

## The products of selenite hydrothermal treatment in lithium chloride solutions

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Selenite was boiled in LiCl solutions of different concentrations (1 M, 2 M, 3 M, 4 M and 5 M) at the respective boiling temperatures and atmospheric pressure. The products were subjected to X-ray diffraction analysis, qualitative infrared analysis, differential thermal analysis, thermogravimetric analysis and microscopic examination. The product obtained in the 1 M LiCl solution was the  $\beta$ -form of calcium sulphate hemihydrate ( $\beta$ -CaSO<sub>4</sub>·0.5H<sub>2</sub>O). In more concentrated LiCl solutions, 2 M and 3 M, the  $\alpha$ -form of calcium sulphate hemihydrate ( $\alpha$ -CaSO<sub>4</sub>·0.5H<sub>2</sub>O) was formed. The product obtained in the 4 M LiCl solution was also the  $\alpha$ -form of calcium sulphate hemihydrate, only mixed with the  $\gamma$ -form of calcium sulphate ( $\gamma$ -CaSO<sub>4</sub>). Finally, in the 5 M LiCl solution the  $\gamma$ -form of calcium sulphate or  $\gamma$ -anhydrite was formed.

*Keywords:* selenite, hemihydrate, hydrothermal treatment, calcium sulphate.

### INTRODUCTION

Hydrothermal treatment of gypsum is performed either in water at an increased pressure,<sup>1,2</sup> or in aqueous solutions of salts and inorganic acids at the respective boiling temperatures and atmospheric pressure.<sup>3-5</sup> This method is new and has not been studied enough nor described in the literature, but it is believed<sup>3</sup> that the dehydration of gypsum under "wet" conditions is a "through solution" process. This means that the dihydrate (CaSO<sub>4</sub>·2H<sub>2</sub>O) dissolves and goes into solution and crystals of the hemihydrate (CaSO<sub>4</sub>·0.5H<sub>2</sub>O) grow from the solution.

The product of the hydrothermal process is usually the  $\alpha$ -hemihydrate ( $\alpha$ -CaSO<sub>4</sub>·0.5H<sub>2</sub>O),<sup>3-6</sup> but also the  $\beta$ -hemihydrate ( $\beta$ -CaSO<sub>4</sub>·0.5H<sub>2</sub>O) and the  $\gamma$ -anhydrite ( $\gamma$ -CaSO<sub>4</sub>),<sup>1,2</sup> depending on the process conditions (temperature, time of hydrothermal treatment, *etc.*), can be formed.

The hydrothermal method offers a great chance for the obtainment of high grade products, it has, however, limitations. Namely, possible reactions between the liquid media (salts) and calcium sulphate may produce undesirable compounds

(double salts or complexes). In this way the double salt ( $\text{K}_2\text{SO}_4 \cdot 5\text{CaSO}_4 \cdot \text{H}_2\text{O}$ ) was formed during selenite hydrothermal treatment in KCl solutions more concentrated than 1 M, when the density of the suspension (mass of selenite in g per volume of solution in  $\text{cm}^3$ ) was  $0.2 \text{ g/cm}^3$  ( $10 \text{ g/50 cm}^3$ ).<sup>7</sup> Consequently, KCl solutions are not favourable liquid media for the hydrothermal treatment (dehydration) of gypsum.

The aim of this work was to investigate the possibility of using LiCl solutions as the liquid media, for the hydrothermal treatment of selenite. Hence, selenite, was boiled in LiCl solutions of different concentrations (1 M, 2 M, 3 M, 4 M and 5 M), in the same manner as had been employed with KCl solutions,<sup>7</sup> and the obtained products were studied by means of X-ray diffraction analysis (XRD), infrared spectroscopy (IR), differential thermal analysis (DTA), thermogravimetric analysis (TGA), and microscopy.

#### EXPERIMENTAL

Natural selenite mineral of very high chemical purity (0.33 mass % impurity) was used in the experiments. Its chemical composition, determined by conventional chemical analysis, is given in Table I.

TABLE I. Chemical composition of selenite (mass. %)

$\text{H}_2\text{O}$	20.75
$\text{CaO}$	32.47
$\text{SO}_3$	46.45
$\text{SiO}_2$ (insol.)	0.03
$\text{MgO}$	0.08

Ten grams samples of selenite,  $-0.250 + 0.125 \text{ mm}$  size fraction, were boiled in  $50 \text{ cm}^3$  of aqueous LiCl solutions of different concentrations (1 M, 2 M, 3 M, 4 M, and 5 M) at the respective boiling temperature and atmospheric pressure. The boiling vessel was a reactor with a magnetic stirrer (200 rpm). The solution concentration was maintained constant by continuously feeding boiling distilled water to balance the water loss due to evaporation.

Selenite boiling periods for the different concentration of lithium chloride solutions were: 300 min for 1 M; 180 min for 2 M; 120 min for 3 M; 75 min for 4 M and 60 min for 5 M (as were used with the KCl solutions<sup>7</sup>).

The solid products obtained after boiling the selenite for the mentioned time intervals were separated from the solution by vacuum filtration, rinsed in boiling distilled water to remove any traces of  $\text{Cl}^-$  ions and dried at  $105^\circ\text{C}$  before analysis.

The chemical composition of the products was determined by the X-ray powder diffraction technique. All samples were examined under the same conditions using a Philips PW 1729 X-ray generator and a Philips PW 1710 diffractometer and the original APD software. The radiation source used was an X-ray LFL tube with copper radiation and a graphite monochromator. The radiation was  $\lambda_{\text{CuK}\alpha 1} = 0.15405 \text{ nm}$ . The anode tube load was 40 kV and 35 mA. The slits of 1.0 and 0.1 mm were fixed. The samples were pressed into standard aluminium frames and measured in the  $2\theta$  range from  $5^\circ$  to  $100^\circ$ . Each  $1/50^\circ$  ( $0.02^\circ$ ) was measured for 0.5 s. The MPDS programme and JCPDS (ASTM) card files were used for identification of the products.

Infrared absorption spectra were recorded using a Perkin-Elmer spectrophotometer 782 in the range from  $4000\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$ , using the KBr pressed disc technique.

A Netsch STA 409 EP instrument was used for differential thermal and thermogravimetric analyses. The sample mass was 40 milligrams (0.040 g), and the atmosphere was air. The samples were heated from 20 to  $500\text{ }^{\circ}\text{C}$  at a heating rate of  $10\text{ }^{\circ}\text{C}/\text{min}$ .

Microscopical examinations were carried out using an American Optical Stereoscopic ZOOM microscope.

## RESULTS AND DISCUSSION

The X-ray analytical results of the obtained products can be interpreted using JCPDS cards: 41-0224 for  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  (hemihydrate) and 37-184 for  $\gamma\text{-CaSO}_4$  (soluble anhydrite).

Table II shows the interplanar spacings  $d$ , the reflection intensities  $I$ , and the  $hkl$  values for the mentioned substances taken from the two cards, and the interplanar spacings  $d$  and reflection intensities  $I$  for each of the obtained products.

The data given in Table II indicate that the product of selenite boiling in 1 M, 2 M and 3 M LiCl solutions is calcium sulphate hemihydrate ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ); that the product in 4 M LiCl solution is a mixture of two substances: calcium sulphate hemihydrate ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ) and  $\gamma$ -calcium sulphate ( $\gamma\text{-CaSO}_4$ ); and that the product in 5 M LiCl solution is  $\gamma$ -calcium sulphate ( $\gamma\text{-CaSO}_4$ ) or soluble anhydrite.

The infrared absorption spectra of the products are shown in Fig. 1.

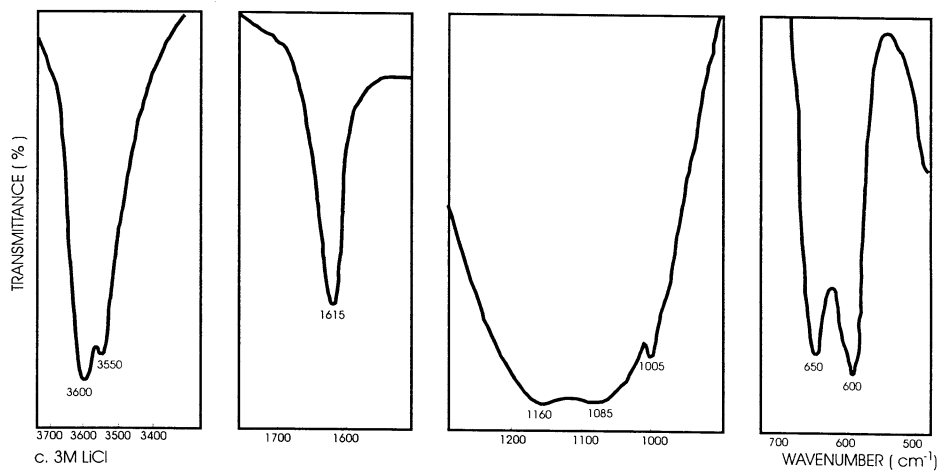
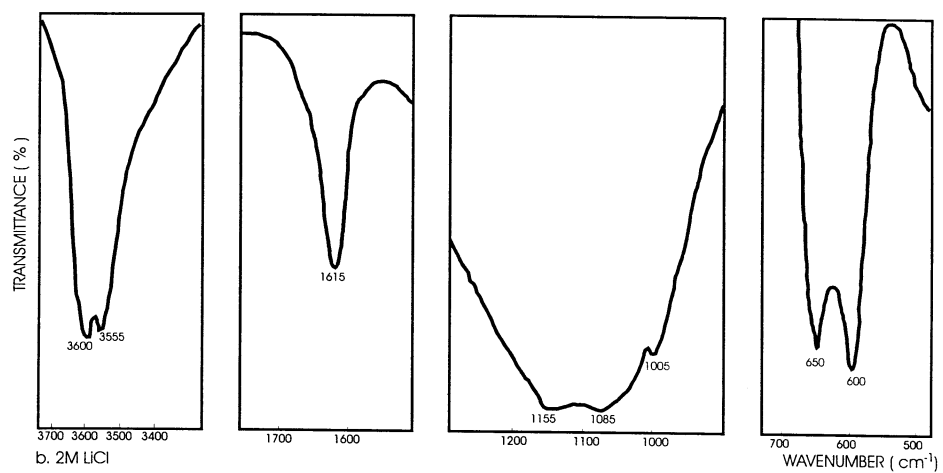
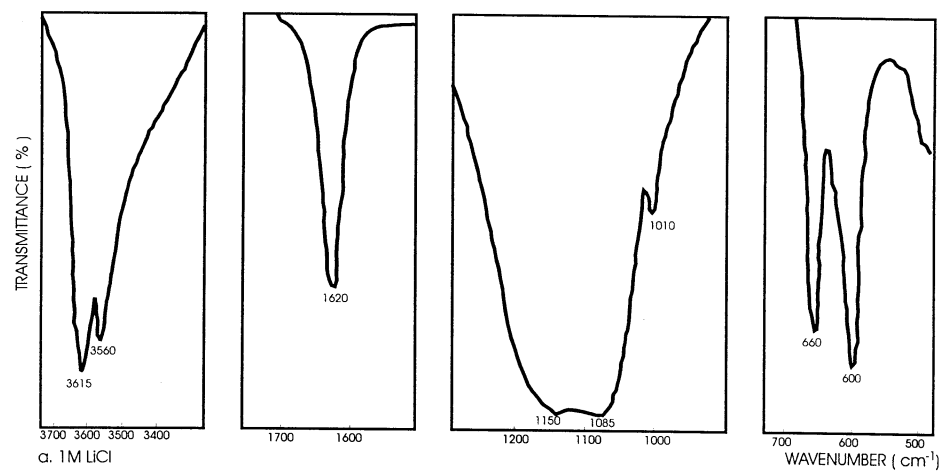
The infrared spectra of the products in 1 M, 2 M and 3 M LiCl solutions are almost identical, which confirms the identity of the chemical composition of these products and which is congruous with the X-ray data (Table II). Namely, the IR spectra of the products in 1 M, 2 M and 3 M LiCl solutions (Fig. 1a, b and c) contain only absorption bands which are characteristic of  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ <sup>8-11</sup> (about  $3600$ ,  $3550$ ,  $1615$ ,  $1150$ ,  $1085$ ,  $1005$ ,  $650$  and  $600\text{ cm}^{-1}$ ).

In addition to the absorption bands characteristic of  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ , the IR spectrum of the product in 4 M LiCl solution (Fig. 1d) contains an absorption band (shoulder) at  $610\text{ cm}^{-1}$  which confirms the presence of soluble anhydrite<sup>8-10</sup> (or  $\gamma\text{-CaSO}_4$ ), in addition to  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ , in the product, as detected in the X-ray analysis (Table II).

Finally, the IR spectrum of the product obtained in 5 M LiCl solution (Fig. 1e) contains absorption bands which are characteristic of  $\gamma\text{-CaSO}_4$ .<sup>8,10</sup> The broad and weak absorption bands in this spectrum at  $3440$  and  $1620\text{ cm}^{-1}$  confirm the presence of a small amount of water<sup>10</sup> in the product, which was reported in the literature for soluble, or  $\gamma$ -anhydrite. Namely, it is known that  $\gamma$ -anhydrite contains residual,<sup>12</sup> *e.g.*, zeolitic<sup>13</sup> water, which can be completely driven off only at higher temperatures,<sup>12</sup> or if heating is prolonged.<sup>14</sup>

The results of DTA of the products are given in Fig. 2.

The differential thermogram of the product obtained in 1 M LiCl solution has an endothermic and an exothermic peak, whereas the differential thermograms of



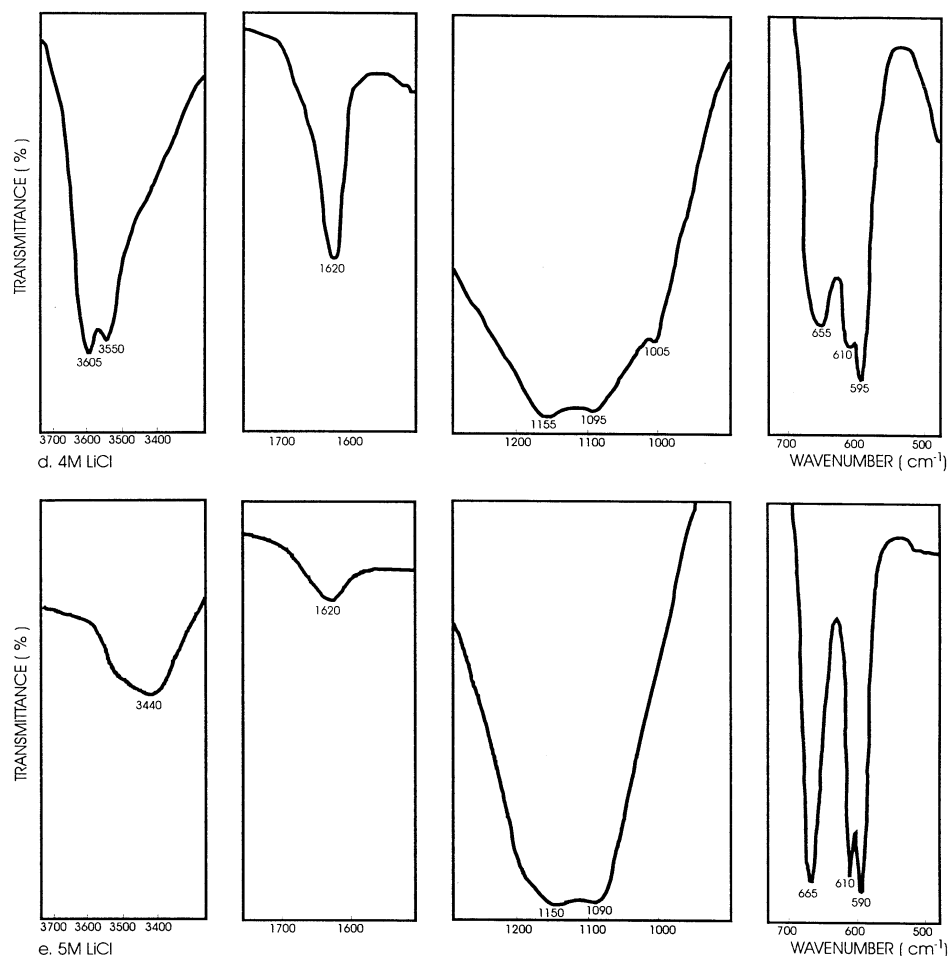


Fig. 1. IR-absorption spectra of the products: a. obtained in 1 M LiCl solution, b. obtained in 2 M LiCl solution, c. obtained in 3 M LiCl solution, d. obtained in 4 M LiCl solution, e. obtained in 5 M LiCl solution.

all other products have only an endothermic peak. The endothermic peak (at 166.5 °C) and the exothermic peak (at 353.4 °C) in the differential thermogram of the product obtained in 1 M LiCl solution belong, according to reference data,<sup>4,5,15</sup> to the differential thermogram of  $\beta$ -CaSO<sub>4</sub>·0.5H<sub>2</sub>O. This means that the product obtained in 1 M LiCl solution was the  $\beta$ -form of the hemihydrate. The endothermic peaks in the differential thermograms of the products prepared in 2 M, 3 M and 4 M LiCl solutions (at 159.5, 161.8 and 158.5 °C) are not followed by exothermic peaks, as in the case of  $\beta$ -CaSO<sub>4</sub>·0.5H<sub>2</sub>O, which is characteristic of  $\alpha$ -CaSO<sub>4</sub>·0.5H<sub>2</sub>O, according to reference data.<sup>16,17</sup> Consequently, the hemihydrate (identified by X-ray and infrared spectroscopic analyses) obtained in 2 M, 3 M and 4 M LiCl



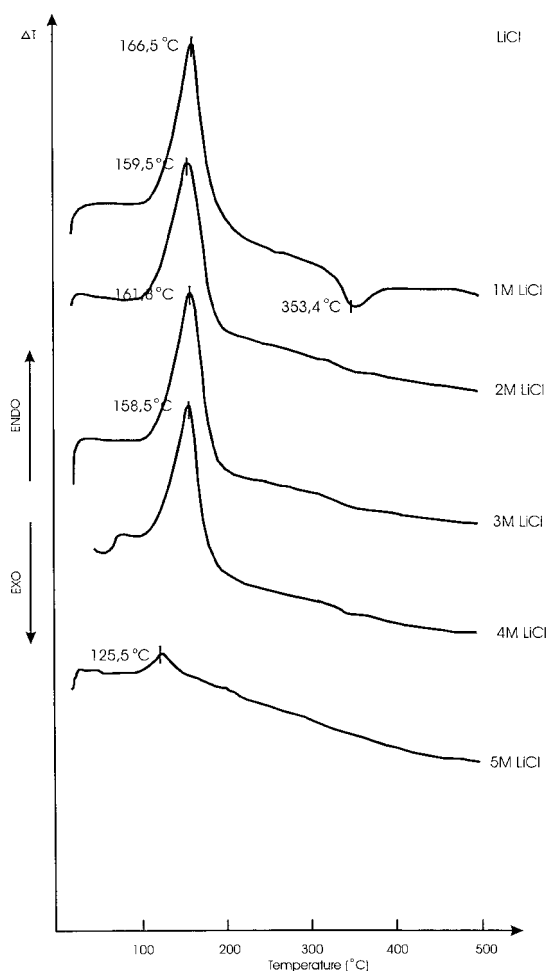


Fig. 2. DTA thermograms of the obtained products.

solutions was the  $\alpha$ -form. The endothermic peak in the differential thermogram of the product obtained in 5 M LiCl solution is weak and at a lower temperature (125.5 °C, Fig. 2). It corresponds to the removal of residual (zeolitic) water in the soluble anhydrite ( $\gamma$ -CaSO<sub>4</sub>), which was detected by infrared analysis (Fig. 1e).

The results of TGA are given in Table III.

The mass losses of the products prepared in 1 M, 2 M and 3 M solutions (Table III), which correspond to the endothermic reaction of dehydration of CaSO<sub>4</sub>·0.5 H<sub>2</sub>O, are in good agreement with the theoretical water content in the hemihydrate (6.2 %). The mass loss of the product prepared in 4 M LiCl solution (Table III) is considerably lower than the theoretical value for the hemihydrate because this product, in addition to CaSO<sub>4</sub>·0.5H<sub>2</sub>O, also contained CaSO<sub>4</sub>, as was primarily identified by X-ray and infrared spectroscopic analyses. Finally, the mass loss of the

product prepared in 5 M LiCl solution (Table III) is in accordance with reference data<sup>12</sup> concerning the amount of residual water (from 0.25 to 1 %) in soluble anhydrite ( $\gamma$ -anhydrite).

TABLE III. DTA and TG data – endothermic peaks and mass losses

Product	Endothermic peak/°C	Mass loss/%
in 1 M LiCl	166.5	6.40
in 2 M LiCl	159.5	6.17
in 3 M LiCl	161.8	6.04
in 4 M LiCl	158.5	4.19
in 5 M LiCl	125.5	0.88

Table IV gives the microscopical examination data of the products discussed in this paper.

TABLE IV. Microscopic examination data for the obtained crystals

Sample	Crystal characteristics (shape, size, <i>etc.</i> )
Product obtained in 1 M LiCl	White irregular, porous, brittle, tabular microcrystal aggregates. (Sample size and shape like those of raw selenite grain)
Product obtained in 2 M LiCl	Single needle-shaped crystals, colourless, clear, average length 108 $\mu\text{m}$
Product obtained in 3 M LiCl	Single needle-shaped crystals, colourless, clear, average length 114 $\mu\text{m}$
Product obtained in 4 M LiCl	Single needle-shaped crystals, colourless, unequal in length which varies from 27 $\mu\text{m}$ to 162 $\mu\text{m}$
Product obtained in 5 M LiCl	Single needle-shaped crystals, colourless, very small - average length 14 $\mu\text{m}$

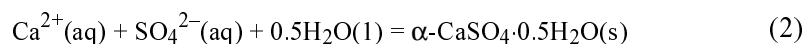
As indicated in Table IV, the crystals produced in 1 M LiCl solution differ from the crystals formed in the higher concentration LiCl solutions, which can be related to the different mechanisms of crystal formation in the different concentration of LiCl in the solutions. Namely, in 1 M LiCl solution the dehydration of selenite takes place in the solid phase and consequently irregular microcrystal aggregates of hemihydrate, like those of raw selenite, form, according to:



Higher concentration of LiCl (2 M and 3 M) in the solutions provide conditions, by higher selenite dissolution, for crystallization of single needle-shaped crystals from the solution, which are the  $\alpha$ -form of the hemihydrate ( $\alpha$ - $\text{CaSO}_4 \cdot 0.5$

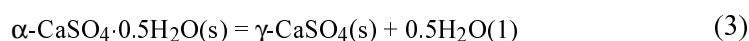


H<sub>2</sub>O), according to the literature.<sup>3,4</sup> Their formation can be represented by the equation:



These results of the microscopic examination of the products prepared in 1 M, 2 M and 3 M LiCl solutions are congruous with the DTA data given above.

The single needle-shaped crystals produced in 4 M LiCl solution are of unequal length (Table IV) which may be explained by their being a mixture of two different compounds:  $\alpha\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  and  $\gamma\text{-CaSO}_4$ , as was detected by IR and X-ray analyses. This means that the  $\alpha$ -hemihydrate partially dehydrates in 4 M LiCl solution giving the  $\gamma$ -anhydrite, according to:



The microscopic examination data of the product prepared in 5 M LiCl solution indicate that the reaction (3) occurred to completion in this solution, giving very small needle-shaped crystals of  $\gamma$ -anhydrite (Table IV).

The occurrence of reaction (3), partially in 4 M LiCl solution and completely in 5 M LiCl solution, can be explained by the selenite hydrothermal treatment time being longer than was necessary for hemihydrate production in these solutions.

#### CONCLUSION

During selenite hydrothermal treatment in LiCl solutions of different concentration (1 M, 2 M, 3 M, 4 M and 5 M), a reaction between LiCl and CaSO<sub>4</sub> (like the one which occurred in KCl solutions giving K<sub>2</sub>SO<sub>4</sub>·5CaSO<sub>4</sub>·H<sub>2</sub>O<sup>7</sup>) did not occur. Consequently, the studied LiCl solutions are favourable for selenite hydrothermal treatment and by an adequate choice of process parameters (concentration of solution and time of treatment) different products of selenite dehydration can be obtained ( $\alpha\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ,  $\beta\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  and  $\gamma\text{-CaSO}_4$ ).

#### ИЗВОД

##### ПРОДУКТИ ХИДРОТЕРМИЧКЕ ОБРАДЕ СЕЛЕНИТА У РАСТВОРИМА ЛИТИЈУМ-ХЛОРИДА

СЛОБОДАНКА МАРИНКОВИЋ, АЛЕКСАНДРА КОСТИЋ-ПУЛЕК и МИРЈАНА ЂУРИЧИЋ\*

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Селенит је исууваан у растворима LiCl различите концентрације (1 М, 2 М, 3 М, 4 М и 5 М) на њиховој температури кључања и атмосферском притиску. Продукти су испитани рендгенском анализом, квалитативном инфрацрвеном анализом, диференцијалном термичком анализом, термогравиметријском анализом и микроскопским прегледом. Продукт добијен у 1 М LiCl раствору био је  $\beta$ -облик полихидрата калцијум-сулфата ( $\beta\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ). У концентрованијим растворима LiCl, 2 М и 3 М, дошло је до обра-

зовања  $\alpha$ -облика полихидрата калцијум-сулфата ( $\alpha$ -CaSO<sub>4</sub>·0,5H<sub>2</sub>O). Продукт добијен у 4 М LiCl раствору представљао је смешу две супстанце:  $\alpha$ -облика полихидрата калцијум-сулфата и  $\gamma$ -облика калцијум-сулфата ( $\gamma$ -CaSO<sub>4</sub>). И на крају у 5 М раствору LiCl образовао се  $\gamma$ -облик калцијум-сулфата, или  $\gamma$ -анхидрит.

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