Thermal Analysis of Molten Salts and their Mixtures with Metals

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ABSTRACT

Salts and their mixtures play an important role for industrial and energy sectors, eg, metallurgy, biomass gasification and combustion, nuclear and solar power plants, and electrochemical processes. Depending on the composition of salts (eg, Li^+,Na^+,K^+,Mg^{2+},Ca^{2+}// NO_3^-,F^-,Cl^-,CO_3^{2-},SO_4^{2-}, etc.), the temperature range for different applications can vary starting from room temperature and going up to 1500°C. For the proper design and modelling of heat exchangers and other equipment, it is necessary to have reliable and validated datasets of thermophysical properties.

The 50 mol% $NaNO_3$ - 50 mol% KNO_3 salt mixture as a well-studied composition was selected for validation of relevant thermophysical properties (heat capacity, enthalpy of phase transitions, thermal expansion, viscosity and thermal conductivity). To study these properties of the liquid phase, special crucibles and approaches should be implemented. Verification of these crucibles for different methods (DSC, TMA, LFA and Rheometers) has been performed.

The low thermal conductivity of salts is one of the main problems in implementing latent heat storage. In this project, the authors intend to develop a fundamental solution to this problem using chemically bonded metals with salts. These are known as metal-salt solutions. To fit the main parameters of new phase change materials to the requirements of thermal energy storage, a wide variety of possible combinations should be considered. CALPHAD modelling is used together with thermal analysis for the development of a consistent thermodynamic database including chloride salts (Li, Na, K, Mg, Ca // Cl) and corresponding metals (Li, Na, K, Mg, Ca). The results of the study of quasi-binary and multicomponent metal-salt (eg, Mg-KCl and Ca-KCl) systems as well as the selection of suitable crucible materials and challenges by studying of these systems will be discussed.

INTRODUCTION

The transition to renewable energy sources, including wind, solar, water, and biomass, necessitates advancements not only in the development of efficient and energy-storage technologies but, given the inherently variable nature of these sources, particularly in the realm of energy storage systems. Beyond electrical and electrochemical storage, thermal storage emerges as a pivotal facet on this new technological landscape. The concept of thermal energy storage (TES) is well known, exemplified by furnaces used for heating homes, and nowadays its contemporary significance lies in its diverse applications across varying temperature ranges. Thermal storage, for example, is integrated into a variety of applications, ranging from heat storage for solar-assisted heating of buildings (0 - 100°C), to applications in industrial processes (100 - 300°C), to high-temperature storage for power plants (300 - 1000°C).

In recent decades, there has been a growing interest in thermal storage technologies, propelled by the advancement of Concentrated Solar Power (CSP) plants. CSP is one of the most promising renewable energy technologies and will play a key role in addressing current and future global electricity demand challenges. Recognizing the potential for further advancements, the current

"SaltMe" project directs its focus toward increasing the capacity of CSP plants. The key strategy involves the development of latent thermal energy storage using innovative phase change materials with enhanced two main parameters: energy density and thermal conductivity.

Currently, in most CSP plants so called SolarSalt (mixture of 60 wt.% $NaNO_3$ and 40 wt.% KNO_3) is used for TES with a large amount of salt (up to several tons of salt). This type of TES uses the heat capacity of the liquid phase, known as sensible heat. There are two other types of TES, latent and thermochemical, which are still under development and have not been applied for CSP plants yet, because of the low thermal conductivity of salts [Cárdenas, 2013; Baharoon, 2015; Liu, 2016], which causes a relatively poor performance of the TES [Jegadheeswaran, 2009]. In latent TES, phase change materials (PCMs) will be used. They can store a large amount of thermal heat in a narrow temperature range. As PCMs for latent TES, in particular salts and salt systems [Kenisarin, 2010; Cárdenas, 2013] are suitable due to thermodynamic, physical, chemical, and economic aspects. Latent TES requires PCMs with a thermal conductivity preferably in the range of 5 – 20 W/(m·K) and additionally high volumetric heat capacity to guarantee high discharging power and high storage density [do Couto Aktay, 2008]. By using different salt mixtures with a relatively high phase transition enthalpy, the energy density of latent TES can be improved. However, these systems usually have very low thermal conductivity (lower than 2 W/(m·K)), which means that charging and discharging of TES takes longer than for materials with higher thermal conductivity. From this point of view, metal systems are an interesting alternative to salts, because they have higher thermal conductivity. Nevertheless, the low energy density and relatively high price of metallic systems make the choice between these two groups of PCMs more complicated and ambiguous.

In the case of metal-salt systems, homogeneous mixtures can be easily prepared. It is sufficient to melt metals with salts according to the existing phase diagrams. There is a miscibility gap between the two liquids. However, if the critical (consolute) temperature is achieved, a homogeneous liquid phase is formed, and the metal can be dissolved in the entire concentration range. It is possible to prepare homogeneous metal-salt solutions in situ with various concentrations of the metals. However, yet it is not clear how the thermal conductivity of these materials is changed by phase transitions, eg, from liquid to solid. It may be the case that the thermal conductivity of the homogeneous liquid phase can be increased significantly. However, it must be determined how the metals are distributed in the salts after crystallization, because it exerts a strong influence on the thermal conductivity of the solid phase.

Even if the thermal conductivity of metal salt solutions can be significantly increased, this does not mean that these materials can be used as PCMs in CSP plants due to the stringent requirements, eg, low costs, no corrosion, thermal stability and suitable temperature of the phase transitions. Therefore, it is important to vary the parameters of metal-salt systems, which can be done by using multicomponent systems. Nevertheless, these systems have not undergone any comprehensive study. In this case, a different kind of possible combinations of components should be considered. Therefore, the fundamental principles of the formation of metal-salt solutions and influences on the phase transition temperatures and on the thermal conductivity need to be understood. Nowadays such tasks can be solved by using thermochemical modelling based on the CALPHAD method, which has been successfully applied in the last few decades for the development of superalloys and slag systems with three and more components. However, in the case of metal-salt systems, this is not yet possible because there is currently no such database that includes both metals and salts. The SaltMe project focuses on developing a consistent thermodynamic database and discovering new correlations between thermodynamic properties and thermal conductivity for metal-salt solutions.

SAMPLES

The pure salts LiCl (Alfa Aesar, ultra-dry, 99.995%), KCl (Thermo Fisher Scientific, ultra-dry, 99.997%), NaCl (Thermo Fisher Scientific, 99.998%), $MgCl_2$ (Thermo Fisher Scientific, 99.9%), $CaCl_2$ (Thermo Fisher Scientific, 99.99%) and pure metals Li (Sigma-Aldrich, ultra-dry, 99 %),K (Thermo Fisher Scientific, ultra-dry, 99%), Na (Thermo Fisher Scientific, 99.95%), Mg (Carl Roth, >=99.8%), Ca (Sigma-Aldrich, 99%) were used to prepare samples for the measurements. Preparation of the samples was performed inside a glove box with argon atmosphere (purity 99.9992%).

The 50 mol% $NaNO_3$ – 50 mol% KNO_3 salt mixture was prepared from the two pure compounds with purity 99.995% of $NaNO_3$ and 99.999% of KNO_3 from Sigma-Aldrich by mixing in a glazed porcelain crucibles and heating up to 300 °C under air atmosphere. Thermogravimetric analysis of the prepared mixture shows minor mass loss (in total 0.06%) by heating the sample up to 400°C with two cycles, which confirms low content of absorbed water.

INSTRUMENTS

Differential Thermal Analysis (DTA)

NETZSCH STA 449C device was used to measure the phase change temperature. Samples were tested at a heating and cooling rate of 5 K/min with an argon gas flow rate of 20 ml/min, the purity of the argon gas is 99.9992%.

Differential scanning calorimetry (DSC)

NETZSCH STA449F3 (Type S thermocouple) and NETZSCH DSC204F1 (Type E thermocouple) have been used for determination of heat capacity of the 50mol%$NaNO_3$-50%KNO_3 mixture. The experiments were performed with a heating rate of 10 K/min and 40 ml/min flow rate of argon (purity of 99.999%) and nitrogen (purity of 99.999%).

X-ray diffractometry (XRD)

Samples were investigated by using XRD with an EMPYREAN diffractometer (Malvern Panalytical, Almelo, The Netherlands) equipped with a Cu LFF X-ray tube (operated at 40 kV and 40 mA), a Bragg Brentano HD mirror, a PIXcel3D detector in 1D mode and a HTK 1200N oven chamber (Anton Paar, Austria).

CRUCIBLE MATERIALS FOR SALT MIXTURES

The choice of crucible material and geometry is highly dependent on the specific requirements of the thermal analysis method (eg DSC, thermomechanical analysis (TMA), laser flash analysis (LFA) and Rheology) to ensure the determination of reliable thermodynamic (heat capacity, enthalpy of phase transitions) and thermophysical (thermal conductivity, thermal expansion, viscosity) properties. The selection depends on several factors such as the temperature range, thermal stability (when using closed or open crucibles), possible reactions with the crucible material and the gas atmosphere. In addition, surface energy and roughness of crucible material can influence the creep behaviour of the sample [Grosu, 2019; Piro, 2021; Hallat, 2019].

In the case of salt systems, the use of graphite and boron nitride crucibles is preferable for DSC and DIL/TMA analyses due to low reactivity and wettability. However, relatively high thermal conductivity of graphite and non-replicable structure can indeed impact the reliability and accuracy of results for the laser flash analysis (LFA) measurements. The irregularities in the graphite structure can introduce variability in thermal properties, affecting the precision of thermal diffusivity measurements. Low wettability can also be considered as a disadvantage when selecting spindle materials for rheological viscosity measurements. In rheological measurements, the interaction between the sample and the spindle or geometry used is critical to obtaining accurate and reliable viscosity data. Spindles with low wettability may not fully immerse or cover the sample, resulting in incomplete interaction. This can result in inaccurate viscosity readings as the instrument may not measure the entire sample.

In the frame of this work, different crucibles were tested for various thermal analysis techniques, including DSC, TMA, LFA, and Rheometry. A 50 mol% $NaNO_3$ - 50 mol% KNO_3 salt mixture was used as the well-studied composition to verify the experimental values. Figure 1 shows the experimental results of heat capacity obtained for the first heating of the sample in aluminium and graphite crucibles. In both cases quite similar results within the uncertainty of 3% can be obtained, however in both cases two different devices STA449F3 (Type S thermocouple) and DSC204F1 (Type E thermocouple) were used. The results are also compared with available heat capacity data from FTSalt and FTfrtz databases from FactSage.

The temperature dependence of the density, thermal diffusivity and viscosity as well as the calculated thermal conductivity of the 50 mol% $NaNO_3$ – 50 mol% KNO_3 mixture will be discussed in the presentation at the MOLTEN 2024 conference. One of the main problems for the determination of these values in the solid phase is the appropriate sample preparation, which should minimise the formation of pores and irreversible solid phase transition in the samples. In the case of viscosity measurements by rotational rheometer, spindle geometries made of different materials have been tested and reliable values have been obtained by using a plate-plate geometry made of copper.

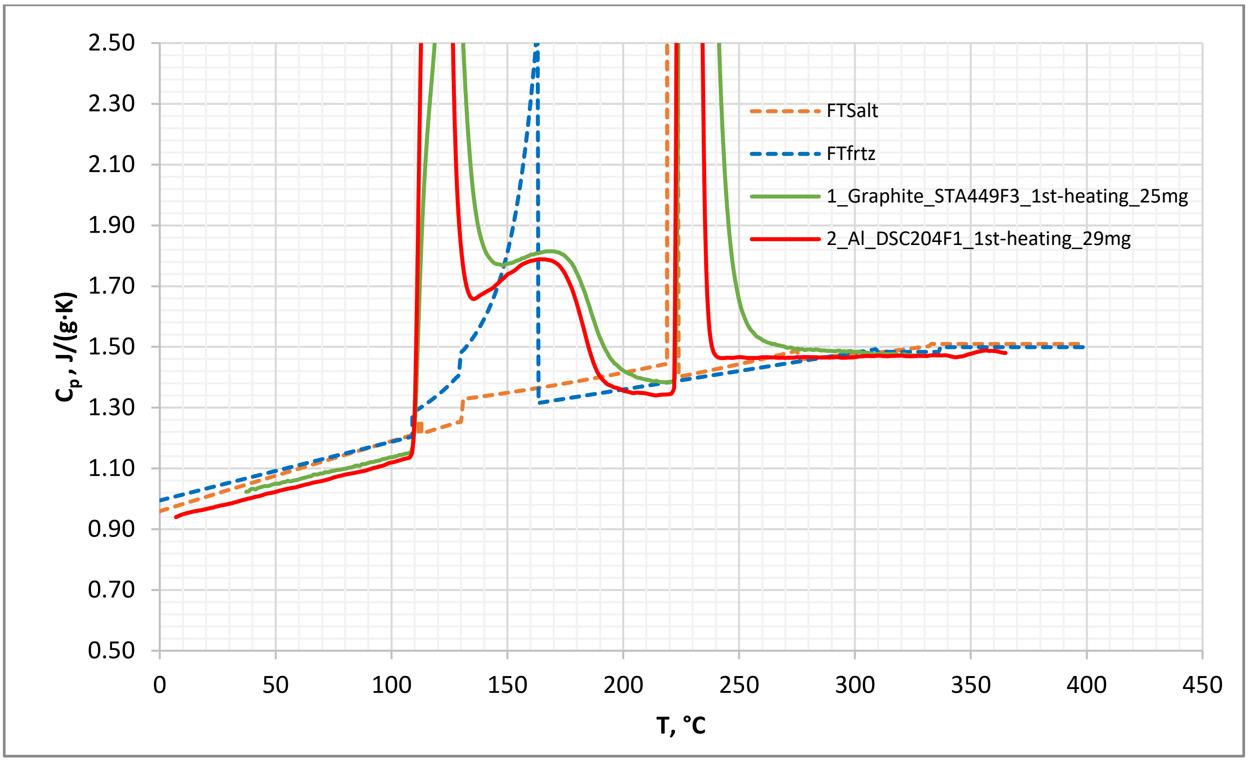

FIG. 1 - Experimental values of the specific heat capacity of a 50mol% $NaNO_3$ – 50mol% KNO_3 mixture measured in aluminium and graphite crucibles and calculated values from FTSalt and FTfrtz databases from FactSage

CRUCIBLE MATERIALS FOR METAL-SALT MIXTURES

The combination of salts and alkaline/alkaline earth metals introduces additional challenges in the selection of crucible materials, especially for high-temperature applications. The corrosive and reactive nature of certain salts, coupled with the reactivity of alkaline and alkaline earth metals, necessitates careful consideration when choosing materials for crucibles.

Table 1 shows the melting and boiling points of the metals, alongside the melting point of the salts. Notably, the boiling point of potassium (K) is lower than the melting points of NaCl and KCl. This implies that it is not advisable to conduct measurements of the K-KCl and K-NaCl mixture in open crucibles. Additionally, all metals within the system are prone to oxidation, and lithium (Li), sodium (Na), and potassium (K) are particularly susceptible to reacting with water (H_2O). To prevent undesirable interactions between the gas flow and the sample, as well as the vaporization of the sample, it is preferable to use closed crucibles for the measurements.

TABLE 1 – Melting and boiling temperatures of pure metals and salts

Metal	Melting temperature, °C	Boiling temperature at 1 atm, °C	Salt	Melting temperature, °C
Li	181	1350	LiCl	610
Na	98	899	NaCl	801

K	64	768	KCl	770
Mg	650	1114	$MgCl_2$	714
Ca	842	1492	$CaCl_2$	772

The K-KCl system was experimentally investigated by [Johnson and Bredig, 1958] utilizing stainless steel crucibles. Similarly, the Na-NaCl system was studied by [Bredig et al., 1955] and [Bredig and Bronstein, 1960] using stainless steel crucibles. As an example, the phase diagram of K-KCl system studied by [Johnson and Bredig, 1958] is shown in Figure 2, which demonstrates the formation of a homogeneous solution between salt and metal in the liquid phase. The Li-LiCl system was measured by [Nakajima et al., 1974] using molybdenum (Mo) cells sealed by means of electron beam welding. For the measurement of the Ca-CaCl2 system, tantalum and stainless-steel crucibles were used [Sharma, 1970; Staffanson, 1960]. The effect of Mg on the corrosion of 316H stainless steel in molten salts $MgCl_2$-NaCl-KCl was investigated by [Zuo, 2021]. These results are summarized in Table 2.

In studies involving liquid sodium (Na) as a heat transfer fluid, [Pacio and Wetzel, 2013] identified suitable structural materials. Their findings indicated that pure iron, ferritic stainless steel, austenitic stainless steel, chromium, nickel alloys (containing iron, chromium, and molybdenum) and refractory metals (molybdenum, niobium, tantalum, and tungsten) exhibited good compatibility with the liquid sodium at 300 °C, 600 °C and 800 °C, ensuing a corrosion rate lower than 25.4 μm/year.

TABLE 2 – Literature data on crucible materials used in previous studies

System	Crucible	References
K-KCl	Stainless steel + glass	Johnson and Bredig, 1958
Na-NaCl	Stainless steel + glass	Bredig et al., 1955
Li-LiCl	Mo cell sealed by means of electron beam welding	Nakajima, 1974
Ca-$CaCl_2$	Tantalum melt container /stainless steel	Sharma, 1970 /Staffanson, 1960
NaCl-KCl-$MgCl_2$-Mg	Stainless steel	Zuo, 2021

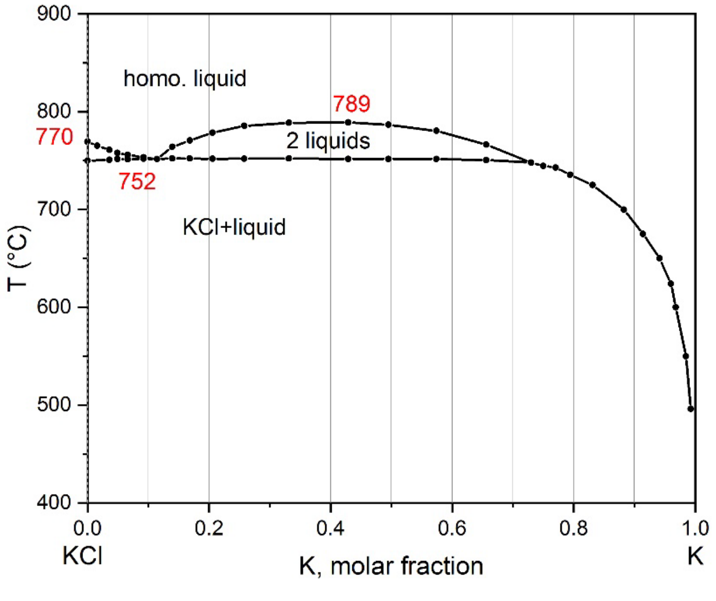

FIG 2. Phase diagram of the metal-salt system K-KCl [Johnson and Bredig 1958]

It is important to ensure that no reactions occur between the sample and the crucible when selecting crucible materials. This validation process involves consideration of the phase diagrams with the present components. If the analysis reveals the presence of intermediate compounds or solid solutions, the crucibles are subsequently excluded from the consideration. The assessment involved examining the phase diagram or the intermediate compounds that may form between the metals and SiO_2, Al_2O_3, graphite, and Pt. The phase diagram of metals and oxide crucible materials were calculated using the FToxid database and SGPS database. As an example, the results of Mg-Al_2O_3 are illustrated in Figure 3. While the liquid phase of the phase diagram may lack accuracy due to the absence of a shared database between metal and oxide, the representation of intermediate compounds and solid solution phases in the solid part of the diagram offers valuable insights into potential reactions between the samples and the crucible materials. Analogously, in the calculated phase diagrams of Al_2O_3 and other metals (ie. Li, Na, K and Ca), intermediate compounds are found formed,eg. Li_5AlO_4, $LiAlO_2$, $LiAl_5O_8$, $NaAlO_2$, $Na_2Al_{12}O_{19}$, $NaAl_9O_{14}$, $KAlO_2$, $K_2Al_{12}O_{19}$, $CaAl_2O_4$, $CaAl_{12}O_{19}$, $CaAl_4O_7$. In the calculated phase diagrams between SiO_2 and sample metals (Li, Na, K, Mg and Ca), various intermediate compounds are found , such as Li_2SiO_3, $Li_2Si_2O_5$, Li_4SiO_4, Li_8SiO_6, Na_2SiO_3, $Na_2Si_2O_6$, Na_4SiO_4, $K_2Si_4O_9$, $K_2Si_2O_5$, K_2SiO_3, $CaSiO_3$, Ca_2SiO_4, $MgSiO_3$, Mg_2SiO_4. In the case of Pt, numerous intermediate compounds such as LiPt, $LiPt_2$, $LiPt_7$, Li_2Pt, $NaPt_2$, MgPt, $MgPt_3$, Mg_2Pt, Mg_3Pt, Mg_3Pt_2, $CaPt_2$, $CaPt_5$ and Ca_2Pt_2 have been identified, as documented in the ICSD database [Belsky et al., 2002]. Notably, no intermediate compound between Pt and K was found in this database. Besides, the phase diagram between other crucible material (Mo, Ni, Fe, graphite) and the sample metals (Li, Na, K Mg and Ca) were calculated with FTlite database in FactSage. In Table 3 possible compatibilities of crucible materials with salts and metals are shown.

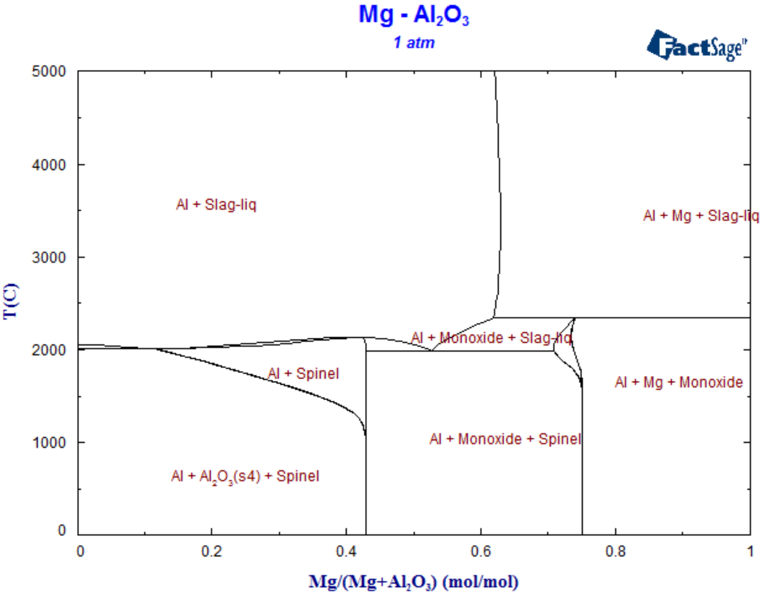

FIG. 3 - Phase diagram of Mg-Al_2O_3 system

TABLE 3 – Compatibility of crucible materials with salts and metals, +: good compatibility, -: not compatible.

Samples	Crucible materials							
	graphite	glass	Pt	Al_2O_3	Mo	Fe	Ni	Stainless steel 316L
Chloride salts	+	+	+	+	+	+	+	+
Na	-	-	-	-	+	+	+	+
K	-	-	+	-	+	+	+	+
Li	-	-	-	-	+	+	+	+

Mg	-	-	-	-	+	+	-	-
Ca	-	-	-	-	+	+	-	-

Two types of closed crucibles were designed for the DTA experiments of the salt-metal system, which are made of Fe-alloy-Mo crucible and of stainless steel 316L, as shown in Figure 4a and 4b, respectively. The threaded structure and the sealing gasket are used to increase the sealing ability of the crucibles. The similar structure was reported by Piro (2021).

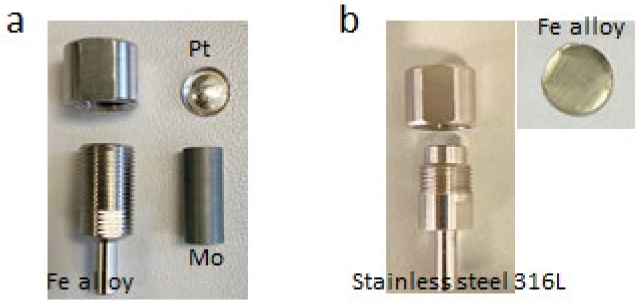

FIG. 4 - DTA crucible from a) Fe-alloy with Mo liner and b) stainless steel 316L

MULTICOMPONENT METAL-SALT SYSTEMS

In addition to quasi-binary metal-salt systems, multicomponent metal-salt systems have great potential for use as phase change materials or as heat transfer fluids. Such systems have not yet been investigated systematically. Binary metal-salt mixtures are limited and not suitable for various application conditions requiring lower phase transition temperatures. In the case of multicomponent systems, the melting temperature can be decreased significantly. For example, we can consider the reciprocal system Na-K-KCl-NaCl. This system includes four binary (K-Na (Figure 5), KCl-NaCl (Figure 5), K-KCl (Figure 2), Na-NaCl) systems. It can be seen, that in all these cases the lowest melting temperature is reduced. Therefore, it can be assumed, that the melting temperatures inside of the reciprocal system will be lower compared to the quasi-binary systems.

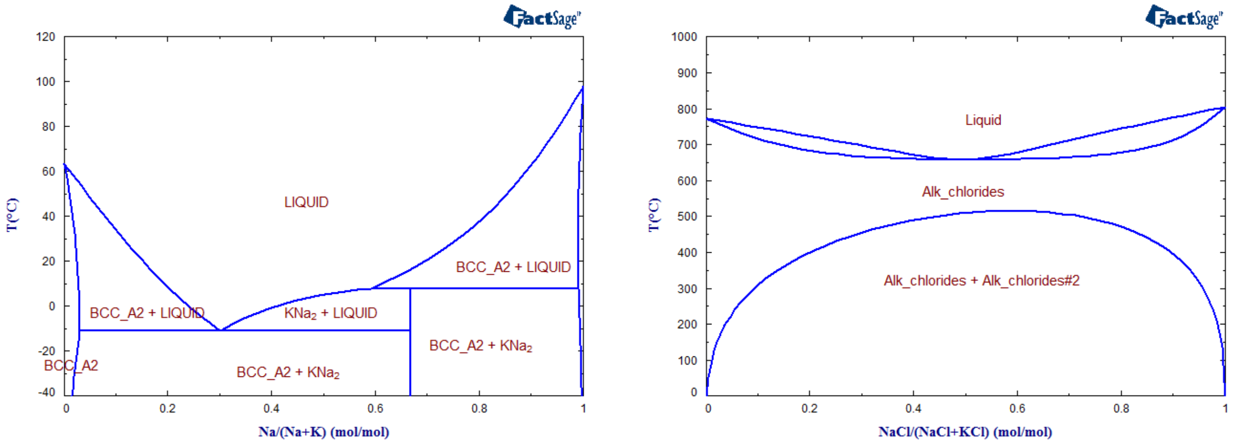

FIG. 5 - Phase diagram of Na-K (SGTE database) and NaCl-KCl systems (PCM database)

One of the features of reciprocal systems is the reciprocal reaction, eg K+NaCl = KCl+Na. Equilibrium conditions of this reaction should be considered. For example, when studying the two-component K-NaCl or Na-KCl systems, four components can be formed according to the equilibrium conditions of the reciprocal reaction. That means it is sufficient to mix just three components, eg Na, KCl, and NaCl, to produce all the compositions in the triangle Na-KCl-NaCl on the phase diagram. This allows the preparation of mixtures with more suitable components. It also avoids the use of highly reactive components such as potassium.

For the reciprocal system, the stable diagonal systems can be confirmed using Ellingham diagonal, calculated with FactSage Reaction using SGTE database, as shown in Figure 6. There are crossings in the Ellingham (Na - Li and Na - Ca). According to this calculation, the stable diagonals at room temperature are not correct for the (Na-Li-NaCl-LiCl) and (2Na-Ca-(NaCl)$_2$-CaCl$_2$) systems, when the temperature is above the cross point. The stable diagonals at 298 K are shown in Figure 7 and listed in Table 4. The reliability of this calculation needs to be tested experimentally. From the application point of view, according to these reactions, when small amounts of metals were added to the salt mixture, only the stable metals remained. For example, when the metal mixture of Na, K and Mg is added into the salt mixture of NaCl, KCl and MgCl$_2$, Na and K will react with MgCl$_2$ to form NaCl and KCl. After the reaction, only Mg remains, and the composition of the salt mixture will be changed. This composition change can lead to changing of transition temperature of the system. Therefore, only the stable diagonals can be used. The stable metal in the ternary systems is given in Table 4. This was also the case when the metals were added to the quaternary salt systems. The five quaternary salt systems and the corresponding metals are listed in Table 4. The information about the eutectic or lowest temperature and corresponding composition in binary and ternary systems are given in Table 5 and Table 6.

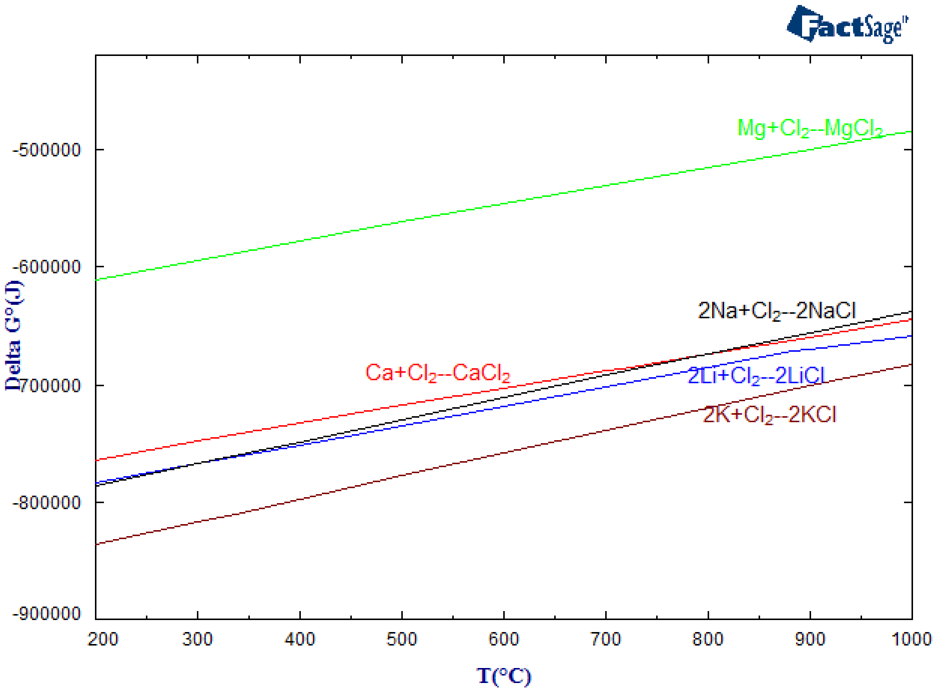

FIG. 6 - Ellingham diagram for the chlorides

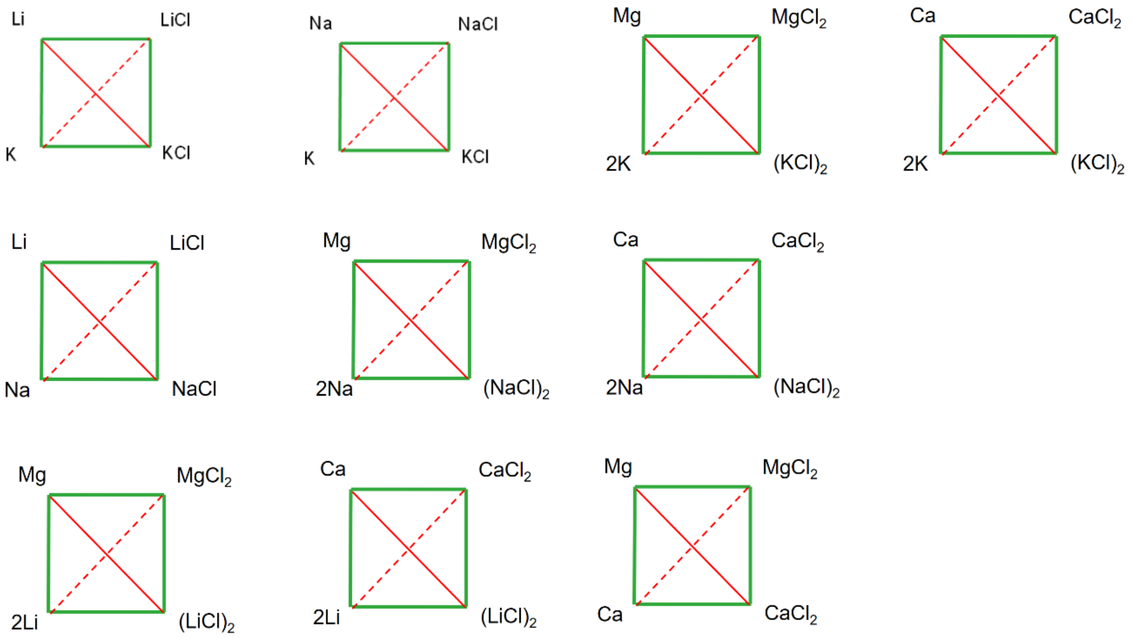

FIG. 7 - Stable diagonals (solid lines) and unstable diagonals (dashed lines) at 298 K for different reciprocal systems

TABLE 4 - Stable diagonal systems in the reciprocal systems and stable metals in the ternary and quaternary systems

Reciprocal system	Stable diagonal at 298 K	Ternary systems	Stable metal	Quatenary system	Stable metal
K-Li-KCl-LiCl	Li-KCl	KCl-NaCl-$CaCl_2$	Ca	KCl-NaCl-$MgCl_2$-$CaCl_2$	Mg
K-Na-KCl-NaCl	Na-KCl	KCl-NaCl-$MgCl_2$	Mg	LiCl-NaCl-$MgCl_2$-$CaCl_2$	Mg
Na-Li-NaCl-LiCl	Li-NaCl	NaCl-$CaCl_2$-$MgCl_2$	Mg	KCl-LiCl-$MgCl_2$-$CaCl_2$	Mg
2K-Mg-$(KCl)_2$-$MgCl_2$	Mg-KCl	KCl-$CaCl_2$-$MgCl_2$	Mg	KCl-NaCl-LiCl-$CaCl_2$	Ca
2Na-Mg-$(NaCl)_2$-$MgCl_2$	Mg-NaCl	KCl-NaCl-LiCl	Li	KCl-NaCl-$MgCl_2$-LiCl	Mg
2Na-Ca-$(NaCl)_2$-$CaCl_2$	Ca-NaCl	NaCl-LiCl-$MgCl_2$	Mg		
2K-Ca-$(KCl)_2$-$CaCl_2$	Ca-KCl	KCl-LiCl-$CaCl_2$	Ca		
Mg-Ca-$MgCl_2$-$CaCl_2$	Mg-$CaCl_2$	NaCl-LiCl-$CaCl_2$	Ca		
2Li-Mg-$(LiCl)_2$-$MgCl_2$	Mg-LiCl	KCl-LiCl-$MgCl_2$	Mg		
2Li-Ca-$(LiCl)_2$-$MgCl_2$	Ca-LiCl	LiCl-$CaCl_2$-$MgCl_2$	Ca		

TABLE 5 - Eutectic or lowest temperature and corresponding composition in binary systems

Binary system	Composition, molar fraction	Temperature, °C

KCl-LiCl (PCMJ)	0.413-0.587	351.9
KCl-NaCl (PCMJ)	0.512-0.488	657
KCl-MgCl$_2$ (FTsalt)	0.70-0.30	422.7
KCl-CaCl$_2$ (FTsalt)	0.751-0.249	601.4
NaCl-LiCl (PCMJ)	0.72-0.28	557
NaCl-MgCl$_2$ (FTsalt)	0.569-0.431	459.3
NaCl-CaCl$_2$ (FTsalt)	0.476-0.524	506.2
LiCl-MgCl$_2$ (FTsalt)	0.68-0.32	571
LiCl-CaCl$_2$ (FTsalt)	0.65-0.35	475.1
MgCl$_2$-CaCl$_2$ (FTsalt)	0.526-0.474	617.4

TABLE 6 - Eutectic or lowest temperature and corresponding composition in ternary systems

Ternary system	Composition, molar fraction	Temperature, °C
KCl-NaCl-LiCl (FTsalt)	-	347.5
KCl-NaCl-MgCl$_2$ (FTsalt)	0.273-0.284-0.444	382.1
KCl-NaCl-CaCl$_2$ (FTsalt)	0.080-0.405-0.515	483.1
KCl-LiCl-CaCl$_2$ (FTsalt)	0.424-0.529-0.047	340.9
KCl-LiCl-MgCl$_2$ (FTsalt)	0.454-0.464-0.08	335.8
KCl-CaCl2-MgCl$_2$ (FTsalt)	0.694-0.025-0.281	416.7
NaCl-LiCl-MgCl$_2$ (FTsalt)	0.431-0.236-0.332	414.4
NaCl-LiCl-CaCl$_2$ (FTsalt)	-	436.2
NaCl-CaCl2-MgCl$_2$ (FTsalt)	0.51-0.25-0.24	416.6
LiCl-CaCl2-MgCl$_2$ (FTsalt)	0.305-0.334-0.36	545.2

EXPERIMENTAL RESULTS

In this work, preliminary results on the study of the reciprocal (2K-Mg-(KCl)$_2$-MgCl$_2$) system will be presented. In this system, the stable diagonal is Mg-(KCl)$_2$ (see Figure 7). MgCl$_2$ and K react to form metallic Mg and KCl. The mixture of 0.2K-0.8MgCl$_2$ was studied by using DTA in a Fe-alloy crucible with Mo liner and Pt sealing (Figure 4a). The result is shown on Figure 8. In this case, the reaction can be represented in the following way:

$$20K + 80MgCl_2 \rightarrow 20KCl + 70MgCl_2 + 10Mg \qquad (1)$$

On the first heating curve the melting temperatures of K and MgCl$_2$ are visible, and the rest of the peaks showed that the reciprocal reaction (1) occurred during the heating. In the second and third cycles, the melting temperature of K was not visible (see Figure 8) and the area of the melting peak of MgCl$_2$ was reduced due to the reciprocal reaction (see Figure 9). In the second and third cycles, two reproducible phase transition temperatures (473°C and 626°C) were detected. According to the reaction (1), the composition of the salt mixture in the sample was recalculated to be 0.22KCl-0.78MgCl$_2$. Therefore, the phase transition temperature of the sample 0.2K-0.8MgCl$_2$ measured by DTA is compared with the phase transition temperatures of the composition 0.22KCl-0.78MgCl$_2$ in the phase diagram calculated using FTsalt database (see Figure 10). The temperatures of phase transition of 0.2K-0.8MgCl$_2$ obtained from DTA (473°C and 626°C) agree well with the calculated eutectic temperature (472°C) and liquidus temperature (626°C) of the salt mixture. The melting of the metallic Mg, formed due to reciprocal reaction (1), was not detected in the heating curve, but in the cooling curves (652°C). The reason for the low signal of Mg may be due to the reaction between the Mg and Pt seal. The XRD results after the DTA experiment of the analysed 0.2K-0.8MgCl$_2$ mixture are shown in Figure 11. The mixture consists of 0.6 KMgCl$_3$ and 0.4 MgCl$_2$ in weight fraction, which is 0.54 MgCl$_2$ - 0.46 KMgCl$_3$ in molar fraction. In the phase diagram (Figure 10), the composition of the stable phase $MgCl_2$ and $KMgCl_3$ was calculated to be $0.56MgCl_2$-$0.44KMgCl_3$ according to the lever rule. The XRD results agree well with the calculated composition.

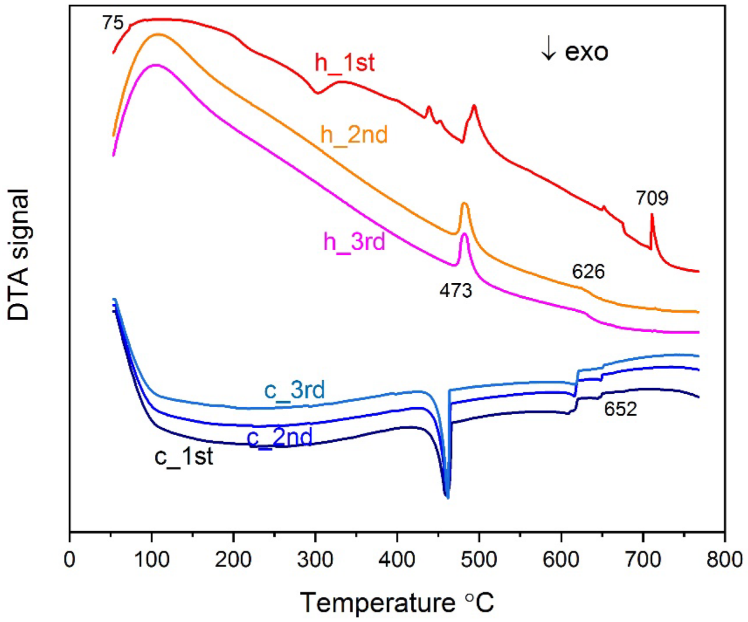

FIG. 8 - DTA results of the 0.2K-$0.8MgCl_2$ composition measured in Fe-alloy-Mo closed crucible

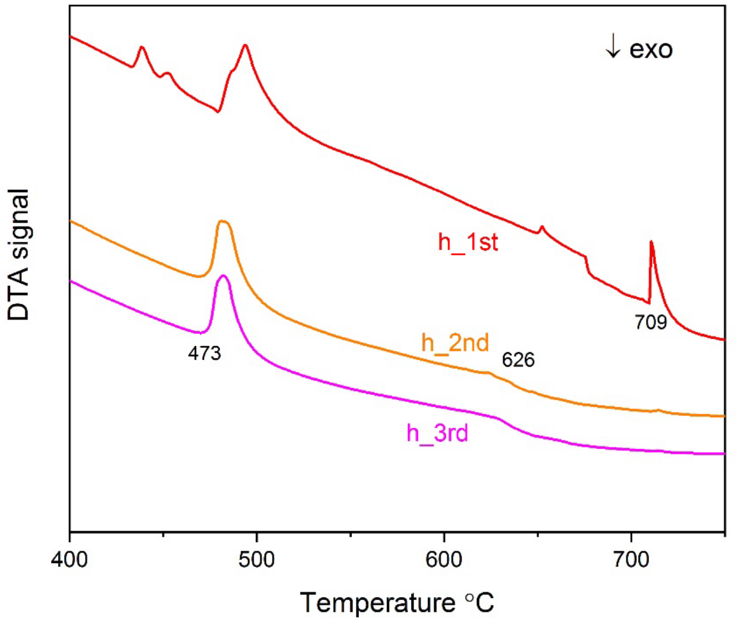

FIG. 9 – DTA heating curves for 0.2K-$0.8MgCl_2$ composition measured in Fe-alloy-Mo closed crucible in the temperature range of 400-750°C

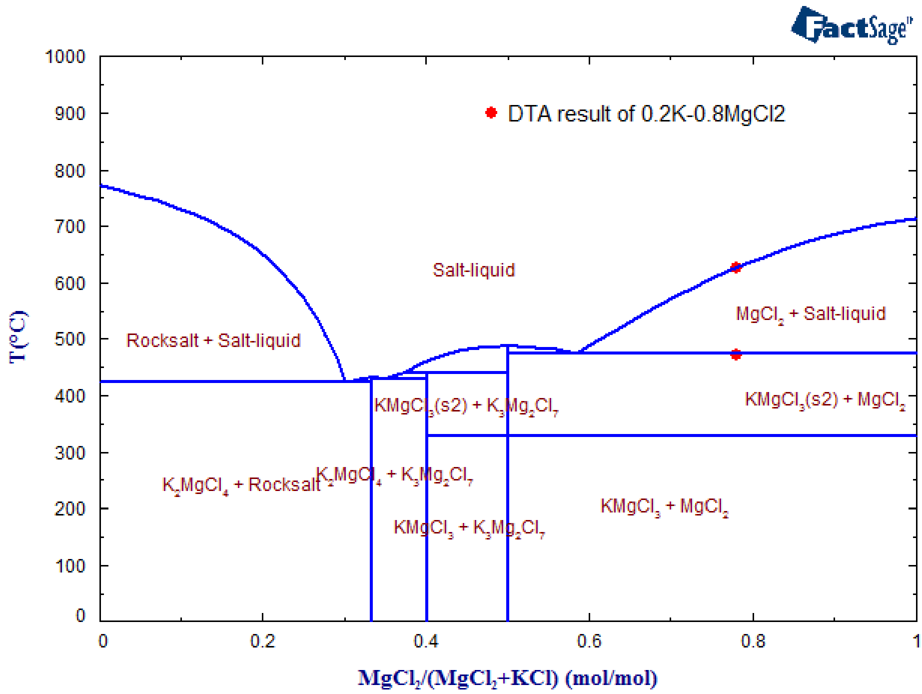

FIG. 10 - Phase diagram of $MgCl_2$-KCl calculated with FTsalt database compared with the phase transition temperature of 0.2K-0.8$MgCl_2$ mixture detected by DTA

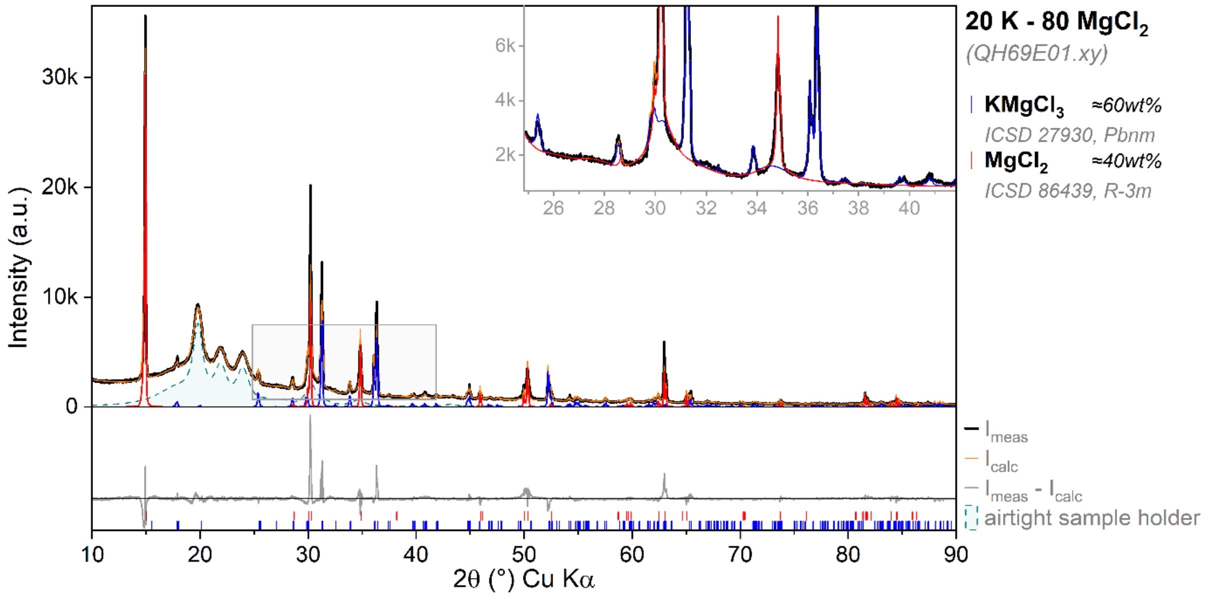

FIG. 11 – XRD results of the mixture 0.2K-0.8$MgCl_2$ after DTA experiment

The mixture of 0.2Mg-0.8KCl from the stable diagonal was measured in a Fe-alloy crucible (Figure 4b), the result is shown in Figure 12. On the DTA curve the melting temperatures of KCl (770°C) and Mg (655°C) are detected like for the pure substance, which means the solubility on both sides is neglectable. An additional peak at 512°C was detected on the heating and cooling curves, however no additional phases besides KCl were detected by XRD (Figure 13). This peak can be related to the Mg-Ni phase diagram, which corresponds to one of the eutectic temperatures. Nickel is one of the components of the stainless steel. Mg was not detected in the sample according to the XRD results (Figure 13) and the DTA peaks reduced in the second and third heating cycles. That is because the Mg reacts with Ni in the container and the rest of Mg is sticked in the wall of the crucible.

Therefore, using Mo liners or crucibles could be the best option for the study of metal salt systems, which do not show any additional reactions with the samples.

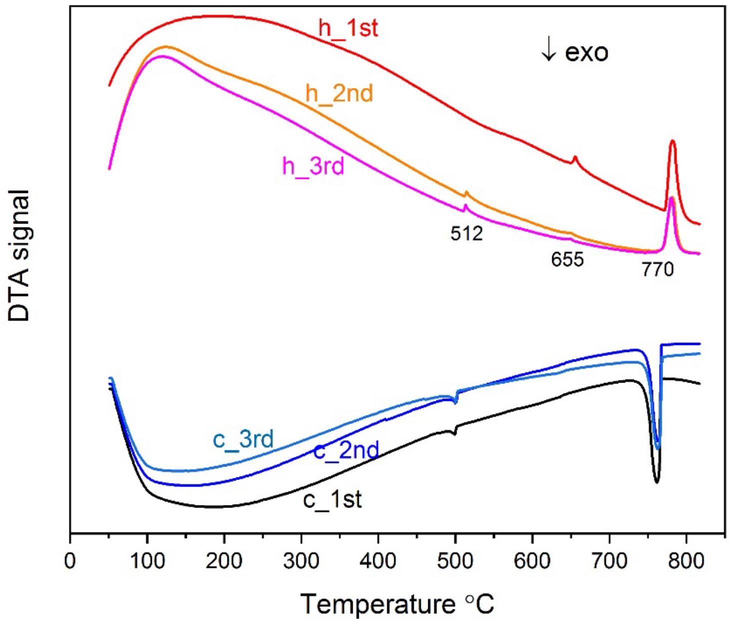

FIG. 12 - DTA result of 0.2Mg-0.8KCl composition measured in SS316L closed crucible

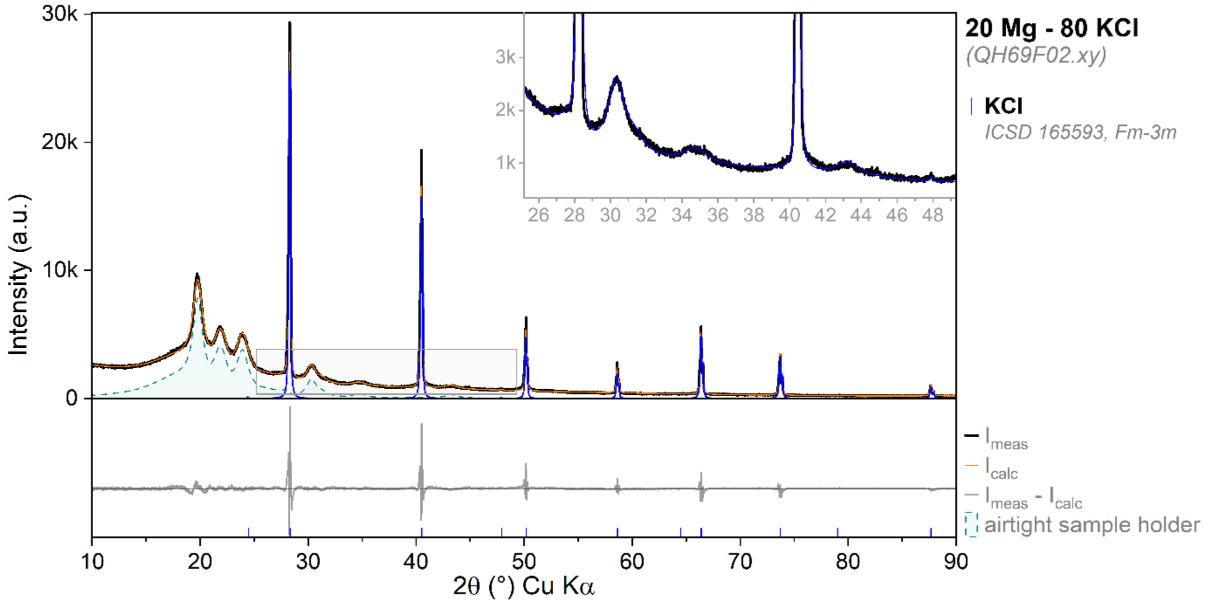

FIG. 13 – XRD results of the mixture 0.2Mg-0.8KCl after the DTA experiment

CONCLUSIONS

In this work, different crucible materials for studying of thermophysical properties of salt and metal-salt mixtures are discussed. Considerations such as temperature range, thermal stability, possible reactions, formation of solid solutions and intermediate compounds, and surface properties influenced the choice of materials. A 50 mol% $NaNO_3$ – 50 mol% KNO_3 mixture was studied by using different techniques of thermal analysis (DSC, TMA, LFA and Rheometry) and the detailed results will be presented on the MOLTEN 2024 conference. A significant challenge in determining these properties of the salt systems is ensuring proper sample preparation to minimize pore formation and consideration of metastable phases as well as creeping and wettability behaviour, which can be influenced by the materials in contact.

Metal-salt systems can play an important role in enhancement of thermal conductivity of salt systems, which is important from the application point of view. However, many challenging questions must be answered first. This work focuses on selecting appropriate crucibles for investigating the thermochemical properties of metal-salt systems and identifying suitable compositions for thermal conductivity tests. Based on the available data in thermodynamic databases, literature review and own experimental results it can be concluded that closed Mo-crucibles and liners are the best option for studying metal-salt systems. Fe-based alloys can be also used as well. DTA and XRD results for the reciprocal 2K-Mg-$(KCl)_2$-$MgCl_2$ system have been obtained and discussed. The formation of the stable Mg-$(KCl)_2$ diagonal in the frame of this system was confirmed, however no solubility between the end members of this system within the 0.2Mg-0.8KCl mixture was detected. Further study of other metal-salt systems will be performed and analysed. All collected data will be used for the development of the new thermodynamic database, which should allow the prediction of stable metal-salt compositions and their miscibility properties.

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