composition reported by Jänecke and Nemecek (Jänecke, 1950; Nemecek et al., 1978) of 45.4 mol% MgCl<sub>2</sub>, 21.6 mol% KCl, 33 mol% NaCl.

As suggested by Fink et al. (Xu et al., 2018b), the ternary system is incomplete in consequence of missing compounds in the binary systems. Variations of the salt compositions from different literature sources in this mixture lead to slight differences in the minimum melting temperature. For this reason, different liquid–solid transitions have been reported with the solid phases NaMgCl<sub>3</sub>, KMgCl<sub>3</sub>, K<sub>3</sub>Mg<sub>2</sub>Cl<sub>7</sub>, Na<sub>2</sub>MgCl<sub>4</sub>, and K<sub>2</sub>MgCl<sub>4</sub> which should be considered in order to select the correct minimum temperature and eutectic composition since discrepancies are linked to incomplete identification of those compounds (Baek et al., 2016).

According to Fink and Neil (Fink and Seifert, 1984; Neil et al., 1965), as well as evidenced by the binary MgCl<sub>2</sub>–NaCl and KCl–MgCl<sub>2</sub> systems presented in Figure 2, the presence of

**TABLE 2** | Different compositions (in mol%) and minimum melting temperature data following the literature review with phase diagram measurements.

Work		Salt composition (mol%)			Reported minimum temperature (°C)
		MgCl <sub>2</sub>	KCl	NaCl	
A	Scholich (Scholich, 1920)	49.0	18.5	32.5	385
B	Jänecke, Mohan, Nemecek (Jänecke, 1950; Nemecek et al., 1978; Mohan et al., 2018a)	45.4	21.6	33.0	385–387
C	Podlesnyak (Podlesnyak et al., 1987)	46.5	22.2	31.3	<400
D	Vidal et al. (Vidal and Klammer, 2019)	44.7	25.8	29.4	385
This work	Average ± Standard deviation	<b>46.4 ± 1.6</b>	<b>22.0 ± 2.6</b>	<b>31.6 ± 1.4</b>	<b>385 ≤ T<sub>m</sub> &lt; 400</b>



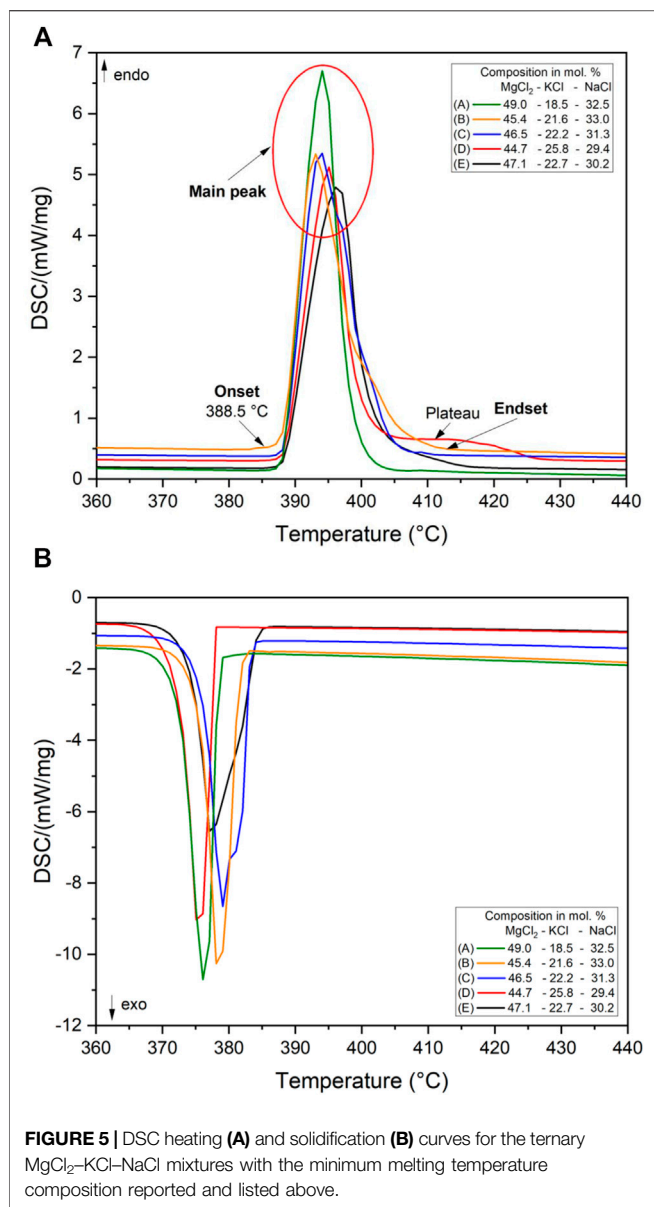
incongruently melting compounds leads to peritectic transformations and intermediate compounds. Podlesnyak and Orekhova (Podlesnyak et al., 1987) have experimentally measured the MgCl<sub>2</sub>-KCl-NaCl ternary system by conductivity techniques in which the ternary compound NaKMgCl<sub>4</sub> is reported and associated with a peritectic at 398°C, and Chartrand et al. (Chartrand and Pelton, 2001) measured the KMgCl<sub>3</sub>-NaCl section in the ternary phase diagram shown in **Figure 3**. The eutectic KMgCl<sub>3</sub>/NaCl mixture has the melting temperature of around 400°C and 35–45 mol% NaCl (Chartrand and Pelton, 2001).

The salt compositions and minimum melting temperature data from literature are summarized for comparison in **Table 2**. The discrepancies of minimum melting temperature compositions are relatively high (standard deviation of about 2 mol% for each salt species), while the reported minimum melting temperatures are in the range of 385–400°C.

### FactSage Thermodynamic Simulation

In this section, a thermodynamic simulation was performed using FactSage 7.2. The ternary phase diagram of MgCl<sub>2</sub>-KCl-NaCl have been estimated using the Phase Diagram module as well as the FTsalt database which contains data of the species Mg, K, and NaCl, and the temperature range was chosen between 350–850°C. This ternary phase diagram was estimated through the first melting temperature projection and, all compositions are referred on mole fractions.

According to FactSage simulation shown in **Figure 4**, the zone in which the minimum temperature is located corresponds to a composition of 30.2 mol% NaCl, 22.7 mol% KCl, and 47.1 mol% of MgCl<sub>2</sub> with a minimum temperature of 385.4°C compared to the minimum temperature of 383°C for 32.96 mol% NaCl, 21.62 mol% KCl, and 45.42 mol% MgCl<sub>2</sub> previously reported by Mohan et al. (Mohan et al., 2018a; Villada et al., 2019), as well as the average and standard



deviation of the minimum melting temperature salt composition from **Table 2**. In addition, the eutectic composition is formed by the compounds  $\text{KMgCl}_3 + \text{NaMgCl}_3$  (36–64 mol%) according to our thermodynamic analysis. This implies that the theoretical exact eutectic composition of  $\text{MgCl}_2$ -KCl-NaCl is 50–18–32 mol%. In the  $\text{KMgCl}_3/\text{NaCl}$  section from the ternary system, it has also been reported previously that the eutectic point at about 400°C (Fink and Seifert, 1984; Chartrand and Pelton, 2001).

## Differential Scanning Calorimetry Measurements

Since there are limited experimental measurements for the  $\text{MgCl}_2$ -KCl-NaCl ternary system, more detailed discussion is useful in understanding the minimum melting temperature and

composition of this mixture. The minimum melting temperature and related eutectic composition of the  $\text{MgCl}_2$ -KCl-NaCl ternary system were validated by DSC experiments on the salt mixtures (Samples A–D) from the literature listed in **Table 2** and the predicted salt mixture (Sample E) 30.2 mol% NaCl, 22.7 mol% KCl, and 47.1 mol% of  $\text{MgCl}_2$  in this work. The DSC heating and solidification curves of the five compositions are given in **Figure 5**.

**Figure 5** (a) shows the melting temperature which is taken from the onset of the main endothermic peak at the heating cycle from the DSC curve, excluding the water losses in the first cycle. There is only one main melting peak at approximately 388.5°C in all curves, as would be expected for a congruent melting compound. Moreover, an overlapping melting peak (Sample B, C, and E) or a plateau (Sample D) can be observed which implies that the salt mixture is not completely eutectic. A similar phenomenon can be observed in the solidification curves. The onset temperature of the main endothermic peak in the heating curve is about 3°C higher than the predicted temperature value by FactSage. The end temperatures of phase transition during heating were between ~405 and 425°C. The melting temperatures for the five salt compositions measured *via* DSC in this work are slightly higher than the melting temperatures reported in **Table 2**. The experimental results show that among these five salt compositions, the composition of Sample A ( $\text{MgCl}_2$ -KCl-NaCl 49.0–18.5–32.5 mol%) is shown to be very close to the exact eutectic composition, as almost no secondary peak can be found in the heating and solidification curve. This also agrees with the fact that the composition of Sample A is closer to the theoretical exact eutectic composition.

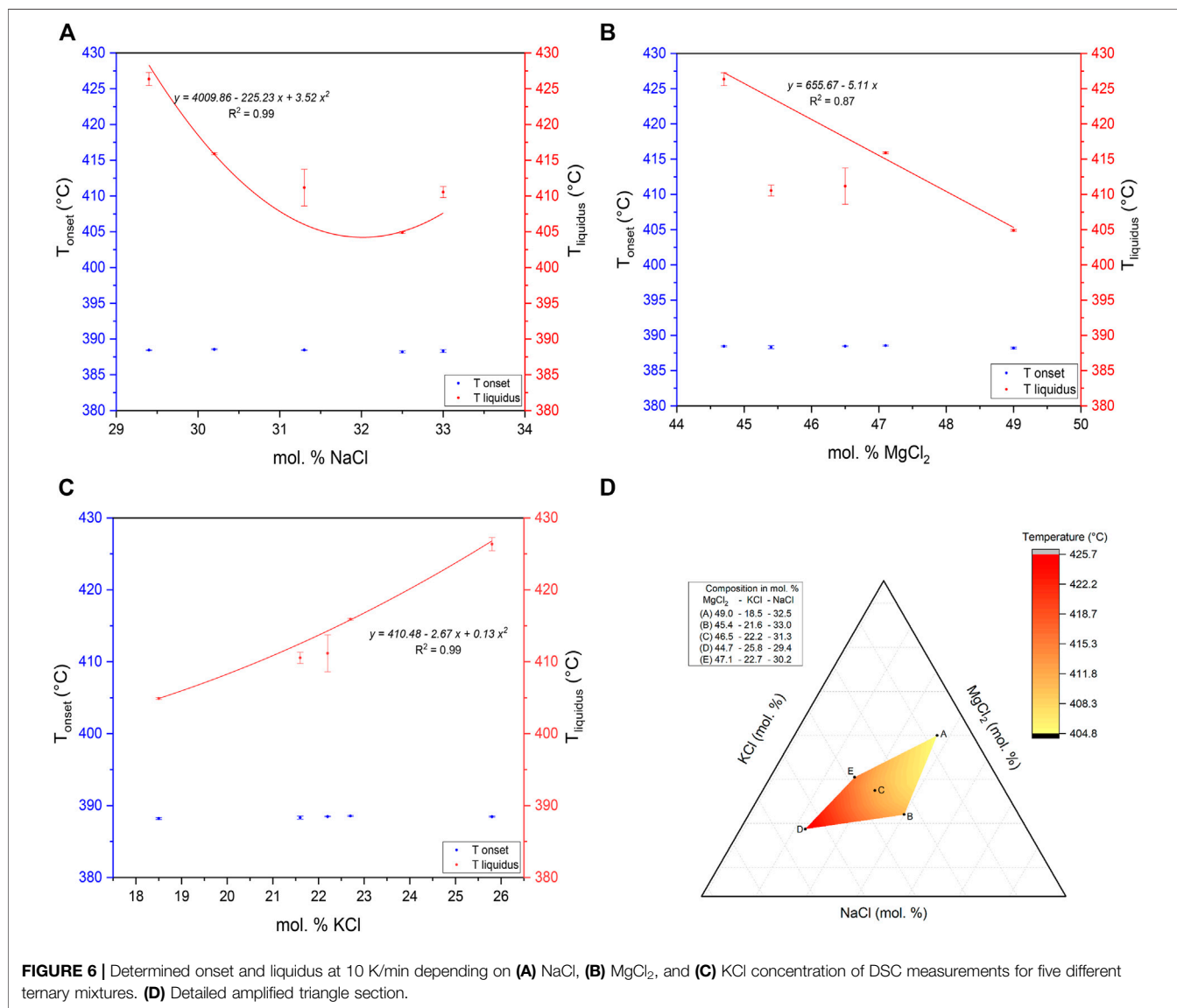
## Discussion

The melting temperature is a key parameter in the development of next-generation molten chloride salts, and it is represented by the onset of the DSC melting peak for a minimum melting temperature or eutectic mixture. From previous experience in our group with molten nitrate salts, the melting temperature of minimum melting temperature compositions can be successfully determined by differential scanning calorimetry—DSC (e.g., ASTM E794 (Bonk et al., 2018)). For mixtures with a melting range, the liquids temperature is relevant. A simple endset or peak maximum measurement as reported by some authors is misleading due to the influence of heating rates, sample mass, and composition (Yu-ting et al., 2017). Overall, the minimum operating temperature of the  $\text{MgCl}_2$ -KCl-NaCl ternary system for sensible TES applications should not exceed 420°C assuming a melting temperature of about 390°C and the recommended safety margin of 30°C for CSP applications (Bonk et al., 2018). It can also be seen from this work that the composition values for the minimum melting temperature are usually referred to compositions of 44.7–49 mol%  $\text{MgCl}_2$ , 18.5–25.8 mol% KCl, and 29.4–33 mol% NaCl.

The melting temperatures of the ternary  $\text{MgCl}_2$ -KCl-NaCl system with different compositions, including this work, are listed in **Table 3**. All onset values are mostly around  $388.40 \pm 0.55^\circ\text{C}$ . The variations of the DSC liquidus temperature for the

**TABLE 3** | Comparison of salt compositions and melting temperatures of the studied five MgCl<sub>2</sub>-KCl-NaCl ternary salt mixtures experimentally obtained by DSC at 10°C/min heating rate. The error of the measured temperatures is the standard deviation of three different measurements.

Salt composition (mol%)	MgCl <sub>2</sub> KCl NaCl			Reported or predicted Temp. (°C)	Onset Temp. (°C)	End Temp. (°C) at 10 K/min
	MgCl <sub>2</sub>	KCl	NaCl			
A (Scholich, 1920)	49.0	18.5	32.5	385	388.20 ± 0.14	404.9 ± 0.14
B (Jänecke, 1950; Nemecek et al., 1978; Mohan et al., 2018a)	45.4	21.6	33	385–387	388.33 ± 0.21	410.55 ± 0.78
C (Podlesnyak et al., 1987)	46.5	22.2	31.3	400	388.47 ± 0.06	411.17 ± 2.57
D (Vidal and Klammer, 2019)	44.7	25.8	29.4	385	388.45 ± 0.07	426.35 ± 0.92
E (This work)	47.1	22.7	30.2	385.4	388.55 ± 0.07	415.90 ± 0.14



**FIGURE 6** | Determined onset and liquidus at 10 K/min depending on (A) NaCl, (B) MgCl<sub>2</sub>, and (C) KCl concentration of DSC measurements for five different ternary mixtures. (D) Detailed amplified triangle section.

five different ternary mixtures at 10 K/min are shown in **Figure 6**, in which the influence of each single chloride from the ternary mixture is notable. Both NaCl and MgCl<sub>2</sub> contribute to a decrease in the liquidus temperature, whereas the KCl content increases the liquidus temperature. The

results confirm the main conclusion in the last subsection that the composition of Sample A (MgCl<sub>2</sub>-KCl-NaCl 49.0–18.5–32.5 mol%), which has the highest MgCl<sub>2</sub> content and lowest KCl content, is closer to the exact eutectic composition.



## SUMMARY AND CONCLUSIONS

This study investigated the binary and ternary phase diagrams of the  $\text{MgCl}_2$ - $\text{KCl}$ - $\text{NaCl}$  system using literature data and FactSage simulation and own DSC measurements in order to determine the minimum melting temperature of the  $\text{MgCl}_2$ - $\text{KCl}$ - $\text{NaCl}$  ternary salt. This mixture is relevant for high temperature TES for next-generation CSP systems.

In this study, five different compositions of the ternary  $\text{MgCl}_2$ - $\text{KCl}$ - $\text{NaCl}$  salt mixture from literature and simulation of this study have been synthesized in an inert atmosphere (i.e., water impurity in the salt mixtures is neglectable) and tested according to the previous reported compositions, and their experimental melting temperatures were determined by the DSC technique.

After detailed analysis of literature, FactSage simulation and own DSC measurements, a minimum melting composition of  $\text{MgCl}_2$ - $\text{KCl}$ - $\text{NaCl}$  49.0–18.5–32.5 mol% or 58.7–17.4–23.9 wt% with the experimental melting temperature of 388.5°C is recommended. In addition, the phase transition that describes this eutectic composition is given by the composition  $\text{KMgCl}_3 + \text{NaMgCl}_3$  (36–64 mol%). This implies that the theoretical exact eutectic composition of  $\text{MgCl}_2$ - $\text{KCl}$ - $\text{NaCl}$  is 50–18–32 mol%, which agrees very well with the recommended composition. Based on these results, the minimum recommended operating temperature for high-temperature TES is 420°C (more than 30°C higher than the melting temperature). However, material cost aspects and larger safety margins may lead to other salt compositions (e.g., less  $\text{MgCl}_2$  and more  $\text{NaCl}$  in salt mixture)

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and operating temperatures higher than 420°C regarding the overall TES costs. Moreover, as the salt composition and melting temperature can be changed (i.e., shift of salt composition) by the by-reactions of the salt with impurities in salt or gas atmosphere during the use, monitoring of salt health is suggested in order to avoid inconveniences such as salt freezing.

## DATA AVAILABILITY STATEMENT

The simulation details have been added to the article. Further inquiries can be directed to the corresponding author.

## AUTHOR CONTRIBUTIONS

CV: conceptualization, investigation, writing—original draft, preparation, and visualization. WD: conceptualization, investigation, writing—original draft, preparation, visualization, review and editing, and revision. AB: Writing—review and editing. TB: Writing—review and editing and funding acquisition.

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