STUDY ON ELECTRO-CONDUCTANCE AND THERMAL ANALYSIS OF LITHIUM CARNALLITE

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Abstract

Lithium carnallite is a hydrated double salt containing lithium and magnesium chlorides. The processes of thermal dehydration and thermal decomposition of lithium carnallite during heating has been studied by the conductance-thermoanalysis which was designed according to Berg and-Wendlandt, and an interpretation of the conductance–thermoanalytical curve has been suggested.

Introduction

The concentrated eutectic magnesium chloride brine containing 1.0% LiCl could be obtained after separating salts, such as NaCl, $MgSO_4 \cdot 7H_2O$, $MgCl_2 \cdot KCl \cdot 6H_2O$ etc., during solar evaporation of salt lake brines of a new type on Qinghai-Tibet plateau, People's Republic of China [1]. The lithium salt in the concentrated brine might be further enriched by freezing in winter and evaporating in the following summer. Hydrogen chloride was used to salt out part of hydrated magnesium chloride from the concentrated brine. Then lithium carnallite might be prepared from the solution by evaporation and crystallization.

Lithium carnallite which was found during studying of $LiCl–MgCl_2–H_2O$ [2] ternary system and $HCl–LiCl–MgCl_2–H_2O$ [3] quaternary system is a hydrated double salt containing lithium and magnesium chlorides. Its thermal behavior has never been reported before. In this paper, the processes of thermal dehydration and thermal decomposition of lithium carnallite during heating has been studied by the conductance–thermoanalysis which was designed according to Berg [4] and Wendlandt [5], and an interpretation of the conductance–thermoanalytical curve has been suggested.

Experimental

Synthesis of material

A composition point was selected from the solubility phase diagram of $LiCl–MgCl_2–H_2O$ ternary system at 25 and 75°C. 113 g $MgCl_2·6H_2O$ and 153 g $LiCl·H_2O$, both of analytical grade from P. R. of China were weighed, and dissolved completely in 170 ml distillated water at 75°C. The solution was transferred into a flask with three necks, the center one neck fitted with a stirrer and one of the side necks fitted with a thermometer. The flask was placed in a water bath, and was allowed to cool slowly at a rate of 2 K per hour to crystallize out lithium carnallite with the size of 3–4 mm in diameter. At last, the crystalline solid phase was separated, and washed quickly with absolute alcohol for three to four times, and dried in a desiccator at room temperature to volatilize all the solvent with no desiccant.

The analytical results of the lithium carnallite sample which was heated at 105°C for 100 h to constant weight were listed in Table 1. It is indicated that the synthesized lithium carnallite contains a very small amount of mother liquor.

Table 1 The composition of synthesized lithium carnallite

	Lithium	Carnallite		
Composition	Dehydration (at 105°C)		Magnesium oxide (fired at 1000°C)	
	Analytical value /%	Theoretical value /%	Analytical value /%	Theoretical value /%
Li^+	3.90	4.00		
Mg^{2+}	14.00	14.01	60.35	60.32
Cl^-	60.73	61.25		
H_2O	21.27*	20.76		

Instrument of conductance–DTA

The conductance–DTA system shown in Fig. 1 is made up of DT-10B DTA made in Japan and the designed AC-conductance meter with an X-Y function recorder (LZ3-204 produced by Shanghai Second Automatic Instrument and Meter plant, P. R. of China). The sample $LiCl·MgCl_2·6H_2O$ and the reference material Al_2O_3 were placed in crucibles. The sensitivity of the DTA is 250 μV and the rate of heating is 20°C per minute. The conductance of sample is measured as follows: At first, 6V-alternative current power is connected with the Pt electrodes. At the beginning, the conductance is zero. When the resistance of the sample begins to change during heating, there is an alternative current that will pass through the distance between the two Pt-electrodes, and this current

will then be fed to the recorder after rectification. The AC-conductance circuit is so designed that it can measure the conductance from zero to infinite. The distance between two electrodes should be so controlled: When the material is partly molten or in a phase transition, the distance between the two Pt-electrodes should be about 1 mm. When the material is molten, the distance between the electrodes should be 10 mm.
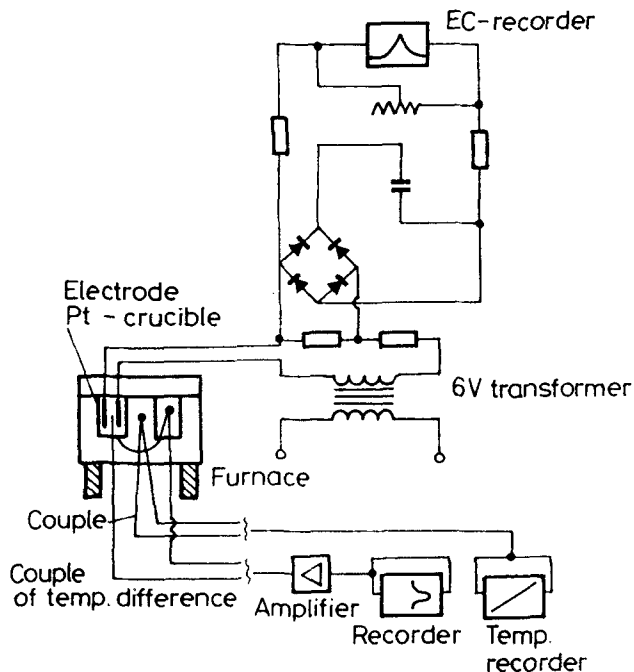

Fig. 1 EC (electric conductance)-differential thermal analysis temperature

X-ray powder diffraction

Model YPC-50u X-ray diffraction meter, made in Japan, is used to identify the lithium carnallite, ground quickly at low humidity, and kept into a closed container. Operating conditions are: Cu target; with a filter; tube voltage 35 KV; current 8 mA; scanning rate 2 deg·s^{-1}; and paper rate 2 cm·s^{-1}.

Results

From the analytical results in Table 1 and X-ray powder diffraction results in Table 2, the lithium carnallite is of good quality and suitable for studying its thermal behavior using the conductance–DTA–TG.

Table 2 X-ray powder diffraction results of lithium carnallite

Line No.	I/I_o	dÅ
1	100	4.78
2	8	4.44
3	10	4.17
4	10	4.08
5	7	3.08
6	5	3.01
7	40	2.88
8	100	2.808
9	5	2.738
10	5	2.637
11	20	2.222
12	5	2.067
13	20	1.817
14	5	1.583

Conductance curve

Two EC (electrical conductance) curves of lithium carnallite are shown in Fig. 2, in which the curve A has been recorded independently using only a conductance pool with lithium carnellite sample and the curve B has been recorded by means of the conductance–DTA system. The conductance peaks on curves A and B almost have the same shape, and only the smaller peaks on the curve A is sharper than those on the curve B. There appears four mainly conductance stages on the conductance curve during heating of lithium carnallite: The first stage including four smaller peaks are from 90 to 230°C, in which the first one is at 110°C, the second at 160°C, the third at 180°C, and the fourth at 220°C. The second conductance stage is from 230 to 470°C. The third stage begins at 550°C. And the fourth stage is from 600 to 700°C, and then reaches its maximum, and finally ends at 930°C.

DTA curve

There are nine differential thermal analytical peaks on the DTA curve of lithium carnallite shown in Fig. 2. The temperatures of the peaks are: Peak 1 at 105°C, Peak 2 at 160°C, Peak 3 at 200°C, Peak 4 at 213°C, Peak 5 at 230°C, Peak 6 at 257°C, Peak 7 at 304°C, Peak 8 at 550°C, and Peak 9 at 600°C.
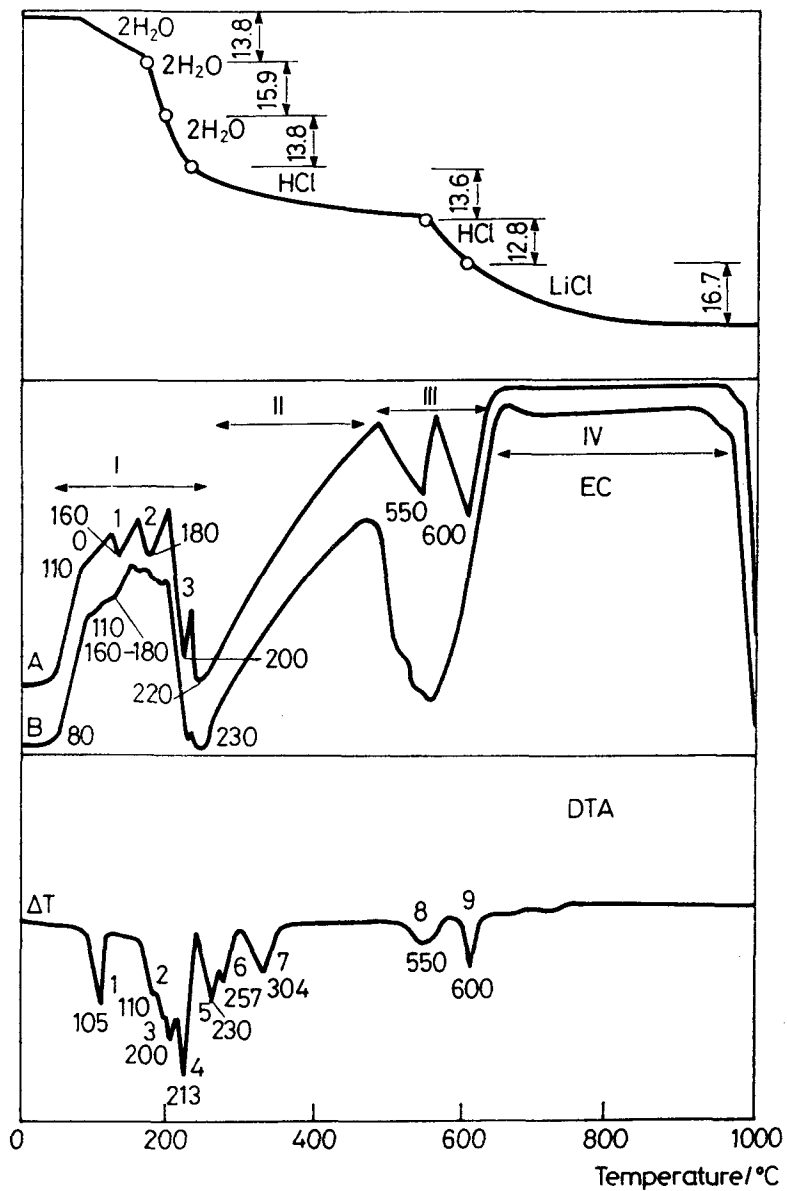
Fig. 2 TG, EC and DTA of lithium carnallite

TG curve

The TG curve was recorded on Stanton HD-D thermobalance, made in Britain. The weight of sample was 0.0999 g, the rate of heating was 5 deg·min^{-1},

moving rate of paper was 2.5 mm·min⁻¹ and the highest temperature was 1000°C.
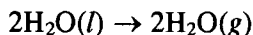
It can be obviously seen that there exists three stages on the TG-curve shown in Fig. 2: The first stage is from room temperature to 230°C, the total amount of loss is 41.6%, and the rate of loss is rapid. Based on the slope of the curve in this period, it is easy to divide this stage into two parts: the first part is from room temperature to 180°C and the loss is 13.6%, and the second part is from 180 to 230°C and the loss is 27.8%. The second stage is from 230 to 550°C, the loss is 13.6%, and the slope of curve in this period is the smallest. The last stage is from 550 to 1000 °C and the loss is only 29.5%. The total loss is 84.7%. It means the weight of the residue is 15.3%, which is in strict accordance with the theoretical content of magnesium oxide in lithium carnallite.
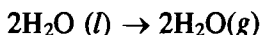
Discussion

It is helpful for explaining the thermal behavior of lithium carnallite by comparing the conductance and thermal analytical results of lithium carnallite with those of $LiCl·2H_2O$ and $MgCl_2·6H_2O$ obtained by the conductance–DTA. There are two conductance peaks on the EC curve of $MgCl_2·6H_2O$, just the same as those in literature [4]: The first one appears at 90°C, reaches its maximum at 150°C, comes back soon to the baseline from 200 to 220°C, no peak appears until 550°C. The second one begins to appear at 550°C, probably a result of the decomposition of MgOHCl [4]. The interpretation of DTA curve of $LiCl·2H_2O$ is in agreement with literature [6] is as follows: The first endothermal peak at 20°C is explained as the loss of the first molecule of water, and the second endothermal peak at 98°C is due to the loss of the second molecule of water.

On the DTA curve the first endothermal peak (at 105°C) is due to fusion, the second peak (at 160°C), the third peak (at 200°C) and the fourth peak (at 220°C) are related to three stages of dehydration, each of which may be regarded due to the loss of two molecules of water. Those three stages of dehydration are in agreement with the results of the TG curve of lithium carnallite. During the period of dehydration, on the EC curve there appears a large peak consisting three smaller peaks, each of which corresponding to a quadruple point of four phases, the initial crystalline phase, the produced new solid phase, liquid phase and gaseous phase.
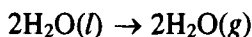
The first quadruple point process at 160°C is

$$LiCl·MgCl_2·7H_2O \rightarrow LiCl·MgCl_2·5H_2O + 2H_2O(l)$$

$$2H_2O(l) \rightarrow 2H_2O(g)$$

The second quadruple point process (at 180°C) is

$$LiCl \cdot MgCl_2 \cdot 5H_2O \rightarrow LiCl \cdot MgCl_2 \cdot 3H_2O + 2H_2O(l)$$

$$2H_2O \ (l) \rightarrow 2H_2O(g)$$

The third quadruple point process (at 220°C) is

$$LiCl \cdot MgCl_2 \cdot 3H_2O \rightarrow LiCl \cdot MgCl_2 \cdot H_2O + 2H_2O(l)$$

$$2H_2O(l) \rightarrow 2H_2O(g)$$

The results recorded by conductance meter are almost the same as those by DTA.

Although the loss of weight from 230 to 550°C on the TG curve is only about one mole water, there are three endothermal peaks on the DTA curve, and they are the fifth peak (at 230°C), the sixth peak (at 257°C), and the seventh peak (at 304°C). These peaks may be considered to correspond with three process. The fifth peak (at 230°C) on the DTA curve of lithium carnallite may be regarded as the last dehydration

$$LiCl \cdot MgCl_2 \cdot H_2O \rightarrow LiCl \cdot MgCl_2 + H_2O(g)$$
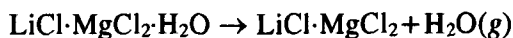
The sixth peak (at 257°C) may correspond with a hydrolysis

$$LiCl \cdot MgCl_2 + H_2O \rightarrow LiCl \cdot MgOHCl + HCl(g)$$

Perhaps the seventh peak (at 304°C) may be thought as the formation of a solid solution LiCl and MgOHCl.

The eighth peak (at 550°C) on the DTA curve may be explained as the decomposition of magnesium oxychloride

$$MgOHCl(s) \rightarrow MgO(s) + HCl(g)$$

And the last (ninth) peak (at 600°C) is due to fusion of lithium chloride.

When the temperature is raised continuously from 230 to 550°C, there appears on the EC curve the second large peak consisting of two smaller peaks. The first one is due to the gaseous hydrogen chloride produced by the hydrolysis of magnesium chloride, and the second one is due to the decomposition of magnesium oxychloride. By heating from 600 up to 930°C, the conductance is increased rapidly to the maximum value, which is the result of the fusion and the evaporation of lithium chloride. The conductant curve does not return to the baseline until the LiCl is volatilized completely at 930°C.

Table 3 Phase reaction of lithium carnallite during heating

T/°C	DTA-peak No.		TG lost wt. /%	Conductance peak	Phase reaction
105	1	sel–melting		liquid	Li–carnallite → solid–liquid
160	2	lost $2H_2O$	13.8	gradruple–phase point (I)	$LiCl \cdot MgCl_2 \cdot 7H_2O \rightarrow LiCl \cdot MgCl_2 \cdot 5H_2O(s)$ $-2H_2O(l) \rightarrow 2H_2O(g)$
200	3	lost $2H_2O$	27.7	gradruple–phase point (II)	$LiCl \cdot MgCl_2 \cdot 5H_2O \rightarrow LiCl \cdot MgCl_2 \cdot 3H_2O(s)$ $-2H_2O(l) \rightarrow 2H_2O(g)$
213	4	lost $2H_2O$	41.6	gradruple–phase point (III)	$LiCl \cdot MgCl_2 \cdot 3H_2O \rightarrow LiCl \cdot MgCl_2 \cdot H_2O(s)$ $-2H_2O(l) \rightarrow 2H_2O(g)$
230	5	dehydrate			$LiCl \cdot MgCl_2 \cdot H_2O \rightarrow LiCl \cdot MgCl_2(s) + H_2O(g)$
257	6	hydrolysis	54.6	gaseous HCl	$LiCl \cdot MgCl_2(s) + H_2O(g) \rightarrow LiCl(s) + MgOHCl(s) - HCl(g)$
384	7	solid soln.			$LiCl + MgOHCl \rightarrow MgOHCl - LiCl$
550	8	decompose	66.9	gaseous HCl	$MgOHCl - LiCl \rightarrow MgO(s) + LiCl(s) + HCl(g)$
600	9	melting and evaporate		gaseous LiCl	$MgO(s) + LiCl(s) \rightarrow MgO(s) + LiCl(l)$ $LiCl(l) \rightarrow LiCl(g)$
1000		return to base–line	83.6	return to base–line	$MgO(s)$

All of the above discussions have been supported by the calculated results from the TG curve of lithium carnallite between 230 and 1000°C. The total loss of weight is equal to the weight of two molecules of hydrogen chloride and one molecules of lithium chloride.

The phase reactions of lithium carnallite during heating is summarized in Table 3.

References

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Zusammenfassung — Lithiumkarnallit ist ein hydratiertes Doppelsalz mit Gehalt an Lithium- und Magnesiumchloriden. Mittels Leitfähigkeits-Thermoanalyse nach L. G. Berg und W. W. Wendlandt wurde der Prozeß der thermischen Dehydratation und der thermischen Zerset-zung von Lithiumkarnallit untersucht und eine Interpretation der Leitfähigkeits-Thermoanalyse-Kurve vorgeschlagen.