

Article

Thermal Characterization of Binary Calcium-Lithium Chloride Salts for Thermal Energy Storage at High Temperature

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Abstract: Due to their excellent thermophysical properties and high stability, inorganic salts and Forsalt mixtures are considered promising thermal energy storage materials for applications operating at high temperatures. A mixture of binary salts, such as CaCl₂ (58 wt.%)–LiCl (42 wt.%), was investigated in this work to understand their thermal properties and stability for use in TES systems. Thermophysical properties, such as onset melting and crystallization temperature, enthalpy of fusion, and crystallization enthalpy, were all investigated experimentally via the use of a simultaneous thermal analyzer. The experimental findings demonstrated a suitable onset melting temperature of 488 °C and a solidification temperature of 480 °C. The heat of fusion was observed as 206 J/g, whereas the heat of crystallization was recorded as 180 J/g. Thermal repeatability tests indicated little variations in melting temperature; however, fusion enthalpies changed significantly over the course of 30 heating-cooling cycles. Additionally, the results obtained from the thermogravimetric analysis showed relatively weak thermal stability with considerable mass changes. This might be caused by the salts decomposing at elevated temperatures. In order to validate this, a high-temperature in-situ X-ray diffraction technique was used to verify the thermal instability of the binary salt mixture with and without thermal cycling. The thermal decomposition of parent salts and the subsequent formation of new phases with the formation of voids were shown to be the cause of thermal instability. It is concluded that the binary mixture of chloride salt showed suitable thermal properties but relatively weak thermal stability, which may limit its use in practical applications.

Keywords: phase change materials; eutectic salt; thermal stability; thermal energy storage



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1. Introduction

In order to generate and utilize energy without emitting any emissions and address the global challenges of environmental pollution and global warming, sustainable sources of energy must be used [1]. Among all energy storage technologies, thermal energy storage is currently the focus of intense research. Sensible heat, latent heat, thermochemical energy, or any combination of these can be used to store thermal energy as a change in a material's internal energy. In sensible heat thermal energy storage (TES) systems, sensible heat storage materials are employed, which store heat in their specified heat capacities without changing phase during the process of heat absorption and the resulting increase in temperature [2,3]. The storage of heat energy through reversible chemical reactions is known as the thermochemical heat type of thermal energy storage. Solar heat can be recovered and used to fuel an endothermic reaction if the chemical reaction is reversible [4]. The latent heat thermal energy storage (TES) system, which harnesses

heat absorption or release during the phase change of a storage material from solid to liquid, liquid to gas, or vice versa, represents a highly promising approach for heat energy storage. The materials used in a latent heat storage system are called phase change materials (PCMs). When comparing phase change materials (PCMs) to the materials used in sensible heat thermal energy storage (TES) systems, it becomes evident that 50 to 100 times more specific heat is produced by PCMs than by sensible heat storage materials. A wide variety of materials, including organic, inorganic, and their combinations, are categorized as PCMs. These materials have distinct thermal properties, such as melting points and fusion enthalpies [4,5]. Among all the classes of PCMs, molten salts have outstanding thermal storage capabilities and cycling stability, due to which they have been extensively utilized in clean energy storage technology as a storage medium or heat transfer fluid. Eutectic salts are much more suited than individual salts for TES because they often have lower melting temperatures than single salts, which reduces the likelihood of freezing. In order to support the hydrogen economy, a major challenge is the efficient production of hydrogen, and with concentrated solar power operating at high temperatures, it is necessary to develop molten salt that melts at high temperatures. More studies have recently been conducted in the field of high-temperature TES materials [6–10].

The desired temperature has a significant impact on the phase change materials (PCMs) that should be used. The salts of carbonate, fluoride, and chloride are potential candidates for high-temperature TES systems. Among them, chloride salts are a particularly convincing choice due to their adequate thermal properties and thermal stability [11]. Furthermore, in a wide range of applications, the plentiful Salt Lake reserves can drastically lower the chloride salt's bulk price. Tian, Wang [12] studied the binary salt mixture NaCl (52 mol%)-CaCl₂ (48 mol%) for its thermophysical properties and the melting temperature was determined to be 512.8 °C. A fusion enthalpy of 178.4 J/g was determined. The assessment of thermal stability and decomposition behavior showed promising results up to the 858 °C temperature range. Xu, Dehghani [13] investigated the NaCl-KCl-ZnCl₂ and NaCl-KCl-MgCl₂ eutectic salt mixtures. Both salt mixtures have been proposed as promising materials for storing thermal energy and heat transport fluid in concentrated solar power CSP plants. The high heat of fusion of 190 J/g with the lowest eutectic point of ternary eutectic chloride salt (CaCl₂, MgCl₂, and NaCl) was discovered by Wei, Song [14]. Du, Ding [15] investigated NaCl-CaCl₂-MgCl₂ for thermal stability, and less than 1% weight loss was revealed during the first two cycles. It was shown that weight loss during early cycles was related to moisture absorption. In fact, it was discovered that moisture loss might be a factor in the salt's thermal instability, with the salt decomposing around 700 °C because of the degradation of magnesium hexahydrate. Thermal characterization of NaCl-KCl-CaCl₂ was carried out by Yin, Wang [16], Zhong, Yang [17], and Wei, Xie [18] to determine the melting temperature, the heat of fusion, and thermal stability. The melting temperature recorded by Yin, Wang [16], Zhong, Yang [17], and Wei, Xie [18] was 496 °C, 531 °C, and 503 °C, respectively. Furthermore, the fusion enthalpy of the salt mixture was determined to be 171.5 J/g by Yin, Wang [16], slightly exceeding the value reported by Zhong, Yang [17] (154.3 J/g) and closely comparable to the value reported by Wei, Xie [18] (178.2 J/g). The salt mixture is thermally stable up to 850 °C with minimal weight loss. Wang and Li [19] investigated the eutectic mixture NaCl-KCl-NaF experimentally for its thermal properties. The salt mixture demonstrated a melting temperature of 604 °C and a heat of fusion of 398 J/g. During thermal stability, a 6% loss in weight was recorded while heating the salt mixture up to 900 °C, indicating good thermal stability. A ternary salt mixture, LiNO₃-NaNO₃-KCl, was investigated for its thermal properties, resulting in a melting point of 172 °C and a solidification temperature of 141 °C. The heat of fusion and heat of crystallization was recorded as 267 J/g and 258 J/g, respectively. The ternary salt mixture was reliable and thermally stable during 30 heating/cooling cycles. The upper working temperature limit was recorded as 550 °C [20].

In one of our previous works, a LiCl-LiOH mixture was investigated for its thermo-physical properties, thermal stability, and chemical stability. The binary mixture melted

in a range of temperatures from 269 °C to 292 °C and crystallized between 289 °C and 265 °C. The enthalpy of fusion and crystallization was recorded as 379 J/g and 375 J/g, respectively. The chosen salt mixture demonstrated excellent thermal reproducibility and thermal stability under 30 heating/cooling cycles. A measurement of 500 °C was recorded as the maximum limit of the working temperature, with verification of thermal instability through XRD [21].

Our initial work intrigued us into varying the cation in the salt while keeping the anions similar and evaluating the effect of these cations in thermal energy storage systems. To the best of our knowledge, the chosen binary salt mixtures are not widely reported. Therefore, in the current work, the binary salt mixture (58 wt.% CaCl₂-42 wt.% LiCl) is investigated for latent heat storage at high temperatures. By using a simultaneous thermal analyzer (STA), the thermophysical properties were all measured and discussed extensively. A thermogravimetric analyzer (TGA) was utilized to determine thermal stability and maximum working temperature. Structural and chemical instability was determined by in-situ X-ray diffraction (XRD). This study will give the engineering details of an inorganic binary salt mixture for use in high-temperature storage applications as a heat storage material or heat transport medium.

2. Experimental and Methodology

2.1. Sample Preparation

To prepare the sample and obtain a uniformly mixed, homogenous binary salt mixture, a direct mixing approach was adopted in this study. The direct approach, in which the two salts are combined while still in a solid form, has been used by the majority of studies. Since some compounds may react with water and change their characteristics, indirect mixing is the mixing of components in deionized water with a resistivity of approximately 10⁸ Ohm, which has not been employed sufficiently in the earlier literature. Sigma Aldrich supplied CaCl₂ and LiCl, both of which had a purity of higher than 99%. To thoroughly evaporate any moisture that could have been trapped, individual salts were subjected to an oven temperature of 100 °C for a duration of 60 min before being mixed. This was carried out to determine the composition of the salt mixture with the greatest degree of accuracy. The next step was to quickly weigh each chemical with the correct composition to prevent moisture capture. In an alumina crucible, both salts were thoroughly mixed to achieve the desired composition and heated in a furnace from 50–550 °C with a heating rate of 5 °C/min. To ensure that the salt had a uniform chemical composition, the mixture was then held at 550 °C for 30 min. The salt mixture was finally brought to an ambient temperature, crushed into small particles, and kept for further processing in a desiccator. The binary salt mixture (58 wt.% CaCl₂-42 wt.% LiCl) was prepared for this study and investigated for the above-mentioned objectives.

2.2. Materials Characterization

Utilizing a simultaneous thermal analyzer (PerkinElmer, STA/TGA-8000, Waltham, MA, USA) operating using the Pyrus software system, the thermal analysis of the binary salt mixture was carried out. This was used to calculate its melting and solidification onset temperatures as well as the fusion and crystallization enthalpies. To investigate the thermal stability of the binary salt mixture, STA was used as a thermogravimetric analyzer (TGA). The STA/TGA-8000 can operate accurately up to a maximum temperature of 25 to 1600 °C. High-purity argon was used to create a furnace Ar atmosphere with a flow rate of 200 mL/min. A crucible made up of graphite with a net mass of a sample of 10–20 mg was used to avoid any large uncertainty toward the experimentation outcomes. The ramps for the heating and cooling were customizable between 0.1 and 100 °C/min. The calibration of STA was carried out by using gold as a standard, as displayed in Table 1. The measurement of enthalpy had a relative error of 3%, while the accuracy of the melting temperature measurement was roughly 0.2%. A 1% relative inaccuracy was noted when the melting temperature and heat of fusion of the pure LiCl sample were also evaluated. In

light of those findings, the instrument appears to be reliable. For verifying the stability of the structural and chemical properties, a SmartLab X-ray diffraction instrument (Rigaku SmartLab XRD, Tokyo, Japan) was utilized. The morphology of the salt mixture was examined using scanning electron microscopy (SEM; Zeiss Neon 40EsB, Akita, Japan). The elemental distribution was examined using energy dispersive spectroscopy (EDS).

Table 1. STA calibration using gold and individual lithium chloride.

Standard Material	Expected Melting Point C	Measured Melting Point C	Relative Error %	Expected Heat of Fusion J/g	Measured Heat of Fusion J/g	Relative Error %
Gold (Au)	1064.2	1061.6	0.2	64.6	67	3
Lithium Chloride (LiCl)	610	602	1	441	449	1

2.3. Experimental Procedure

The STA-8000 instrument was utilized to measure thermophysical properties such as melting and solidification temperature, heat of fusion, and crystallization. For all measurements, the samples were placed in a graphite crucible, and between 10 and 19 mg was used for the samples for each test. The samples underwent a continuous heating process from 50 to 550 °C, employing heating ramps set at a rate of 10 °C/min and ensuring a steady flow rate of argon gas purging at 20 mL/min. By using the same rate, the sample was cooled down to 50 °C. The procedure was repeated many times, and the initial cycles were discounted due to uncertainty in the results due to absorbed moistures. Subsequently, a heat flow versus temperature curve was plotted, enabling the determination of the thermal characteristics.

The STA-8000 was used to assess the binary salt's thermal repeatability during multiple cycles. The sample, weighing about 19 mg, was melted and frozen between 50 and 550 °C 30 times at 10 °C/min heating/cooling rate. The latent heat and transition temperature of each cycle were recorded. In doing so, cycling stability was also attained by measuring the binary salt's weight loss throughout the course of these 30 cycles. TGA was used to assess the chemical stability as well as thermal decomposition. The binary salt mixture was thermally treated by heating it from 50–700 °C at the rate of 10 °C/min while being exposed to an argon atmosphere with a 20 mL/min flow rate, and by examining weight loss, the decomposition performance was investigated. Powdered X-ray diffraction (XRD) analysis was conducted on a SmartLab Rigaku XRD instrument, utilizing a 2 θ range of 20°–90° and a step size of 0.013 to verify chemical instability. SEM/EDS was utilized for morphological assessment and elemental distribution.

3. Results and Discussions

3.1. Thermophysical Properties

The FactSage software tool was used for the derivation of the phase diagram of eutectic salt [22], as shown in Figure 1. The phase diagram shows the eutectic composition of CaCl₂-58 wt.% and LiCl-42 wt.% at 476 °C, as displayed in Figure 1.

Different heating/cooling ramps were employed to measure the binary salt mixture's thermophysical characteristics. This led to the conclusion that the thermal characteristics were impacted only a little by varying heating/cooling rates. In order to go forward with the STA measurements of the thermophysical characteristics in this study, the heating/cooling ramp was changed to 10 °C/min while taking the effectiveness and accuracy of the experiments into consideration.

Two endothermic peaks, as shown in Figure 2a, were obtained, with the initial peak representing the transition of phase in a solid state. Following the peak of solid-phase change, the absorbing heat increased significantly once more and reached a maximum peak temperature. So, the two peaks indicated the non-eutectic behavior of the chosen salt mixture. As a result, the melting process of the binary salt mixture occurred at a variety of

temperatures, with the solid phase starting to melt at 440 °C and the liquid phase finishing at 520 °C. After comparing those results with the phase diagram obtained from FactSage, as shown in Figure 1, CaCl₂-58 wt.% and LiCl-42 wt.% are not eutectic compositions. Similarly, Figure 2b represents the cooling in which the solidification of the binary salt mixture took place within the range 480 °C to 390 °C. The melting and crystallization temperature of a binary salt mixture should be the same; however, the results indicated a minor variation in melting and crystallization temperature ranges, which is likely attributed to the fast sub-cooling rates [23].

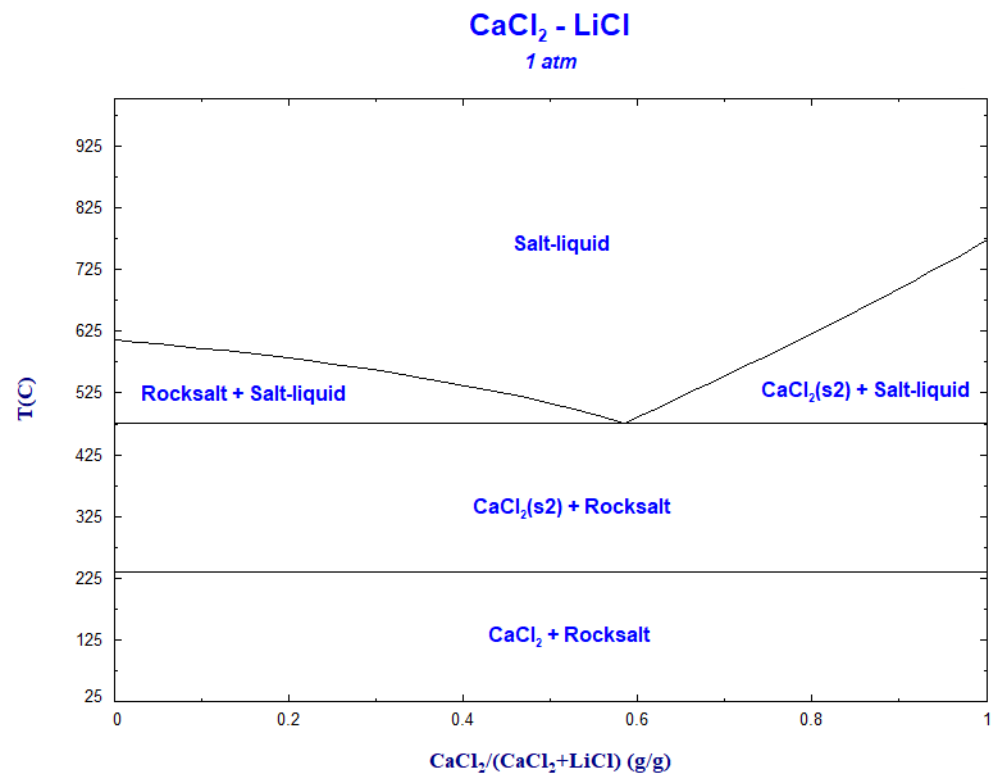
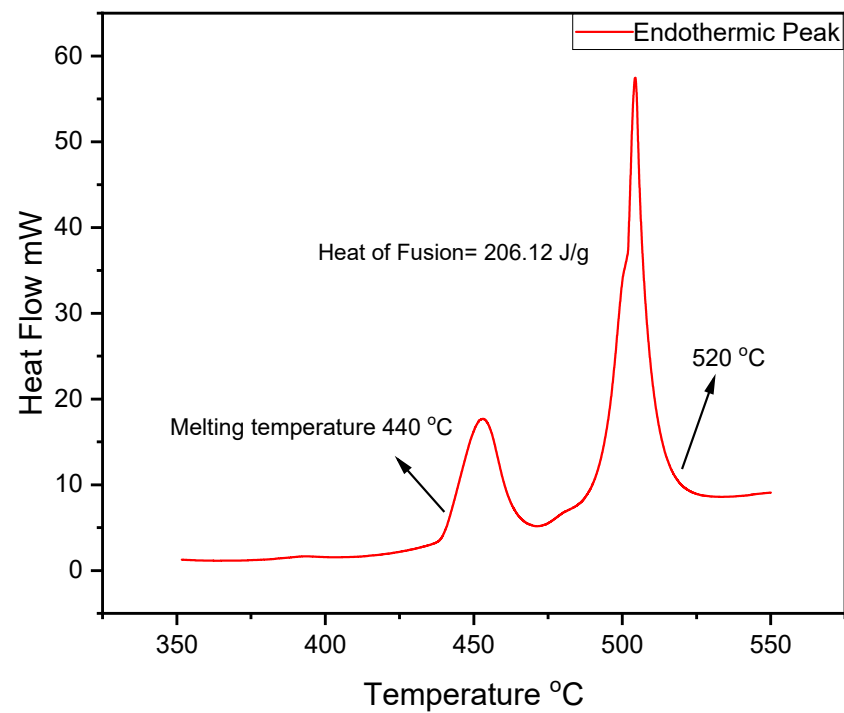


Figure 1. Phase diagram of eutectic CaCl₂-LiCl obtained from FactSage (FactSage, 28 March 2022).

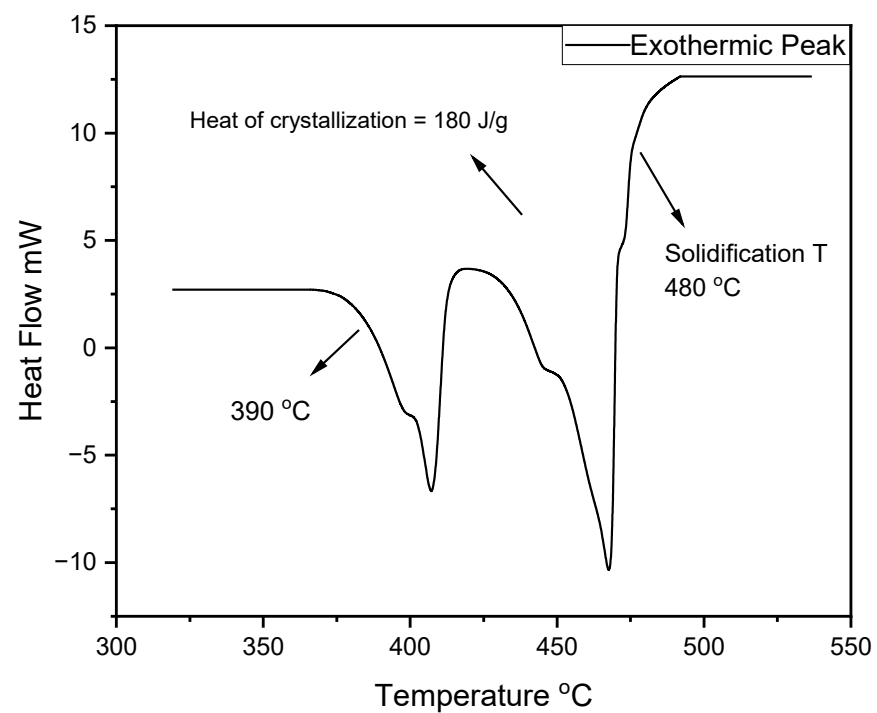
The area under the STA curve was calculated to determine the heat of fusion. By doing so, the heat of fusion was determined to be 206 J/g and the heat of crystallization 180 J/g. Evaporation may have contributed to the discrepancy between these measurements. Creeping could also be the cause since certain salts, primarily chloride salts, tend to move towards the crucible's wall during heating after multiple cycles of STA measurement, which may reduce the sample's heat of fusion. If just mechanical mixing is taken into account, a mixture of the salt's fusion enthalpy allows for the simple mixture rule, which is given by Equation (1) [24].

$$\Delta_{fusion}H_{eutectic} = \sum_{i=1}^n x_i \Delta_{fusion}H_{component_i} \quad (1)$$

where $\Delta_{fusion}H_{eutectic}$ is the enthalpy of fusion, $\Delta_{fusion}H_{component_i}$ is the fusion enthalpy of an individual salt, and x_i represents individual salt composition. Table 2 illustrates the theoretical enthalpies of the fusion of CaCl₂ and LiCl with the calculated and experimental values of the binary salt mixture. The obtained experimental value is 35.9% lower than the values calculated by the mixture rule, indicating the salt mixture is not just a regular mechanical mixture. It can be said that the cluster that formed in the binary salt mixture may have led to the deviation [25].



(a)



(b)

Figure 2. (a) STA curve of 58 wt.% CaCl₂-42 wt.% LiCl, indicating the melting temperature and heat of fusion. (b) STA curve of 58 wt.% CaCl₂-42 wt.% LiCl, indicating the solidification temperature and heat of solidification.

Table 2. Calculated and experimental heat of fusion.

System	The Heat of Fusion J/g
CaCl ₂	253
LiCl	416
58 wt.% CaCl ₂ -42 wt.% LiCl (Calculated)	321.46
58 wt.% CaCl ₂ -42 wt.% LiCl (Experimental)	206

3.2. Thermal Repeatability

A key factor in establishing the long-term stability of a PCM across several cycles is its thermal repeatability. During several heating and cooling cycles, the material must be capable of melting and solidifying with little or no change in thermal properties. In this experiment, the salt mixture (58 wt.% of CaCl₂ and 42 wt.% of LiCl) underwent 30 cycles of heating and cooling in an argon atmosphere, ranging from 50 to 550 °C, with a heating and cooling rate of 10 °C/min. Salt is soluble in water and can absorb moisture (hygroscopic). In order to prevent weight calculation mistakes during sample preparation, which might, in turn, affect the experiment's results, preventive measures were taken to limit moisture absorption. The initial few cycles were discounted due to uncertainty in the measurements because of moisture absorption.

Over the course of all 30 cycles, the salt melted on average at 456 °C and 53 J/g of latent heat. The discrepancies in these results may be caused by contamination or impurities in the mixture. Equations (2) and (3), which are depicted in Figures 3 and 4, were used to determine the deviations in melting temperature and heat of fusion in each cycle from the average values.

$$T_{\text{deviation}} = \frac{T_n - T_{\text{avg}}}{T_{\text{avg}}} \quad 1 \leq n \leq 30 \quad (2)$$

$$\Delta H_{\text{deviation}} = \frac{\Delta H_n - \Delta H_{\text{avg}}}{\Delta H_{\text{avg}}} \quad 1 \leq n \leq 30 \quad (3)$$

where $T_{\text{deviation}}$ represents the deviation in melting temperature, while $\Delta H_{\text{deviation}}$ represents the deviation in fusion enthalpy. T_n and ΔH_n refer to the onset melting point and fusion enthalpy, respectively, observed in the n th cycle. T_{avg} is the average melting point, and ΔH_{avg} is the average fusion enthalpy of 30 cycles. Except for the first four cycles, the salt mixture's onset melting point was nearly constant by a minimal variance of $\pm 1.5\%$ from the average value; however, the difference between the measured and average value for latent heat was within the relatively high range of $+75\%$ and -52% . From the error bars, the maximum error for melting temperatures, excluding the first few cycles, was recorded as ± 1.2 , whereas for the heat of fusion, it was ± 50 , which is high. This significant deviation in latent heat from the average value may be caused by weight loss by gas evolution because of repeated heating. After multiple cycles, creeping may also be the cause of a decline in the enthalpy of fusion. The molten salt mixture showed poor thermal repeatability from the results of the heat of fusion deviations.

3.3. Thermal Stability

Another crucial consideration when choosing a material for an energy storage system using latent heat is the thermal stability of the PCM. Assuming the salt mixture exhibits good thermal stability between 120 and 550 °C, this is adequate, as, at these temperatures, a very large amount of heat might be available. TGA was used to determine thermal stability under the same conditions as the other tests. As shown in Figure 5, the binary salt mixture's hygroscopic properties were the cause of a loss in weight in the initial few cycles. The remaining 27 thermal cycles each led to a continuous loss of weight similar to the first two thermal cycles. Figure 6 shows the weight loss percentage for each cycle. Huge weight loss was observed in the first two cycles, and a consistent weight loss was observed

after the initial two heating/cooling cycles. Minimal weight gain was observed during certain cycles; this may be because of the argon atmosphere, assuming it was not fully dry, absorbing moisture from the air, as the salt in the mixture has substantial characteristics of absorbing moisture. The potential reasons for weight loss could include the accuracy of the TGA instrument, which has a precision of 0.01%. In the first two cycles, the binary salt exhibited a weight loss of 21%. Following the second cycle, the cumulative weight loss reached 72%, with an approximate 2% weight loss observed in each subsequent cycle, which made the chosen material less competitive for practical applications.

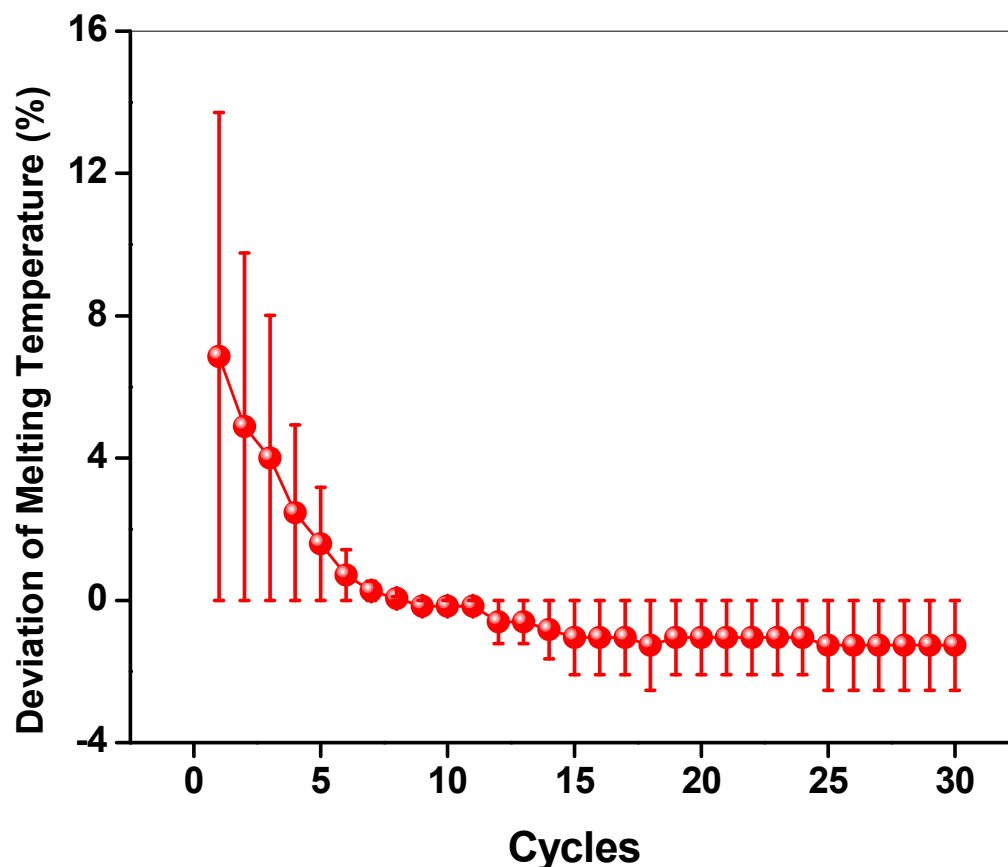


Figure 3. Deviation in melting temperature for each cycle from the average calculated value for all other cycles for sample 58 wt.% CaCl_2 -42 wt.% LiCl .

The huge weight loss might be due to the decomposition of parent salts in the mixture. Individual salts (CaCl_2 and LiCl) were tested through TGA for weight loss determination using the same conditions as for other experiments. The CaCl_2 was found to be a stable material up to 700 °C with no weight loss, excluding the initial weight loss, which is due to moisture, as shown in Figure 7. However, the continuous weight loss of LiCl was observed from 200 °C to 650 °C, as shown in Figure 8. Thus, CaCl_2 showed high stability within a temperature range of 120–550 °C; however, LiCl decomposed within that temperature and resulted in weight loss. LiCl is highly hygroscopic, and it absorbs moisture very quickly. This property might lead the LiCl to decompose into Cl_2 or Li_2O etc. Based on the findings from these investigations, it is evident that the selected binary salt mixture is not suitable for thermal energy storage (TES) applications due to its lack of thermal stability.

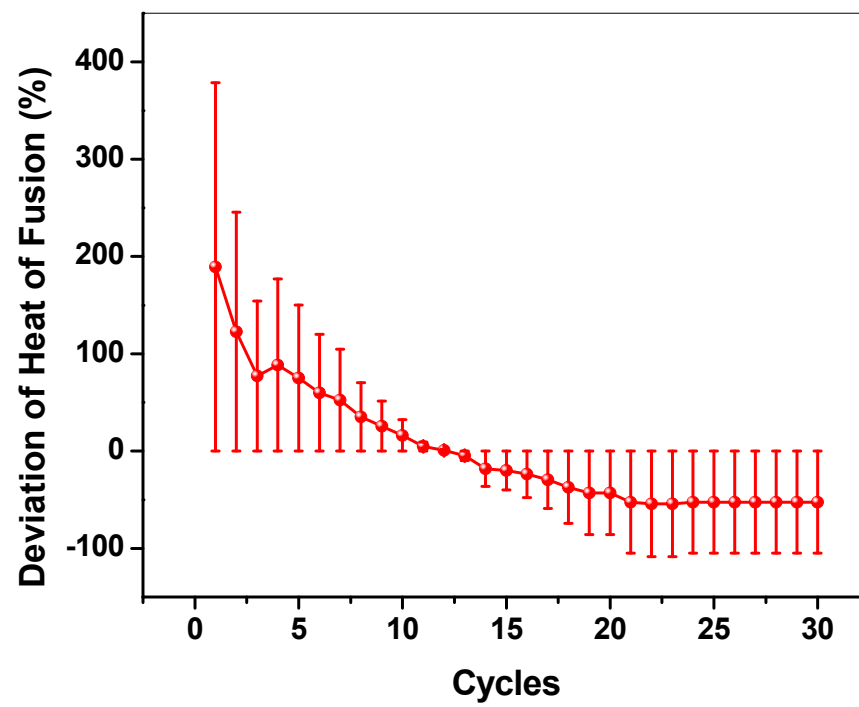


Figure 4. Deviation in the heat of fusion for each cycle from the average calculated value for all other cycles for sample 58 wt.% CaCl₂-42 wt.% LiCl.

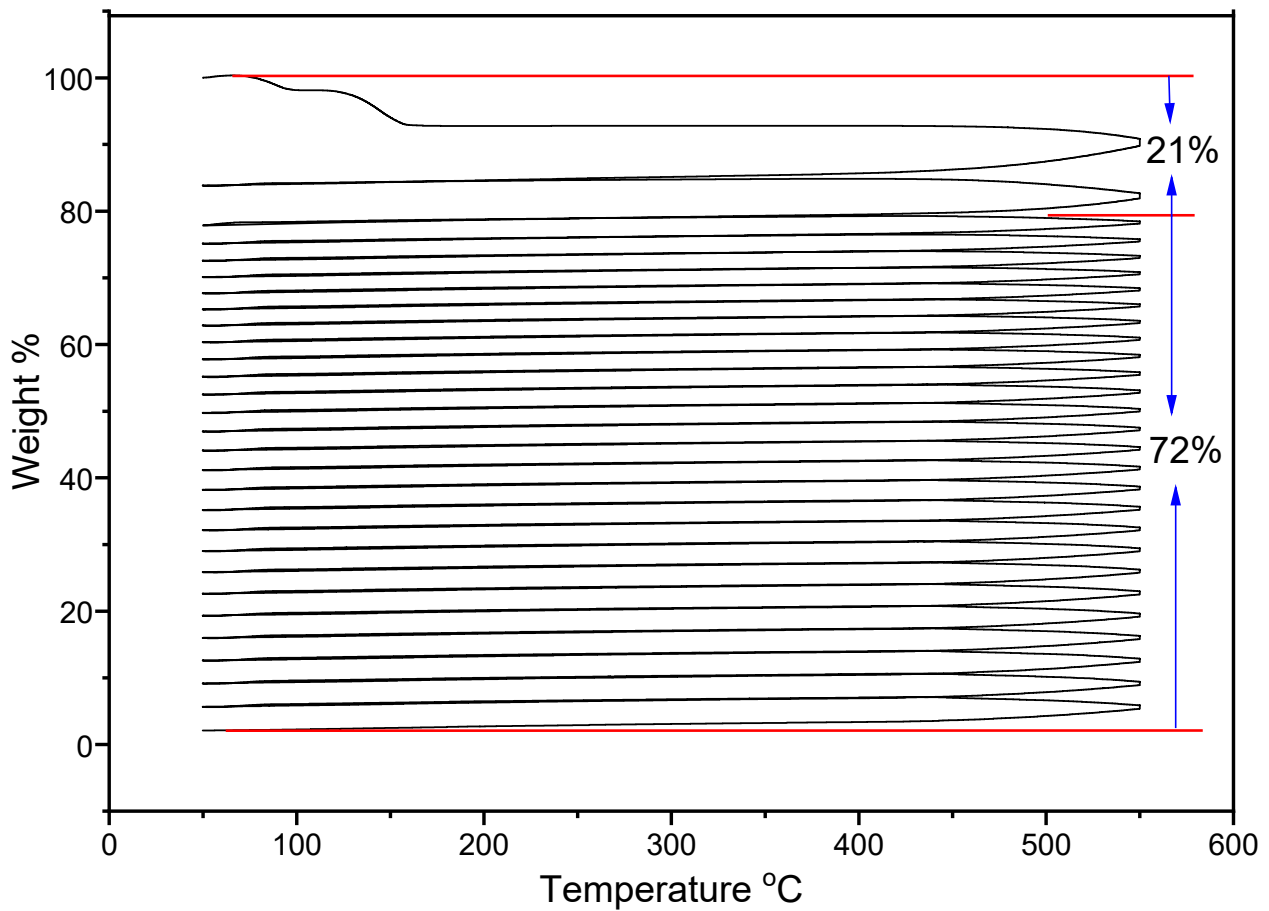


Figure 5. Weight loss vs. temperature plot of 58 wt.% CaCl₂-42 wt.% LiCl for 30 cycles.

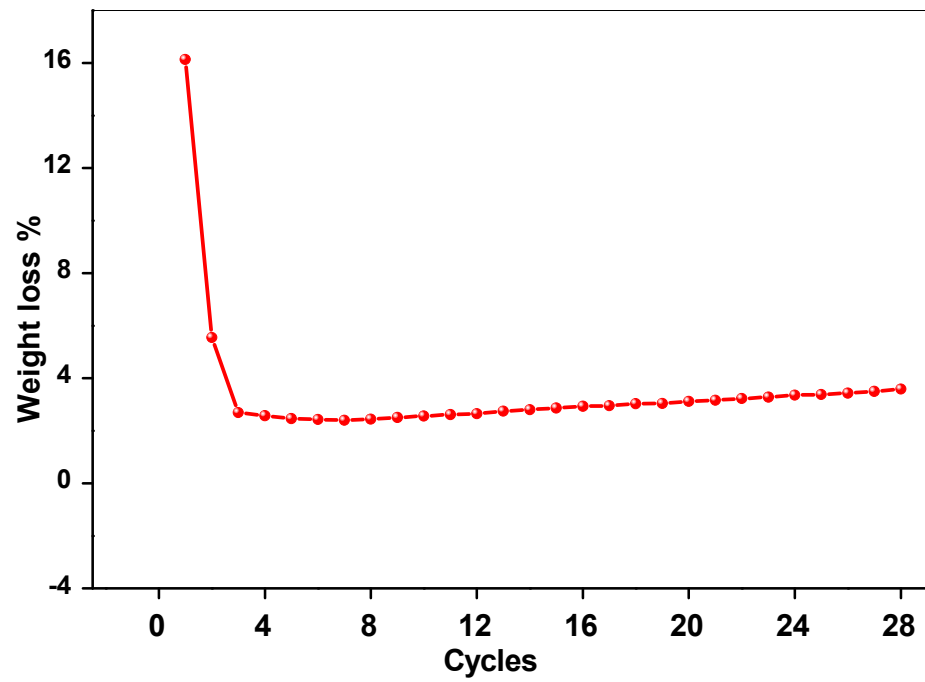


Figure 6. Weight loss % of 58 wt.% CaCl₂-42 wt.% LiCl for each cycle.

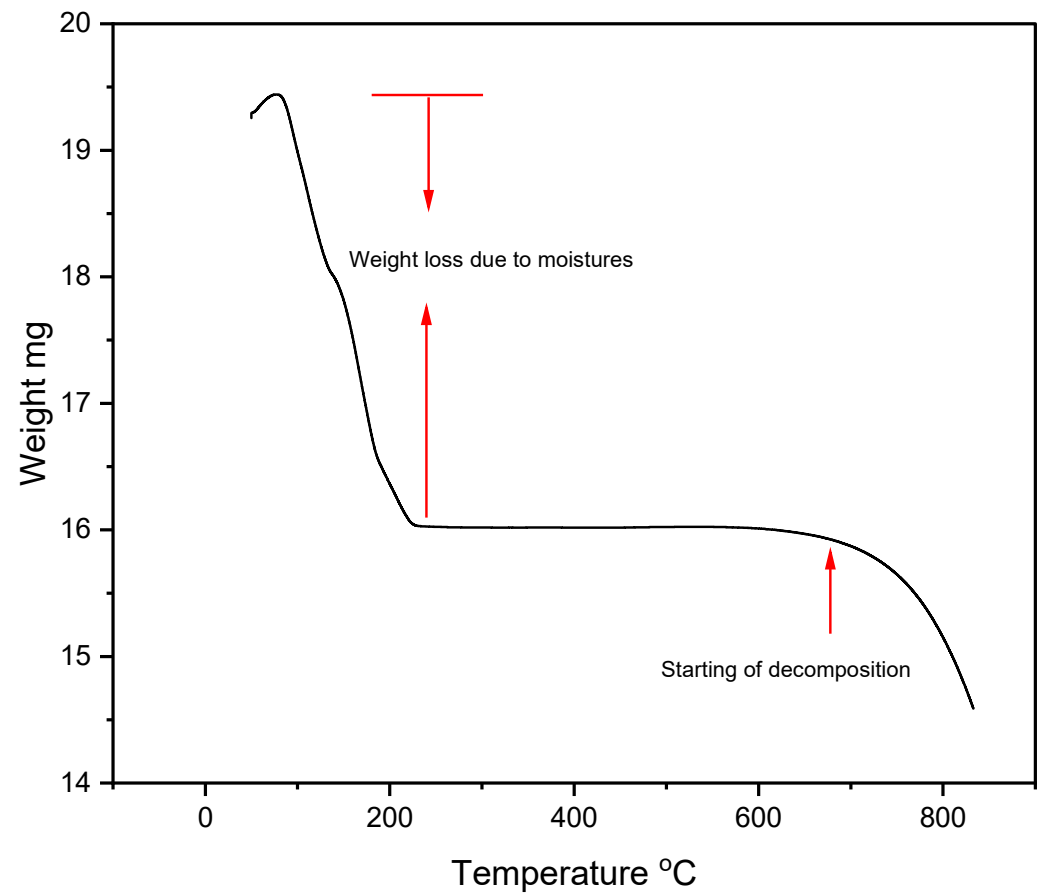


Figure 7. Weight vs. temperature plot of 99% pure CaCl₂.

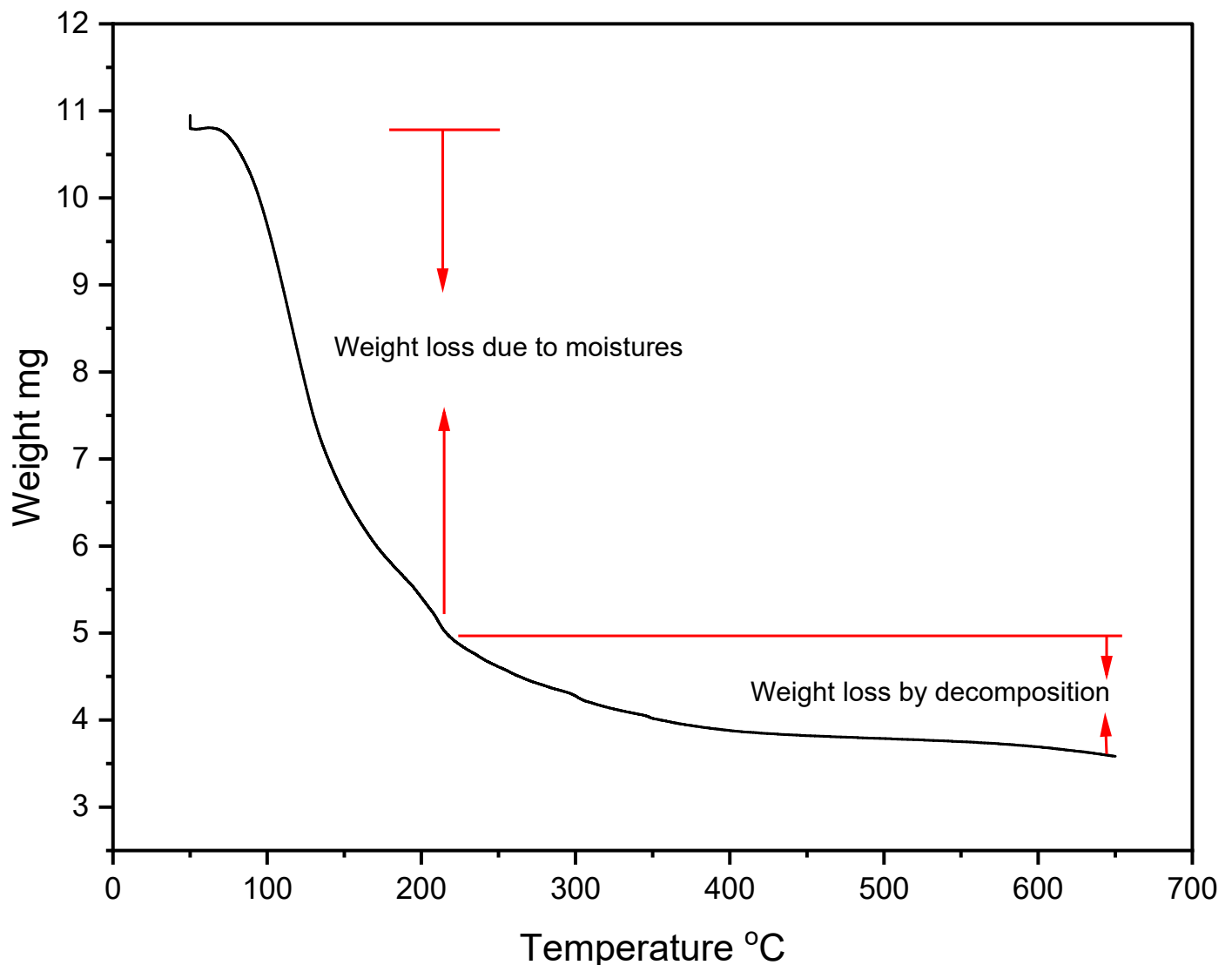


Figure 8. Weight vs. temperature plot of 99% pure LiCl.

3.4. Chemical/Structural Stability

The chemical stability of salts is regarded as one of the crucial criteria taken into account when selecting a phase change material (PCM) for energy storage systems. Understanding the binary salt mixture's decomposition behavior is essential as it establishes the material's maximum allowable temperature for real applications. A stability test to suit the higher temperature was conducted with the use of TGA to determine the temperature at which decomposition would begin. The weight reduction of the salt mixture was assessed during the heating process, ranging from 50–700 °C, with a heating rate of 10 °C/min. Figure 9 clearly demonstrates that the application of heat up to 130 °C resulted in a notable reduction in weight, primarily attributed to the presence of absorbed moisture.

A significant amount of weight was lost after heating to 500 °C, which was the lowest weight loss that could have been considered safe. This indicated that the binary salt began to degrade and transformed into gases at 500 °C. Based on the findings shown in Figures 7 and 8, CaCl_2 is stable up to 500 °C; however, LiCl is not, and it can thermally disintegrate into a new product.

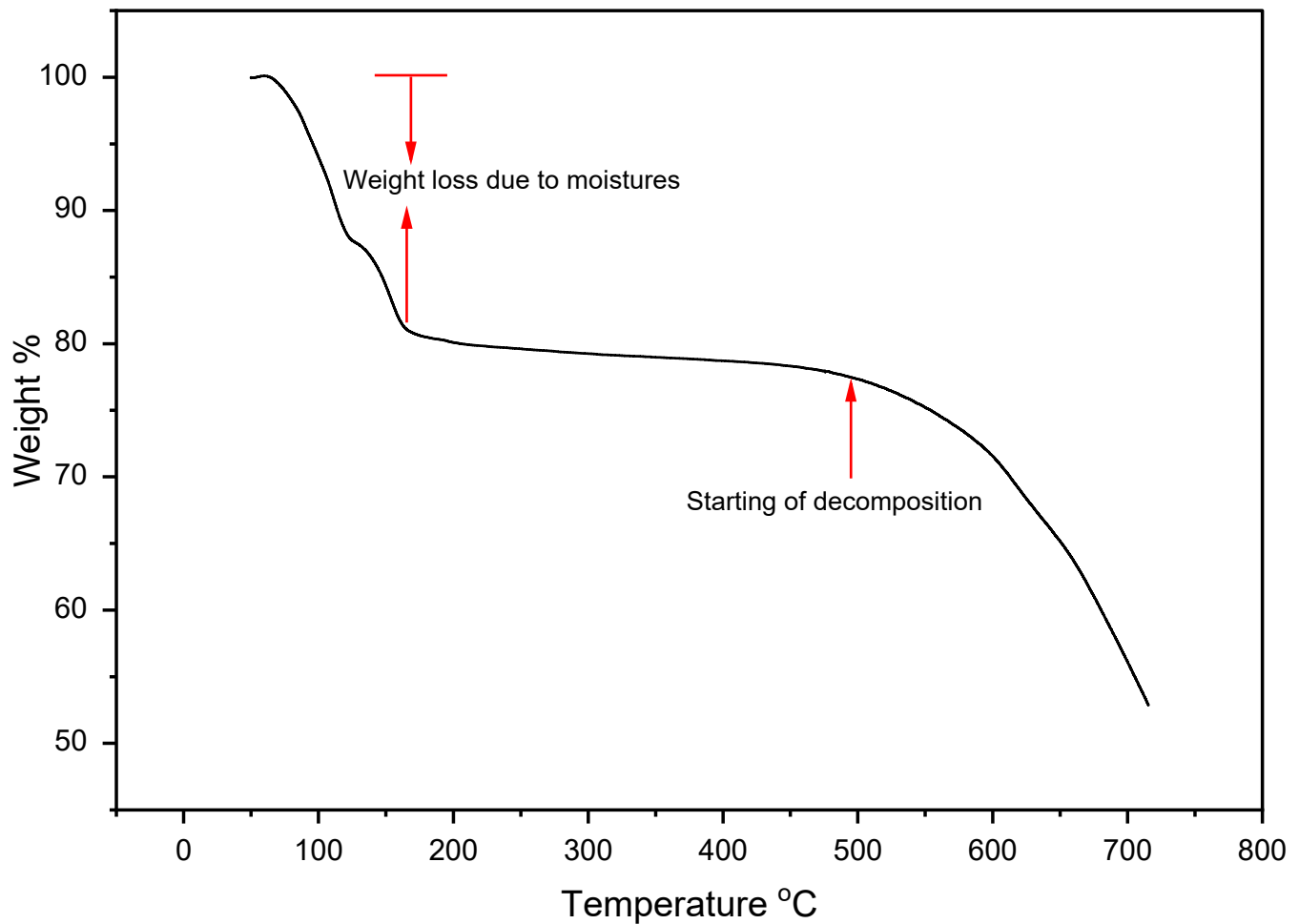


Figure 9. Binary salt of 58 wt.% CaCl_2 -42 wt.% LiCl heated up to 700 °C starts to decompose.

The thermal and structural stability of the three samples was assessed by analyzing their XRD patterns to detect any potential formation of new phases. According to the findings presented in Figure 10, all three binary salt samples exhibited consistent and uniform phase formations, identified as the parent compound. The XRD patterns obtained for the three samples were predominantly similar in nature. Slight variations in the intensities of certain peaks were observed between the original sample and the sample cycled 10 times, suggesting the absence of any significant phase changes in the salt mixture. The intensities of peaks in the decomposed sample increased, representing a change in phases. The detection of a small CaO_2 peak in the decomposed sample can be attributed to the thermal decomposition of CaCl_2 at elevated temperatures. Moreover, in all three samples, Li_2O_2 peaks with higher intensities were detected, which might have resulted from the reaction of LiCl with moisture, as LiCl has strong moisture-absorbing properties. Moreover, Li_2O can be produced via the thermal decomposition of Li_2O_2 at 450 °C [26]. Thus, from the above thermal and structural insights, it appears that the binary salt mixture did not exhibit adequate chemical stability, which could be the limiting factor for its use in thermal energy storage applications.

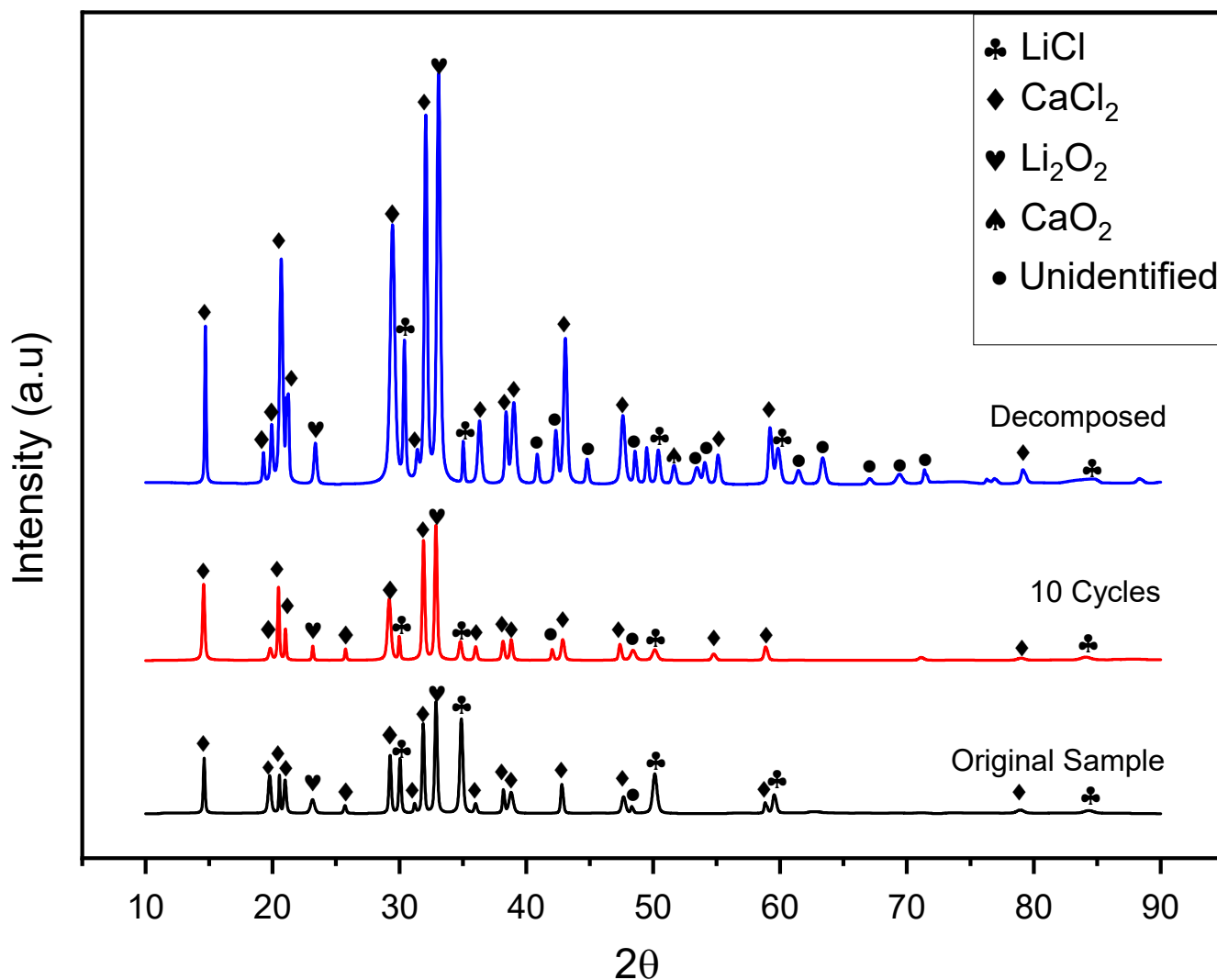


Figure 10. XRD patterns of three samples of 58 wt.% CaCl_2 -42 wt.% LiCl as prepared, 10 times cycled, and decomposed at 700 °C.

The micrographs, along with elemental distributions for the samples before and after cycling, are shown in Figure 11a,b. From the images, it is determined that there is a contrast in particle texture. The particles in the cycled sample had agglomerated when compared to the uncycled sample, in which the particles are discrete and distinctive. Furthermore, some small voids were present after cycling; this could have arisen from the decomposition of the parent salts, transforming into a gaseous product at high temperatures. The EDS analysis at the chosen area represents Ca, Cl, O, and C, which were the core elements except for C and O. Li was not detected by the instrument because of its low atomic mass. The elements, such as Ca and Cl, represented CaCl_2 and LiCl , while O and C might be derived from atmospheric oxygen and carbon tape, respectively. Thus, no external elements were detected, proving the binary salt to be chemically stable. However, a minor diffraction peak is unidentified, which could plausibly be due to the adsorption of Cl_2 on the Li and Ca species.

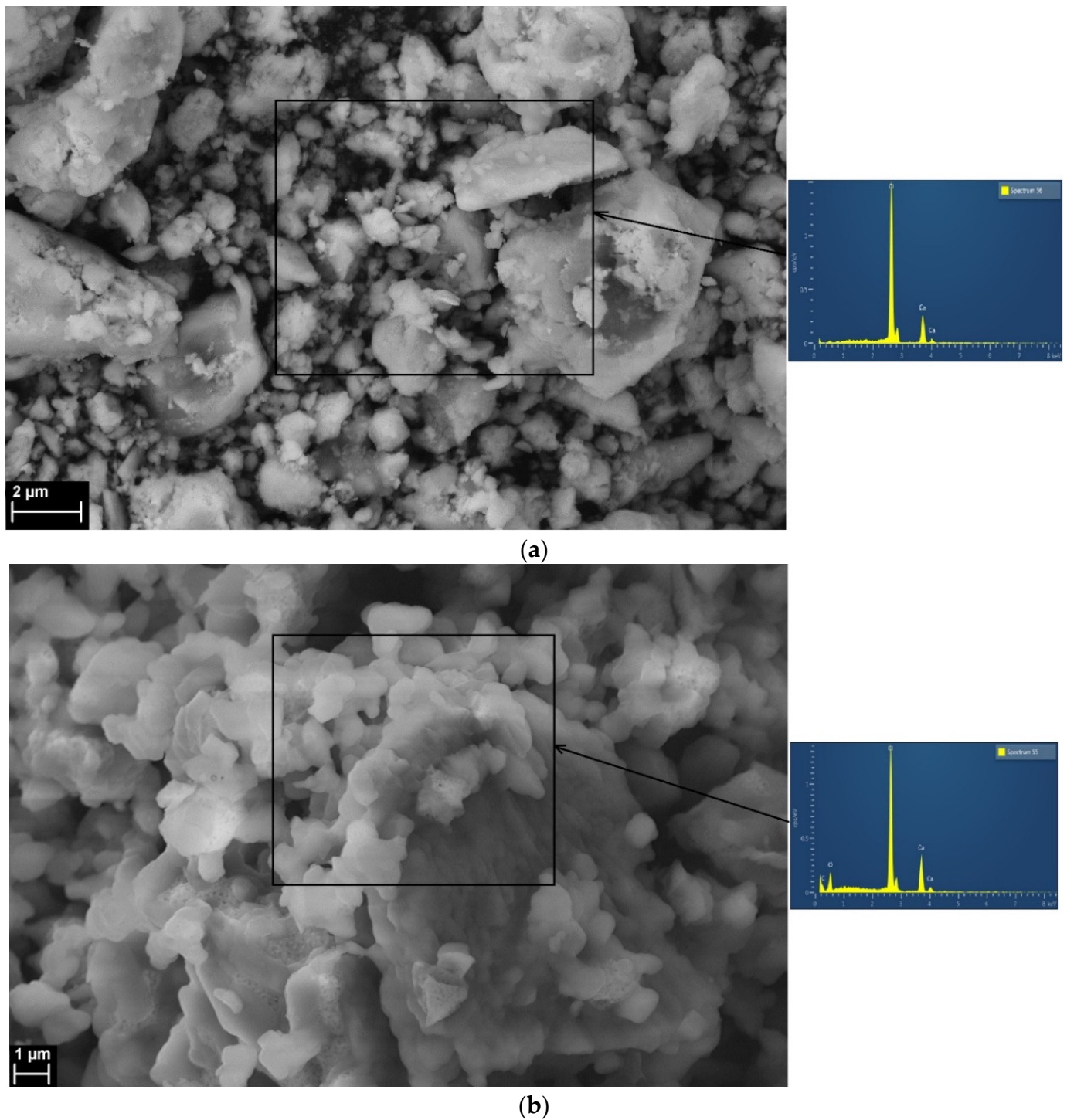


Figure 11. (a) SEM/EDS of uncycled 58 wt.% CaCl₂-42 wt.% LiCl. (b) SEM/EDS of 58 wt.% CaCl₂-42 wt.% LiCl decomposed at 700 °C.

4. Conclusions

The thermophysical properties of the CaCl₂-LiCl mixture were investigated for the use of TES systems operating at high temperatures. The STA measurements of the salt mixture indicated a melting temperature range from 480–520 °C and a fusion enthalpy of 206.12 J/g. The solidification temperature ranged from 480 to 390 °C, and the heat of solidification was determined to be 180 J/g. The subcooling mechanism was observed from the difference between the melting temperature and solidification temperature ranges but was negligible.

Likewise, thermal repeatability was examined through 30 cycles of heating and cooling, revealing minimal deviations in the melting temperature from the average value for each cycle. However, significant variations were observed in the heat of fusion values for each cycle. Furthermore, weight loss was also examined during 30 cycles, indicating relatively weak thermal stability for binary salt, as large weight loss was observed in every cycle caused by parent salt decomposition. The upper limit temperature was determined to be 500 °C, and from the verification of chemical instability via XRD and SEM, new phases were found with the formation of voids and agglomerated morphology, which resulted from the decomposition of LiCl and CaCl₂.

Overall, it can be concluded that the binary salt mixture has the appropriate thermal properties for high-temperature TES systems; however, relatively weak thermal/chemical stability may limit its use in real applications.

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