

Influence of alkaline chlorines on bischofite properties for thermal energy storage

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Abstract

Brines coming from salt lakes such as that of the Atacama desert in Chile produce by-products or wastes stored in the nearby from the production areas. Bischofite is one of those by-products and therefore its composition may vary from batch to batch. Since bischofite has been identified as a good candidate to be used as phase change material for latent heat thermal energy storage, the influence of the variation of bischofite composite with its main impurities in this potential used needs to be evaluated. The main impurities of bischofite are the cations sodium, potassium and lithium and the anion chloride and sulfate. The results of this investigation established that the presence of KCl and NaCl in bischofite (up to 5 wt.%) does not affect its use as phase change material (PCM), since its melting enthalpy and temperature do not vary significantly. Interesting is that small contents of LiCl in bischofite do not change significantly its melting enthalpy but decrease the melting temperature, an curious change that may enable this material as PCM in other applications at lower temperatures.

Keywords: Thermal energy storage; Latent heat; Phase change material; Non-metallic industry; valorisation of by-product.

Abbreviations

TES	Thermal energy storage
SHTES	Sensible heat thermal energy storage
LHTES	Latent heat thermal energy storage
TCS	Thermochemical storage
PCM	Phase change material
DSC	Differential scanning calorimetry
XRD	X-Ray diffraction
wt. %	weight percentage
T_m	Melting temperature
ΔH_m	Enthalpy of fusion

1. Introduction

The growth of industrial and agriculture activities the last four decades has been tremendous. This results mainly from the increase of population during that period of time; hence the CO₂ emissions have also increased [1]. In order to reduce the negative environmental impact of greenhouse gases emissions and global warming is important to look for new energy sources to produce electricity and thermal energy. In this regard, renewable energy sources such as solar, wind, geothermal, etc., have been studied and applied, either at lab scale or at industrial scale, instead of the traditional sources which have been mainly used up to now such as oil, coal and natural gas; besides, it is also an important requirement to use energy efficiently [2]. Since renewable energy sources are not continuously available, it is necessary to store the energy while the source is available to use it when demand requires, designing and using efficient thermal energy storage (TES) systems. In order to achieve this, materials need to have suitable thermophysical properties, such as long-term stability, suitable phase change temperature, and high enthalpy of phase change, among others. Also, they need to be commercially available at low price and in large amounts. Materials that have been applied commercially or those, which are potential to be applied as TES medium, are classified based on their mechanism to store energy; these can be latent heat thermal energy storage (LHTES) materials, sensible heat thermal energy storage (SHTES) materials and thermochemical storage materials (TCM) [3-5]. LHTES materials are also known as phase change materials (PCM). They can be sub classified as organics (fatty acids, paraffin, mineral oil, synthetic oils, etc.), and inorganics (salt, salt hydrates, mixtures) [6-7]. But due to the high prices of PCM as final products, the potential of all wastes studied to be applied as TES materials have been previously reported [8].

The northern Chile has an important presence of mining industry, both metal and non-metallic, with tones of by-products [9-10] and wastes accumulated. Most of them have few or none applications nowadays, thus some materials are very cheap and others don't even have a listed price. In the case of the non-metallic mining, the products are usually obtained from brines. The products and processes to obtain them will depend on brines composition.

Table 1 shows the main salt lakes in the world and their respective composition. The picture varies greatly by region.

Table 1. Characteristic composition in (wt.%) of brines [11]

Element	Wt.%				
	Atacama Chile	Uyuni Bolivia	Silver Peak Nevada	Seawater	Great Salt Lake, Utah
Li	0.16	0.045	0.04	0.000017	0.006
Na	7.6	8.0	7.5	1.08	7.0
K	1.8	1.1	1.0	0.04	0.4
Mg	1.0	1.0	0.06	0.13	0.8
Ca	0.02	-	0.05	0.04	0.03
B	0.07	0.009	-	-	-
Si	-	-	-	0.0003	0.0004
Al	-	-	-	-	-
Fe	-	-	-	-	-
SO4	1.9	1.0	0.75	0.27	1.5
Cl	15.7	16.0	11.7	1.94	14.0
B	-	-	0.0	0.0004	0.0

The salt lakes content are used as raw materials to feed the obtaining processes of salts, as was mentioned before, from brines. To be able to design the process for obtaining a specific salt, it is necessary to build the phase equilibrium diagram of the salt system, which can be a ternary, quaternary, quinary and even more. Based on this diagram and determining the salt of interest, the evaporation pathway can be established. In Chile, the chemical composition of brines coming from the Salar de Atacama corresponds to a complex multicomponent aqueous system. Usually the most used quinary aqueous system contains the following cations and anions to represent the phase equilibrium; Na^+ , K^+ , Mg^{2+} // Cl^- , $(\text{SO}_4)^{-}$ and H_2O (see Figure 1). From the Salar de Atacama Li_2CO_3 and KCl are mainly obtained.

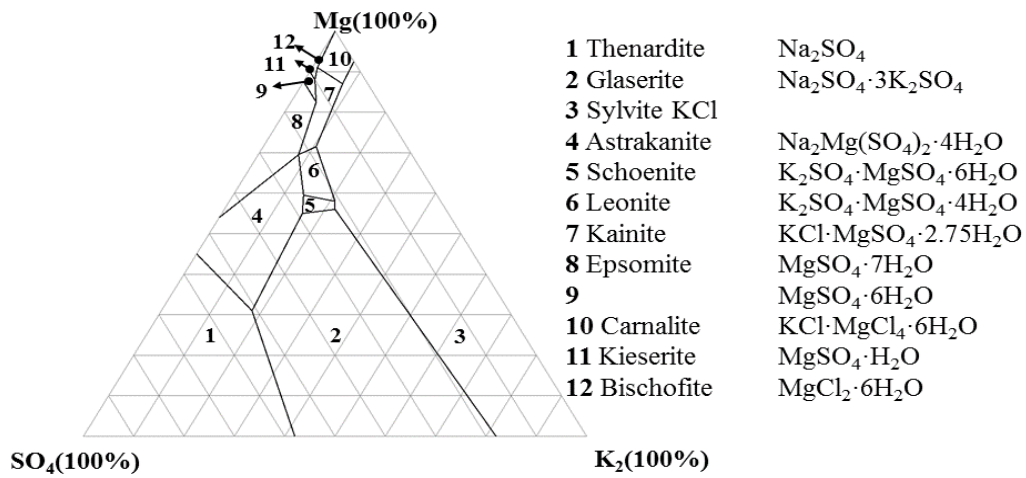


Figure 1. Janecke diagram for the system Mg-K₂-SO₄ at 25 °C (Molar % of K₂, Mg, SO₄ saturated in NaCl) [12]

Another source of non-metallic materials is the “caliche”, which corresponds to sandy-clay soils with high content of nitrates, halite, sodium anorthite and quartz [13]. From this material is mainly obtained the NaNO₃ by leaching and crystallization processes based on the phase diagram shown in Figure 2.

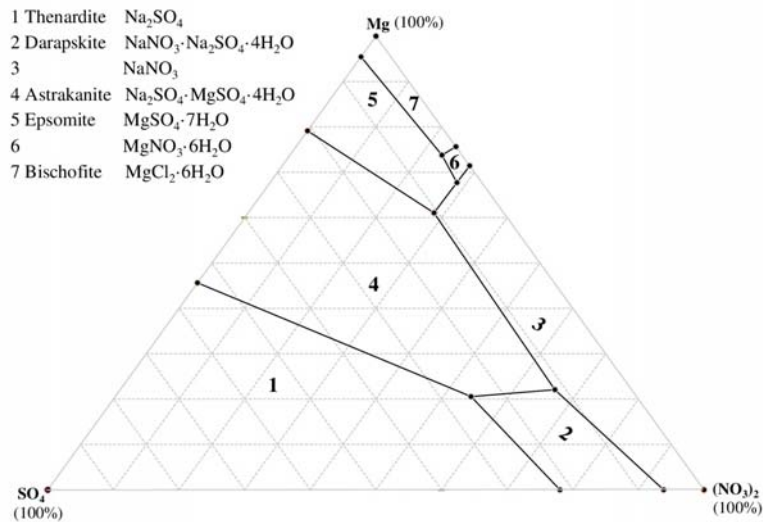


Figure 2. Phase diagram of crystallisation in caliche brines of Mg -SO₄-(NO₃)₂ at 25°C.

(Molar % of Mg -SO₄-(NO₃)₂ saturated in NaCl) [14].

The process established to obtain nitrates is shown in Figure 3. This starts with the blasting of the first layer of land, afterwards the sandy-clay rich in salts are heaped and the leaching process with water takes place. The solution coming from the leaching process is pumped

to the solar evaporation ponds, where different salts precipitate. At the end of this process, NaNO_3 is obtained and then, by chemical reaction with potassium chloride, KNO_3 is obtained.

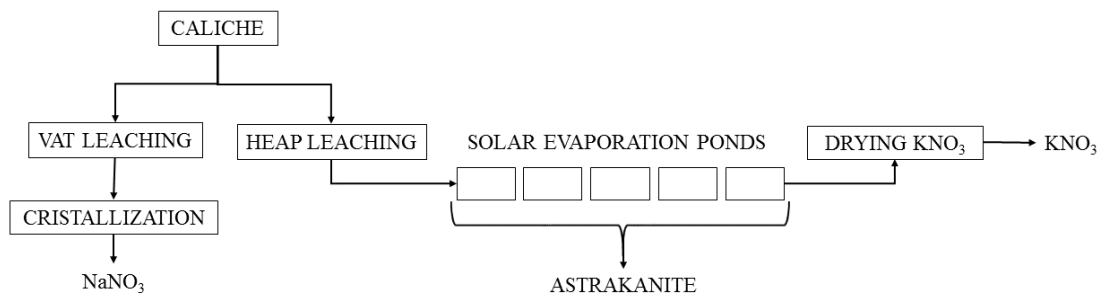


Figure 3. Schematic simplified process to obtain nitrate salts from caliche [15]

Regarding to brines, one of the processes established in Chile to obtain Li_2CO_3 and KCl , due to its low price and based on Janecke diagram [16], is shown in Figure 4. It can be seen that different salts precipitate in the process as wastes and as by-products. In the first and second stages precipitate halite (NaCl) and sylvinite (NaCl-KCl) respectively. The second one is transported to the flotation process to obtain KCl that it is widely used as fertilizer globally [17]. In the next step carnallite precipitates, a double salt hydrate ($\text{KCl}\cdot\text{MgCl}_2\cdot 6\text{H}_2\text{O}$), which can be also used as raw material to obtain KCl but the flotation process is more difficult due to the presence of magnesium increasing the prices of this stage [18-20]. This is why carnallite is mainly accumulated in the mine sites with no specific applications up to now. In the last solar evaporation step bischofite precipitates, which is a salt hydrate that is mainly composed by $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ [10]. This inorganic material is applied to abate dust in copper mines roads and for de-icing roads.

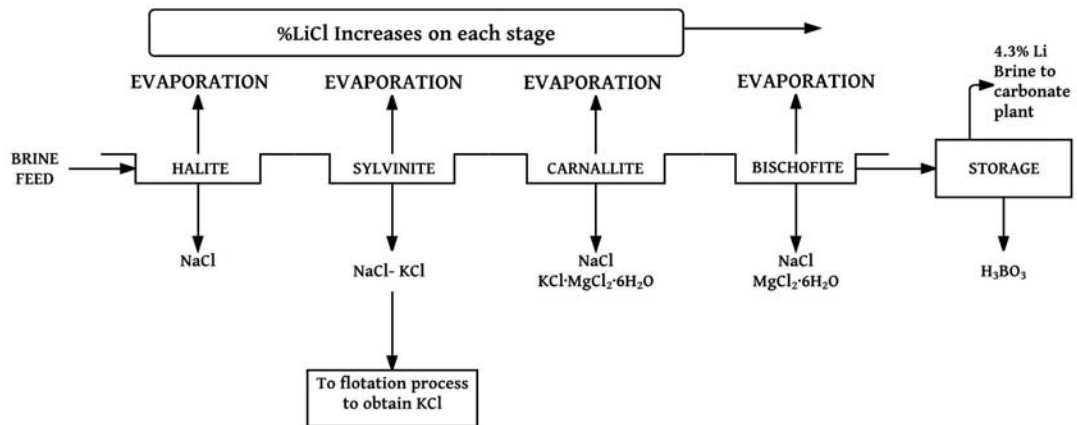


Figure 4. Process for obtaining KCl and lithium concentrated brines [14].

Since bischofite appears in the process together with other products, the goal of this paper is to see the influence that some of those compounds, in this case sodium, potassium and lithium chlorides, have on the thermophysical properties of bischofite. The overall aim is to see if the potential composition variation of the bischofite obtained as by-product would compromise its application as thermal energy storage (TES) material (studied in a previous work [10]) or would suggest use in different potential applications (domestic hot water production, waste heat recovery, solar cooling, etc.).

2. Materials and methods

2.1. Materials

Bischofite is commercialized in two different qualities, the so-called *standard* and *Grade A* bischofite. The main difference between both products is that in *Grade A* bischofite a minimum $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ content of 95% is ensured due to an additional purification process, and that *standard* bischofite is sold as obtained in the precipitation process without further control. This quality commercial difference is reflected in the price of bischofite, *standard* bischofite is sold at around 40 US\$/ton, while *Grade A* bischofite is close but lower to that of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, which is sold at around 155 US\$/ton in the north of Chile [10]. The composition of bischofite *Grade A* as reported by Ushak et al. [10] is presented in Table 2. In the present study, two samples of *Grade A* bischofite and two samples of *standard* bischofite were obtained from Salmag (Antofagasta, Chile).

Table 2. Chemical composition of bischofite [10]

Element	Average concentration range [%]	Concentration used in this study [%]
Sodium, Na	0.321-0.360	0.536
Potassium, K	0.259-0.301	0.474
Calcium, Ca	0.007-0.008	0.008
Magnesium, Mg	10.84-11.45	10.67
Lithium, Li	0.298-0.351	0.250
Chloride, Cl	33.66-34.92	33.62
Sulfate, SO ₄	1.29-1.51	1.49
Boron, B	-	0.193
Moisture	1.42-1.50	13.13

All the additives used for this study were analysis quality LiCl ($\geq 99\%$), NaCl ($\geq 99\%$), KCl ($>99.5\%$) and are commercialized by Merck.

2.2. Sample preparation

In order to evaluate the influence of alkali chlorines, only the new batch of *Grade A* bischofite was mixed with LiCl, NaCl, or KCl (from 1 wt.% to 5 wt.% additive). The top limit (5 wt.%) was selected because in the real product it is not possible to have more chloride in the bischofite, since in the case of NaCl and KCl it would have precipitated before, and in the case LiCl more concentration has no sense since this is the final product of this stage and having more in the bischofite or any other by-product/waste means losses for the production company.

2.3. Chemical characterization

X-ray diffraction (XRD) analyses were performed on an X-ray diffractometer SIEMENS model D5000 (40 kV, 30 mA); radiation of Cu K α 1 ($\lambda=1.5406 \text{ \AA}$); Vertical Bragg–Brentano; Scan Range: 3–70° 2 θ ; Step Size: 0.0201 2 θ ; Step Time: 1.0 s.

The temperature and enthalpy of fusion were determined by differential scanning calorimetry (DSC) method. The DSC 204 F1 *Phoenix*® NETZSCH equipment with N₂

atmosphere (volumetric flow 20 mL/min) and heating rate of 0.5K/min was used. Aluminium crucibles of 25 uL hermetically sealed was used. These crucibles were selected based on previous results reported, which show better thermal stability of the tested material than when using them open crucibles [10].

3. Results and discussions

The chemical analysis for a new batch of bischofite *Grade A*, and two other batches of bischofite *standard* were performed, in order to evaluate the difference on their compositions. Results presented in Table 3 show that magnesium and chloride contents remain within the range determined by Ushak et al. 2015 for bischofite *Grade A* and synthetic $MgCl_2 \cdot 6H_2O$. However, the main difference between bischofite *Grade A* and *standard* is the presence of Na, Ca, Li, B, which present higher concentrations than those contained in the reference *Sample A*.

Table 3. Chemical composition of bischofite and $MgCl_2 \cdot 6H_2O$ (wt.%)

Compound	Synthetic $MgCl_2 \cdot 6H_2O$ * (wt.%)	Bischofite			
		<i>Grade A</i>		<i>Standard</i>	
		Sample A* (wt.%)	Sample B (wt.%)	Sample C (wt.%)	Sample D (wt.%)
Sodium, Na	≤0.001	0.321-0.360	0.536	0.983	0.397
Potassium, K	≤0.001	0.259-0.301	0.474	0.257	0.207
Calcium, Ca	≤0.003	0.007-0.008	0.008	0.025	0.018
Magnesium, Mg	11.49-12.51	10.84-11.45	10.67	10.11	11.377
Lithium, Li	-	0.298-0.351	0.250	0.502	0.437
Chloride, Cl	33.51-36.49	33.66-34.92	33.62	34.62	34.53
Sulfate, SO4	≤0.002	1.29-1.51	1.49	0.37	0.257
Boron, B	-	-	0.193	0.517	0.465
Moisture	-	1.42-1.50	1.313	4.29	-

*Reported in Ushak et al. [10]

It is important to highlight that since bischofite is a by-product or waste, different batches of bischofite mean slight changes in their composition. Furthermore, the composition of bischofite has a slight variation depending on the exact location of salt lake the brines are coming from, which will be different over time. Additionally, bischofite *Grade A* assures at least 95% of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, according to results of XRD (Table 4).

Table 4. XRD analyses of bischofite *Grade A* and two samples of bischofite *standard*

	Compound (crystalline phase)	Chemical composition
<i>Grade A</i>	Bischofita	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
<i>Sample B</i>	Halita	NaCl
<i>Standard – Sample C and Sample D</i>	Bischofita	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
	Halita	NaCl
	Carnallite	$\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
	Lithium sulphate monohydrate	$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$

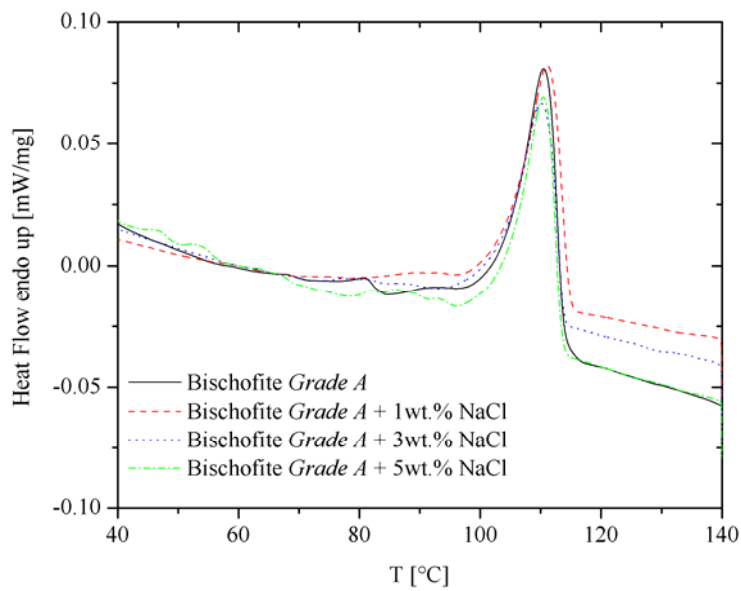
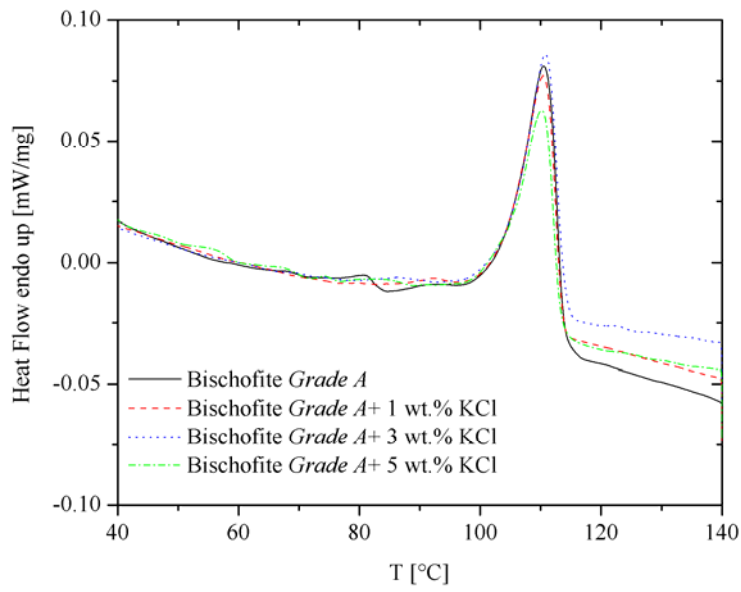
Grade A bischofite (Sample B) and the mixtures with up to 5 wt.% NaCl, KCl, and LiCl were analysed with DSC, and the results are presented in Table 5. Results show that the presence of up to 5 wt.% KCl in bischofite does not affect the melting temperature and enthalpy to compromise to be used as PCM; melting temperature decreases from 104 °C to 102.5 °C, and melting enthalpy decreases from 119.7 J/g to 107 J/g with 3 wt.% KCl. The presence of NaCl means no change in the melting temperature, but 3 wt.% NaCl shows a decrease from 119.7 J/g to 95 J/g (not seen with 5 wt.% NaCl), that it is a significant decrease but still giving a material with good enough thermophysical properties to be used as PCM [8,21-23]. Very interesting is the effect that the presence of LiCl has on bischofite; in this case, the melting enthalpy remains close at the initial value, going from 119.7 J/g to 108.8 J/g. However, the melting temperature change from 104 °C to 91.8 °C showing the possibility to use the new compound in applications such as solar heating, heat load leveling and industrial waste heat recovery [21, 24]. Similar thermophysical properties were observed for bischofite *standard* with a melting temperature of 90.9 °C. However, the

melting enthalpy is lower than Bischofite *Grade A* + 5 wt.% LiCl, this may be explained by the presence of other impurities at higher concentration showed by XRD results.

Table 5. Melting temperature enthalpy of bischofite *Grade A* and *standard*, and mixtures of bischofite *Grade A* with KCl, NaCl and LiCl.

Sample	T _m [°C]	ΔH _m [J/g]	T _m [°C]	ΔH _m [J/g]	T _m [°C]	ΔH _m [J/g]
Bischofite <i>Grade A</i>	104.0	119.7	--			
Bischofite <i>standard</i>	90.9	87.4	--			
	+ KCl		+ NaCl		+ LiCl	
Bischofite+1%	102.5	117.5	104.0	108.7	92.7	118.4
Bischofite+3%	103.5	107.0	103.0	95.0	93.4	108.8
Bischofite+5%	102.7	113.5	104.1	107.8	91.8	113.7

The Figure 5 shows the DSC curves for bischofite, and their mixtures with LiCl (from 1wt.% to 5wt.%). The effect on the curves shape due to the increase of the weight composition of LiCl can be observed. The addition of LiCl in the bischofite means one additional peak to appear until that at 5 wt.% there is only one peak, which is displaced to a lower melting temperature. In other words, two transition stages appear at 1 wt.% and 3 wt.%, which support the hypothesis that a new compound is being obtained.



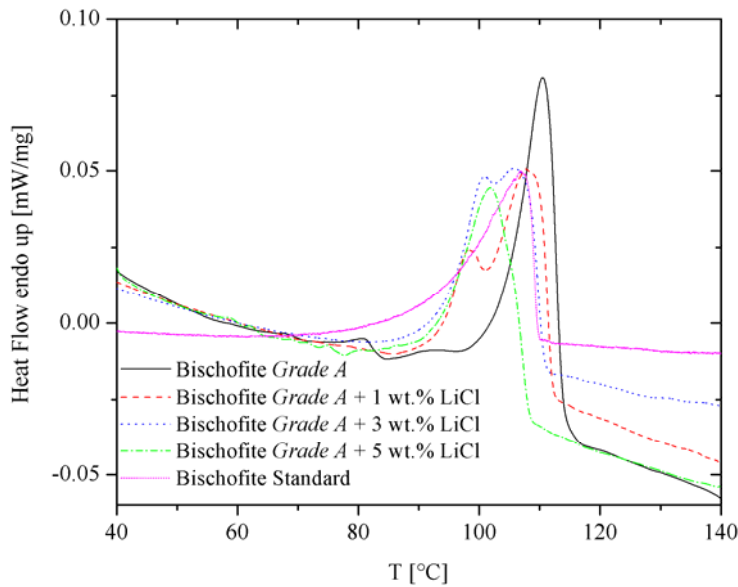


Figure 5. DSC heating curves for Bischofite *Grade A*, their mixtures with NaCl, KCl and LiCl up to 5 wt.%, and Bischofite *standard* without additives.

4. Conclusions

Bischofite is a by-product from the non-metallic industry, and therefore its composition varies from batch to batch. On the other hand, the authors of this paper demonstrated in a previous paper that bischofite is a good candidate to be used as phase change material. Therefore, the influence of the variation of bischofite composite by its main impurities needs to be evaluated. The main impurities of bischofite are the cations sodium, potassium and lithium and the anion chloride.

This paper shows that the presence of KCl (up to 5 wt.%) do not affect the use of bischofite as PCM, since its melting enthalpy and temperature do not vary significantly. Increasing the amount of NaCl do not change bischofite melting temperature but decrease its melting enthalpy, but not enough to compromise the use of bischofite as PCM. Finally, small contents of LiCl in bischofite do not change significantly its melting enthalpy but decrease the melting temperature, an interesting change that may enable this material as PCM in other applications at lower temperature.

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