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PHASE DIAGRAM FOR THE TERNARY SYSTEM $LiCl–CaCl_2–CaCrO_4$*

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ABSTRACT

The phase diagram for the system $LiCl–CaCl_2–CaCrO_4$ has been studied using differential thermal analysis. $LiCl–CaCl_2–CaCrO_4$ has been shown by X-ray diffraction to be a stable, diagonal section of the Li, Ca//Cl, CrO_4 reciprocal ternary system. The three binary systems are: $LiCl–CaCl_2$ which exhibits a double salt ($LiCaCl_3$), which decomposes without melting at 439°C and a eutectic at 36.3 mole % $CaCl_2$ (m.p. 487°C); $CaCl_2–CaCrO_4$ which shows a eutectic at 23.4 mole % $CaCrO_4$ (m.p. 660°C); and $LiCl–CaCrO_4$ with a eutectic at 14.3 mole % $CaCrO_4$ (m.p. 538°C).

In the ternary system, a eutectic exists at 63.2 mole % LiCl–32.9% $CaCl_2$–3.9% $CaCrO_4$ (m.p. 479°C). In addition, a four-phase equilibrium, involving all solid phases, exists at nearly all compositions at 435°C.

Isotherms are shown for the liquidus surface (primary crystallization) and for the secondary crystallization surface. Isothermal and vertical sections through the ternary phase diagram are shown.

INTRODUCTION

Thermal cells (voltaic cells employing a molten salt electrolyte) frequently employ the electrochemical cell system[1]: $Ca/LiCl–KCl–CaCrO_4/Fe$. At the elevated internal temperatures (500 to 600°C) attained in thermal cells, the Ca anode will react chemically[2] with the LiCl to form $CaCl_2$. During the course of this reaction the salt system $LiCl–KCl–CaCl_2–CaCrO_4$ exists, and a knowledge of the phase relationships in that system is important to thermal cell technology. The system $LiCl–CaCl_2–CaCrO_4$ is one of four ternary systems which make up the overall salt mixture. The other three ternaries have been previously studied: the $LiCl–KCl–CaCl_2$ phase diagram has been reported by Plyushchev and Kovalev[3], and the other two systems, $LiCl–KCl–CaCrO_4$ and $KCl–CaCl_2–CaCrO_4$, have been studied in this laboratory[4,5].

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$LiCl-CaCl_2-CaCrO_4$ is a stable diagonal section of the Li, Ca//Cl, CrO_4 reciprocal ternary system. The three binary systems, $LiCl-CaCl_2$, $LiCl-CaCrO_4$, and $CaCl_2-CaCrO_4$, have been previously investigated. The phase diagram for $LiCl-CaCrO_4$ was reported as part of a general investigation of the $LiCl-KCl-CaCrO_4$ ternary system[4], and the $CaCl_2-CaCrO_4$ binary phase diagram was also reported recently[6]. The $LiCl-CaCl_2$ binary system has been studied several times, most recently by Golubeva and Bergman[7]. Because of variances in previously reported data, the $LiCl-CaCl_2$ phase diagram was redetermined in the present work.

EXPERIMENTAL

The samples used in this investigation were ultra-pure anhydrous $CaCl_2$ (99.95%) from Research Organic/Inorganic Chemical Corporation, Sun Valley, Calif.; high-purity $CaCrO_4$ (assay 99.85%) prepared from reagent grade $CaCO_3$ and Na_2CrO_4 using a method previously described[4]; and reagent grade LiCl. LiCl and $CaCl_2$ were vacuum dried for 16 h at 120°C, and $CaCrO_4$ was vacuum dried at 400°C for 4 h.

Phase change data were determined by DTA using a technique previously described in detail[5]. The DTA samples were prepared in a controlled atmosphere "dry room" in a manner described in the same reference. Data were obtained for mixtures which had a liquidus temperature below 800°C. Above that temperature thermal decomposition of $CaCrO_4$ began to occur.

A few samples of selected composition were analyzed using X-ray diffraction. The X-ray diffraction results were used to confirm the stability of the $LiCl-CaCl_2-CaCrO_4$ system.

RESULTS

$CaCl_2-CaCrO_4$ binary system

The phase diagram for this system has been previously reported[6] and is shown in Fig. 1. This diagram shows a simple eutectic system with a eutectic composition of 23.4 mole % $CaCrO_4$ which melts at 660°C.

$LiCl-CaCrO_4$ binary system

LiCl and $CaCrO_4$ form a simple eutectic melting at 538°C with a eutectic composition of 14.3 mole % $CaCrO_4$. This diagram, which has been previously published[4], is shown in Fig. 2.

$LiCl-CaCl_2$ binary system

The diagram for this system has been redetermined and is shown in Fig. 3. A double salt ($LiCaCl_3$) forms at 50 mole % $CaCl_2$ and is stable at temperatures below 439°C. The $LiCaCl_3$ decomposes without melting at 439°C to form LiCl and $CaCl_2$. A eutectic exists at 36.3 mole % $CaCl_2$ with a melting point of 487°C.

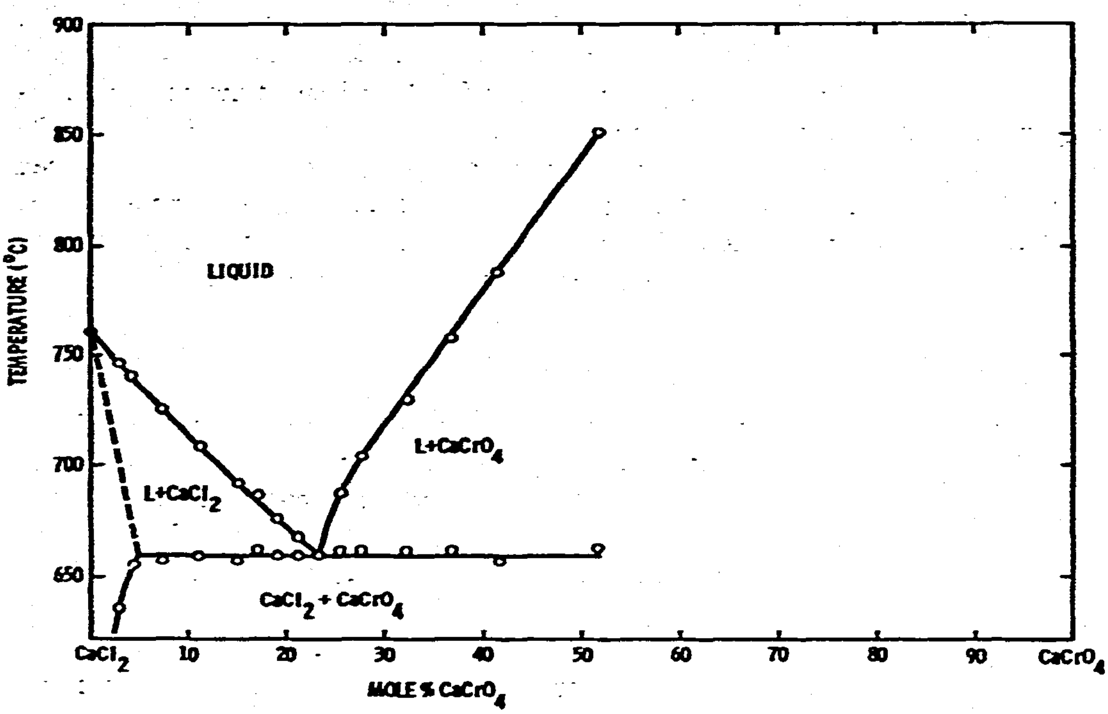


Fig. 1. $CaCl_2$–$CaCrO_4$ binary phase diagram.

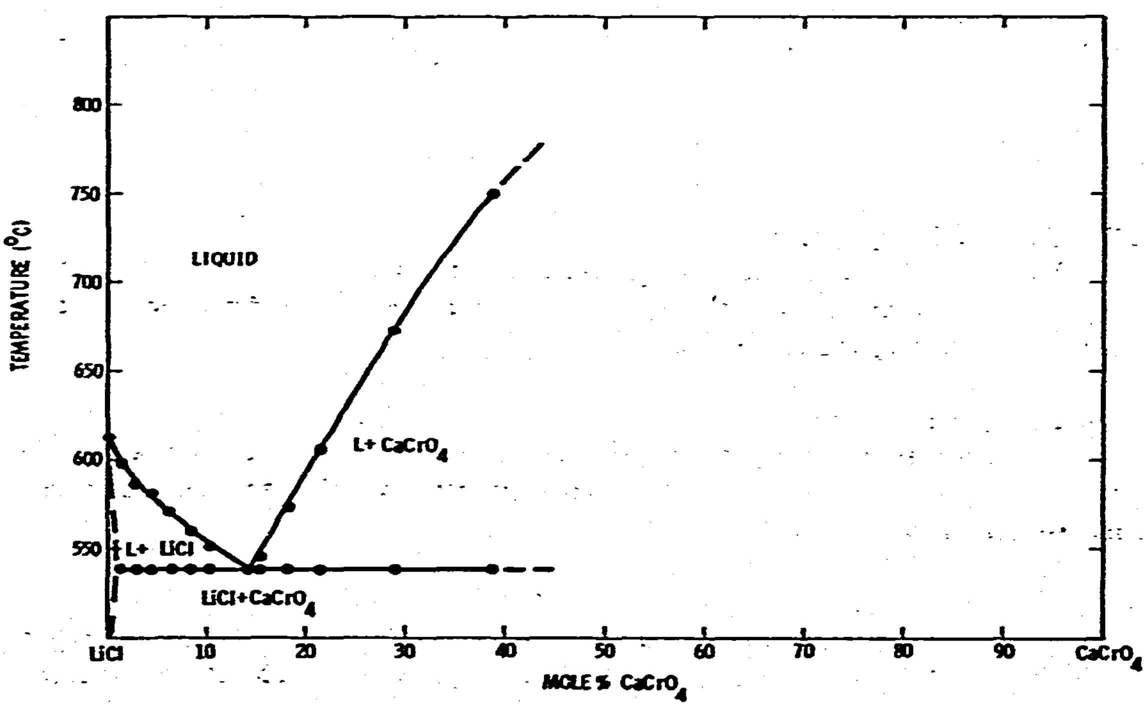


Fig. 2. $LiCl$–$CaCrO_4$ binary phase diagram.

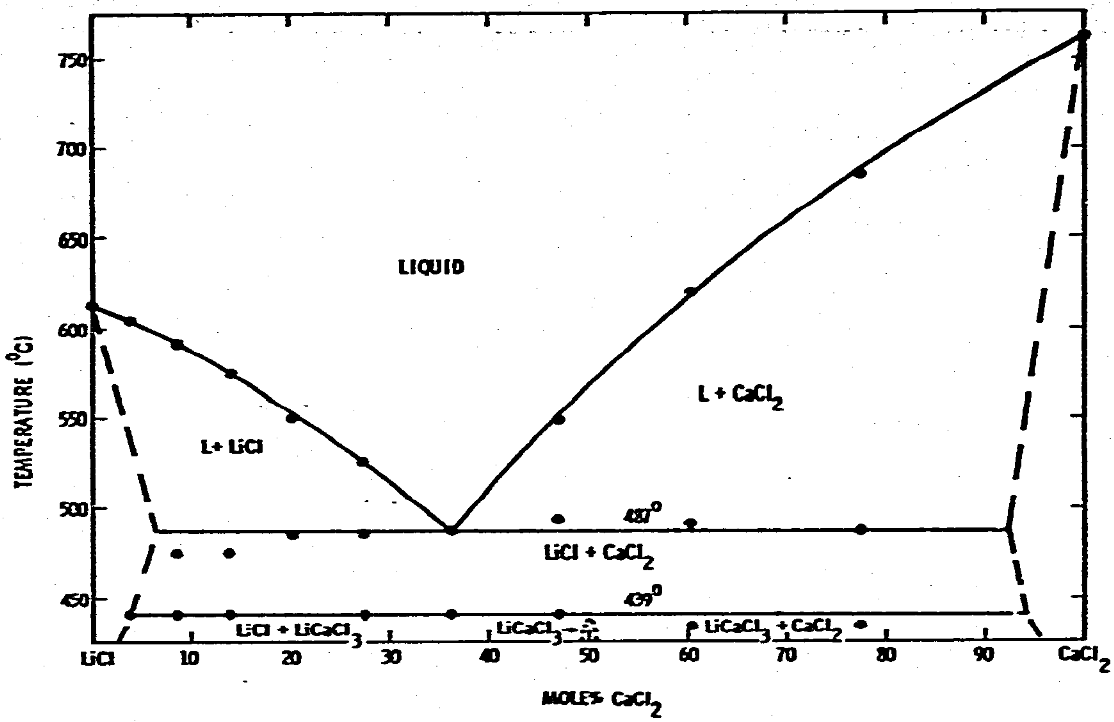


Fig. 3. LiCl–$CaCl_2$ binary phase diagram.

LiCl–$CaCl_2$–$CaCrO_4$ ternary system

The DTA data obtained for the LiCl–$CaCl_2$–$CaCrO_4$ ternary system are shown in Table 1. In this table the temperatures shown are those where the designated phase disappears on heating. The reactions for the disappearance of the four solid phases can be written as follows:

$$\alpha\,(\mathrm{LiCl}) \rightleftharpoons \mathrm{L}$$
$$\beta\,(\mathrm{CaCl_2}) \rightleftharpoons \mathrm{L}$$
$$\gamma\,(\mathrm{CaCrO_4}) \rightleftharpoons \mathrm{L}$$
$$\delta\,(\mathrm{LiCaCl_3}) \rightleftharpoons \alpha+\beta$$

A few representative DTA curves are illustrated in Fig. 4. These particular curves show a variety of phase transformations. Curve (a) is for a composition such that, on heating, the decomposition of the δ phase ($LiCaCl_3$) is observed at 435°C; the disappearance of the α crystals (LiCl) is noted at 479°C; the β phase ($CaCl_2$) is liquid above 552°C; and finally the γ phase ($CaCrO_4$) completely disappears at 761°C. Curve (b) illustrates a mixture in which the β ($CaCl_2$) and γ ($CaCrO_4$) phases become totally liquid at the same temperature (610°C). The decomposition of the δ phase ($LiCaCl_3$) and the transformation of the α phase (LiCl) to liquid occur at 435 and 479°C, respectively, just as they do in curves (a) and (c). Curve (c) is for the ternary eutectic composition and shows the disappearance of the α (LiCl), β ($CaCl_2$) and γ ($CaCrO_4$) phases at a single temperature (479°C).

TABLE 1

DTA DATA FOR PHASE DIAGRAM FOR $LiCl$–$CaCl_2$–$CaCrO_4$ SYSTEM

Mole %			*Temperature of phase disappearance (°C)*			
LiCl	*CaCl₂*	*CaCrO₄*	α (*LiCl*)	β (*CaCl₂*)	γ (*CaCrO₄*)	δ (*LiCaCl₃*)
100	—	—	614			
95.9	4.1	—	605			439
91.3	8.7	—	590	475		439
85.9	14.1	—	574	475		439
79.7	20.3	—	550	487		439
72.4	27.6	—	525	485		438
63.6	36.4	—	487	487		439
52.9	47.1	—	496	548		439
39.6	60.4	—	490	618		432
22.5	77.5	—	486	686		432
—	100	—		759		
98.6	—	1.4	600		538	
96.5	2.0	1.5	599		532	
91.8	6.6	1.6	587	465	520	438
86.5	11.8	1.7	572	474	505	438
80.3	17.9	1.8	552	474	490	439
72.9	25.1	2.0	523	477	483	439
64.1	33.7	2.2	485	479	481	439
53.4	44.2	2.4	479	530	488	438
40.0	57.3	2.7	479	594	492	438
22.8	74.1	3.1	465	667	523	437
—	96.4	3.6		740	660	
97.1	—	2.9	589		538	
92.5	4.4	3.1	583	455	536	438
87.1	9.5	3.4	570	470	525	438
80.9	15.4	3.7	550	477	512	438
73.5	22.5	4.0	521	479	499	438
64.7	30.9	4.4	492	479	484	437
53.9	41.2	4.9	481	499	491	437
40.4	54.1	5.5	481	574	526	436
23.1	70.6	6.3	476	645	575	434
—	92.7	7.3		725	660	
95.4	—	4.6	578		538	
93.1	2.2	4.7	579		538	
87.7	7.2	5.1	568	469	538	437
81.5	13.0	5.5	548	477	528	434
74.1	19.8	6.1	523	479	514	436
65.3	28.0	6.7	495	480	536	435
54.5	38.1	7.4	481	498	547	435
40.9	50.8	8.3	480	556	545	434
23.4	67.1	9.5	476	632	591	435
—	88.9	11.1		708	660	
93.6	—	6.4	568		538	
88.3	4.8	6.9	565	459	537	435
82.1	10.5	7.4	549	473	536	434
74.8	17.1	8.1	531	478	548	434

(*Table continued on p. 26*)

TABLE 1 (*continued*)

Mole %			Temperature of phase disappearance (°C)			
LiCl	$CaCl_2$	$CaCrO_4$	α (LiCl)	β ($CaCl_2$)	γ ($CaCrO_4$)	δ ($LiCaCl_3$)
65.9	25.2	8.9	501	481	558	434
55.0	35.0	10.0	481	490	569	434
41.4	47.4	11.2	481	547	578	436
23.7	63.4	12.9	479	612	602	436
—	84.9	15.1		693	660	
91.7	—	8.3	559		538	
89.0	2.4	8.6	556		542	
82.7	7.9	9.4	546	471	546	435
75.4	14.4	10.2	528	479	572	436
66.5	22.2	11.3	505	481	593	436
55.6	31.8	12.6	481	481	603	435
41.8	44.0	14.2	481	541	616	435
24.0	59.7	16.3	479	603	632	436
—	80.8	19.2		670	660	
89.6	—	10.4	552		538	
83.4	5.3	11.3	547	465	547	436
76.0	11.6	12.4	536	473	583	436
67.1	19.2	13.7	517	481	612	436
56.1	28.6	15.3	485	479	625	434
42.3	40.4	17.3	480	524	640	436
24.4	55.8	19.8	476	593	651	432
—	76.6	23.4		660	660	
87.2	—	12.8	545		538	
84.0	2.7	13.3	538		562	
76.6	8.8	14.6	538	471	602	434
67.7	16.2	16.1	520	474	624	435
56.7	25.3	18.0	486	478	648	436
42.8	36.8	20.4	481	527	665	434
24.7	51.8	23.5	478	594	686	429
—	72.3	27.7		660	700	
84.7	—	15.3	538		546	
77.3	5.9	16.8	532	465	612	436
68.4	13.0	18.6	525	474	643	434
57.3	21.9	20.8	495	476	670	434
43.3	33.1	23.6	481	503	688	435
25.0	47.8	27.2	479	583	715	434
—	67.8	32.2		660	724	
81.8	—	18.2	538		572	
78.0	3.0	19.0	537		625	
69.0	9.9	21.1	536	470	666	437
57.9	18.5	23.6	507	477	692	434
43.9	29.3	26.8	481	481	713	437
25.4	43.6	31.0	478	574	736	434
—	63.2	36.8		660	754	
78.6	—	21.4	538		604	
69.7	6.6	23.7	532	469	672	435
58.6	14.9	26.5	518	472	703	435
44.4	25.4	30.2	477	477	732	434
25.7	39.3	35.0	479	567	758	434

TABLE 1 (*continued*)

Mole %			*Temperature of phase disappearance (°C)*			
LiCl	$CaCl_2$	$CaCrO_4$	α ($LiCl$)	β ($CaCl_2$)	γ ($CaCrO_4$)	δ ($LiCaCl_3$)
—	58.4	41.6		660	784	
75.1	—	24.9	538		639	
70.4	3.3	26.3	532	450	686	434
59.2	11.3	29.5	525	470	722	436
44.9	21.5	33.6	483	478	749	434
26.1	34.9	39.0	474	548	778	425
—	53.5	46.5		660	>800	
71.1	—	28.9	538		673	
59.9	7.6	32.5	522	463	734	432
45.5	17.4	37.1	472	472	776	436
26.5	30.3	43.2	477	541	>800	434
66.5	—	33.5	538		710	
60.5	3.9	35.6	535	452	755	436
46.1	13.2	40.7	512	470	792	435
61.2	—	38.8	538		749	
46.7	8.9	44.4	525	469	>800	434
63.2	32.9	3.9	479	479	479	435
20.0	65.0	15.0	479	610	610	435
28.5	36.5	35.0	479	552	761	435

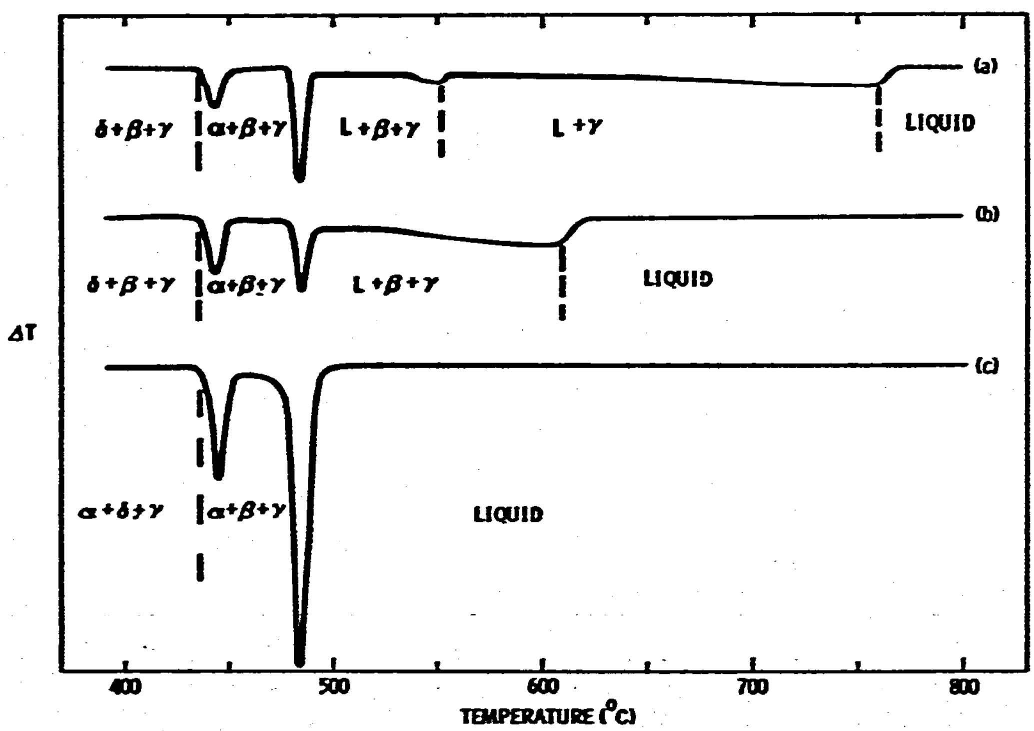


Fig. 4. Typical DTA curves for the system $LiCl–CaCl_2–CaCrO_4$. (a) 28.5% LiCl–36.5% $CaCl_2$–35.0% $CaCrO_4$; (b) 20.0% LiCl–65.0% $CaCl_2$–15.0% $CaCrO_4$; (c) 63.2% LiCl–32.9% $CaCl_2$–3.9% $CaCrO_4$.

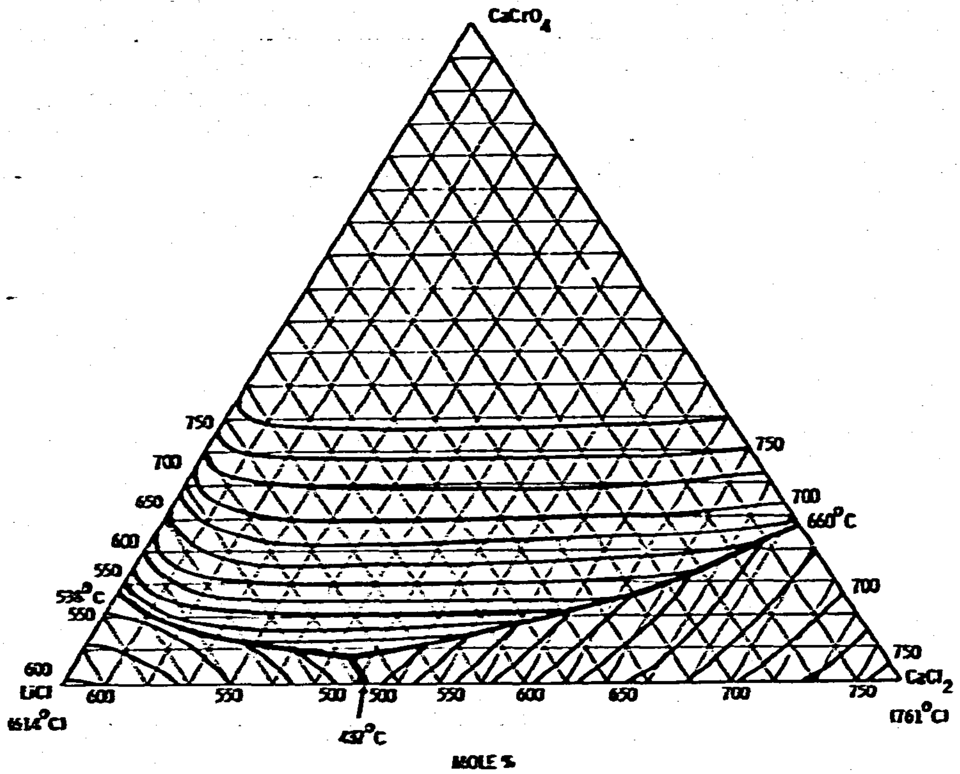


Fig. 5. An isothermal representation of the liquidus surface for the LiCl–$CaCl_2$–$CaCrO_4$ system.

The phase diagram for the LiCl–$CaCl_2$–$CaCrO_4$ system is shown with the isothermal representation of the liquidus surface in Fig. 5. The ternary eutectic that is seen at 63.2 mole % LiCl–32.9% $CaCl_2$–3.9% $CaCrO_4$ has a melting point of 479 °C. In Fig. 6 the three-phase lines connecting the three binary eutectics with the ternary eutectic are observed. The arrows represent the direction of decreasing temperature.

An isothermal representation of the secondary crystallization surface is shown in Fig. 7. At temperatures above this surface, but below the liquidus surface (Fig. 5), both a liquid phase and one solid phase will exist. The particular solid phase present will depend on the composition of the mixture.

TABLE 2

SUMMARY OF DATA FROM THE LiCl–$CaCl_2$–$CaCrO_4$ PHASE DIAGRAM

System	*Significant point*
LiCl–$CaCl_2$	Compound at 50.0 mole % $CaCl_2$, decomposes at 439 °C
	Eutectic at 36.3 mole % $CaCl_2$, m.p. 487 °C
LiCl–$CaCrO_4$	Eutectic at 14.3 mole % $CaCrO_4$, m.p. 538 °C
$CaCl_2$–$CaCrO_4$	Eutectic at 23.4 mole % $CaCrO_4$, m.p. 660 °C
LiCl–$CaCl_2$–$CaCrO_4$	Eutectic at 63.2 mole % LiCl–32.9% $CaCl_2$–3.9% $CaCrO_4$, m.p. 479 °C
	Four-phase equilibrium at 435 °C

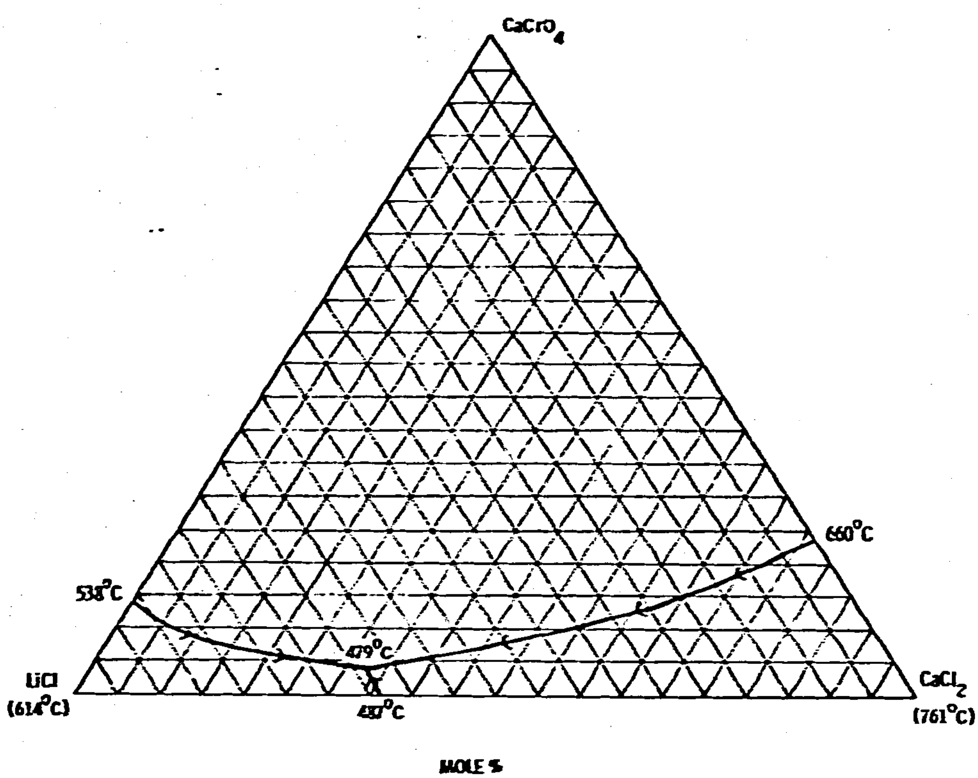


Fig. 6. The three-phase equilibrium lines for the LiCl–$CaCl_2$–$CaCrO_4$ system.

A summary of data from the LiCl–$CaCl_2$–$CaCrO_4$ phase diagram is shown in Table 2.

Examination of both vertical and isothermal sections through the phase diagram is useful in developing a more complete understanding of the diagram. Figures 8 and 9 are vertical sections in which the LiCl to $CaCl_2$ mole ratio is held constant. The section in Fig. 8 (LiCl to $CaCl_2$ ratio equal to 30/70) intersects the three-phase line connecting the $CaCl_2$–$CaCrO_4$ eutectic with the ternary eutectic. The section in Fig. 9 (LiCl to $CaCl_2$ ratio equal to 65/35) intersects two three-phase lines; one connecting the LiCl–$CaCrO_4$ binary eutectic with the ternary eutectic and the other connecting the LiCl–$CaCl_2$ binary eutectic with the ternary eutectic. Both sections intersect the four-phase equilibrium plane.

Figures 10–13 are vertical sections with constant $CaCrO_4$ concentrations ranging from 5 to 30 mole % $CaCrO_4$. Figures 14–19 are isothermal sections, each of which shows the phases present as a function of composition for one constant temperature. At 425°C (Fig. 14) all four solid phases are present, depending on composition. At 450°C (Fig. 15), it is observed that the δ phase ($LiCaCl_3$) has disappeared. At 500°C (Fig. 16) the appearance of a liquid phase is observed. Figures 17–19 show the diappearance of the various solid phases as temperature increases.

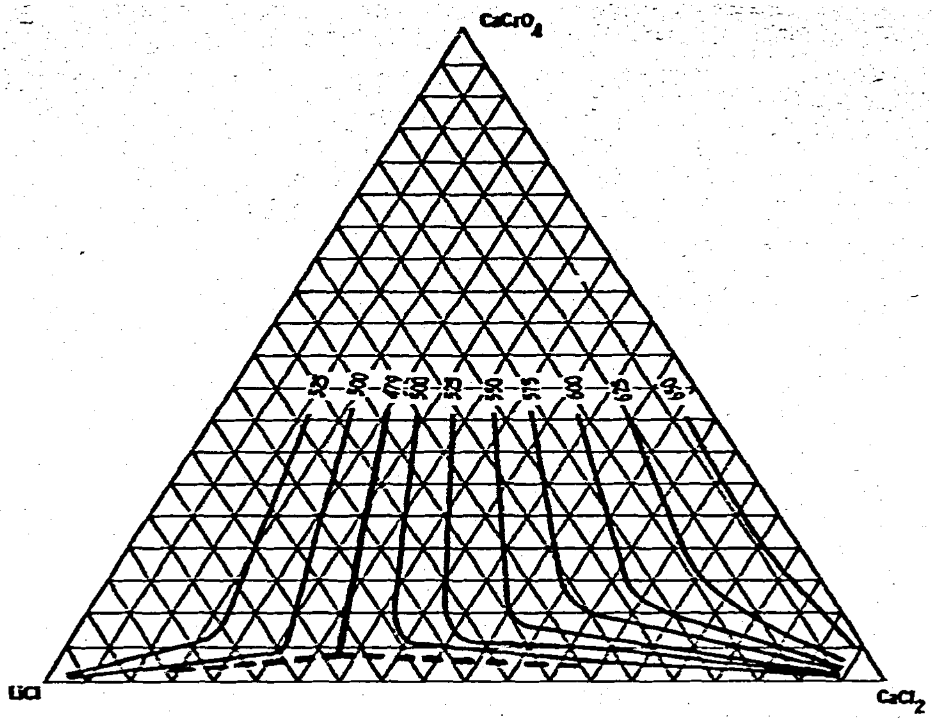


Fig. 7. An isothermal representation of the secondary crystallization surface for the $LiCl-CaCl_2-CaCrO_4$ system.

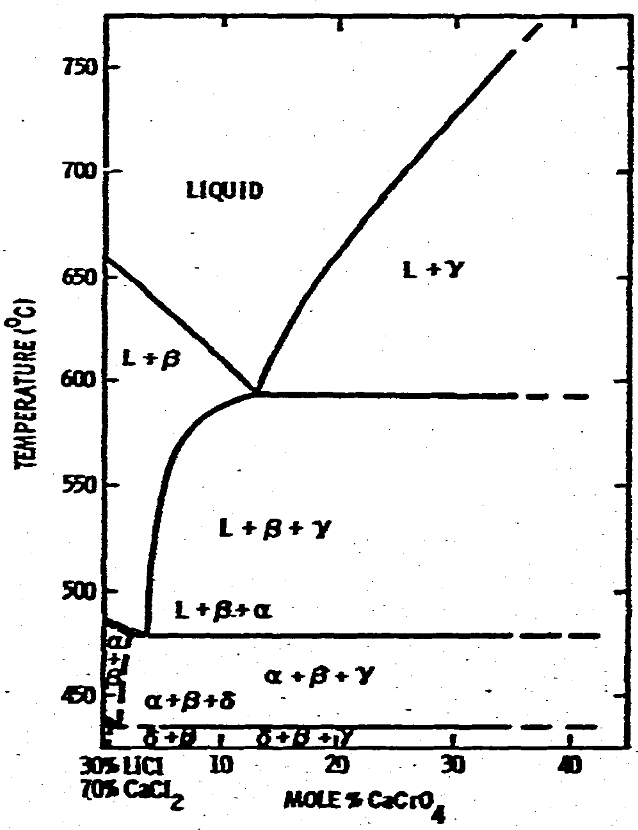


Fig. 8. A vertical section through the $LiCl-CaCl_2-CaCrO_4$ phase diagram ($LiCl$ to $CaCl_2$ mole ratio constant at 30/70).

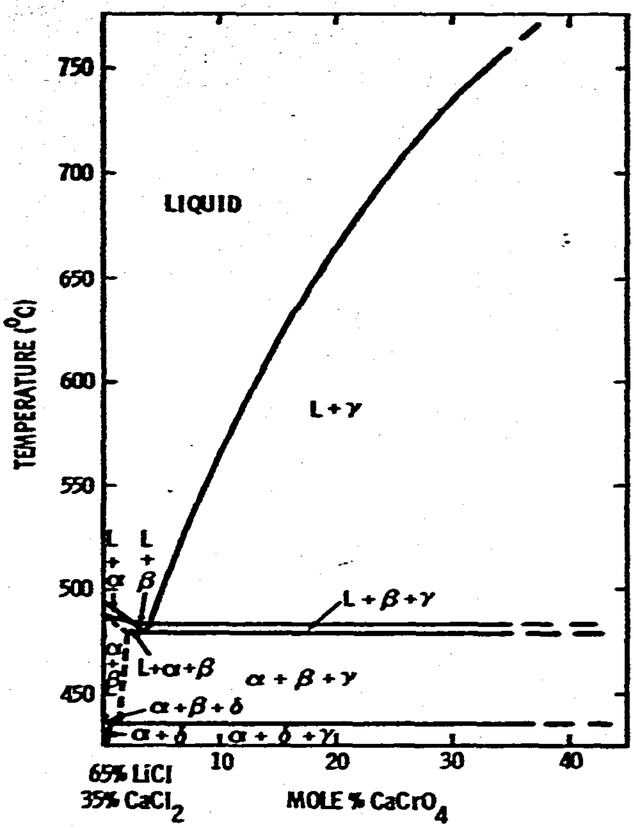


Fig. 9. A vertical section through the $LiCl$–$CaCl_2$–$CaCrO_4$ phase diagram ($LiCl$ to $CaCl_2$ mole ratio constant at 65/35).

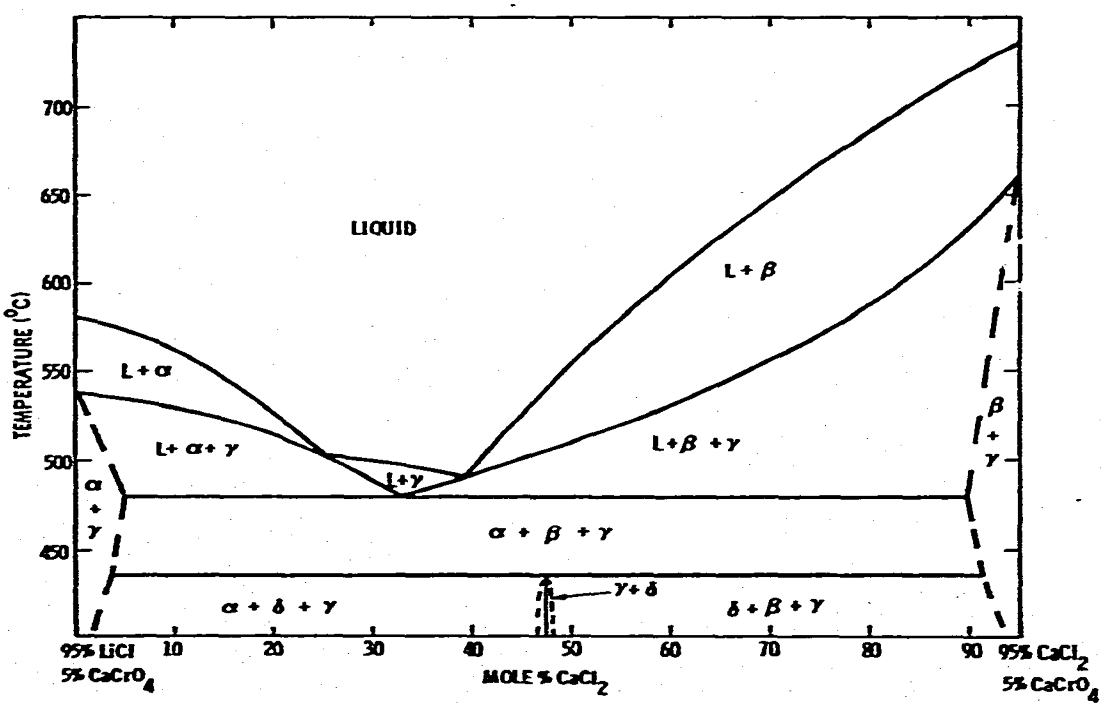


Fig. 10. Constant 5 mole % $CaCrO_4$ vertical section through the $LiCl$–$CaCl_2$–$CaCrO_4$ phase diagram.

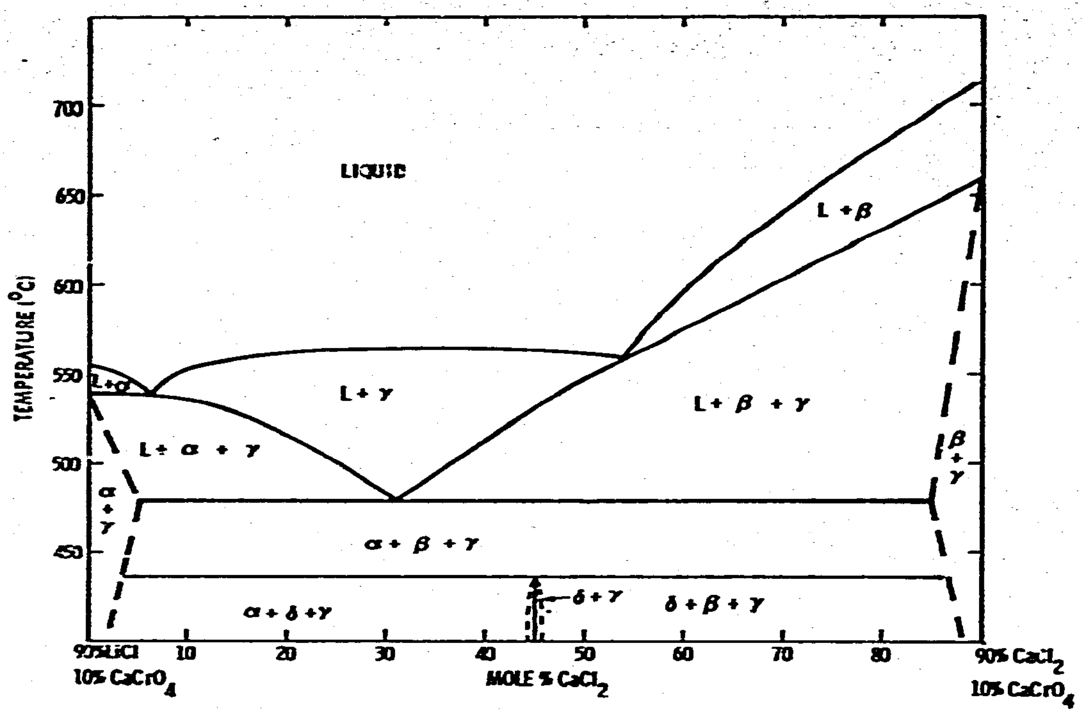


Fig. 11. Constant 10 mole % $CaCrO_4$ vertical section through the $LiCl$–$CaCl_2$–$CaCrO_4$ phase diagram.

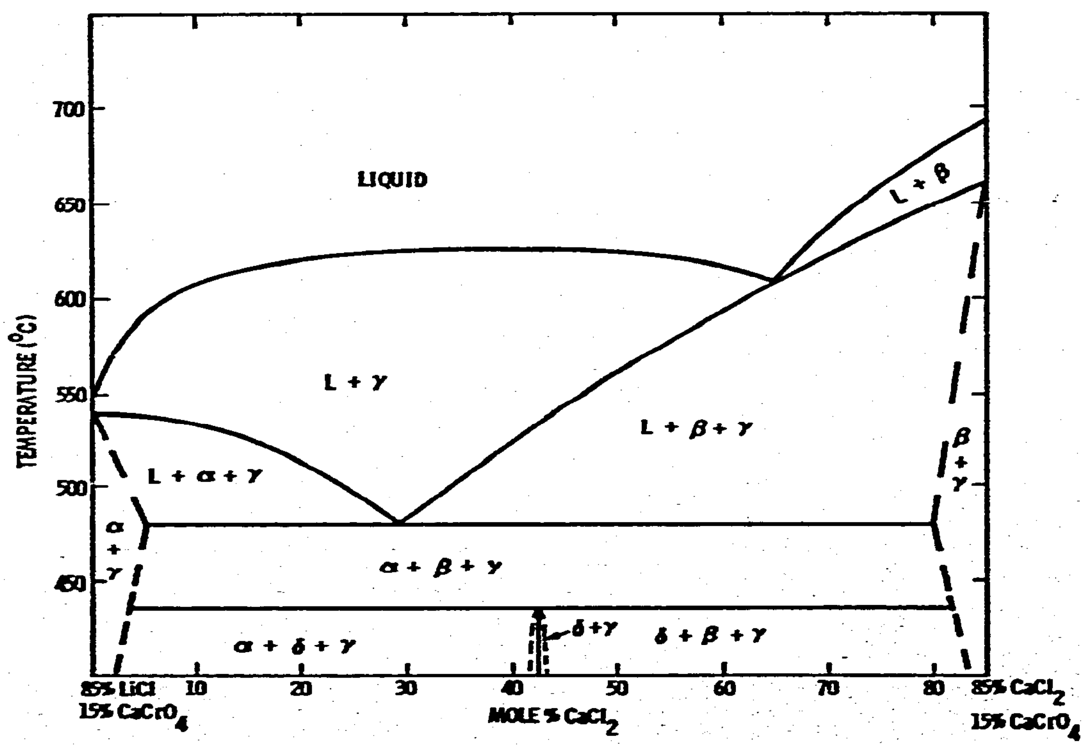


Fig. 12. Constant 15 mole % $CaCrO_4$ vertical section through the $LiCl$–$CaCl_2$–$CaCrO_4$ phase diagram.

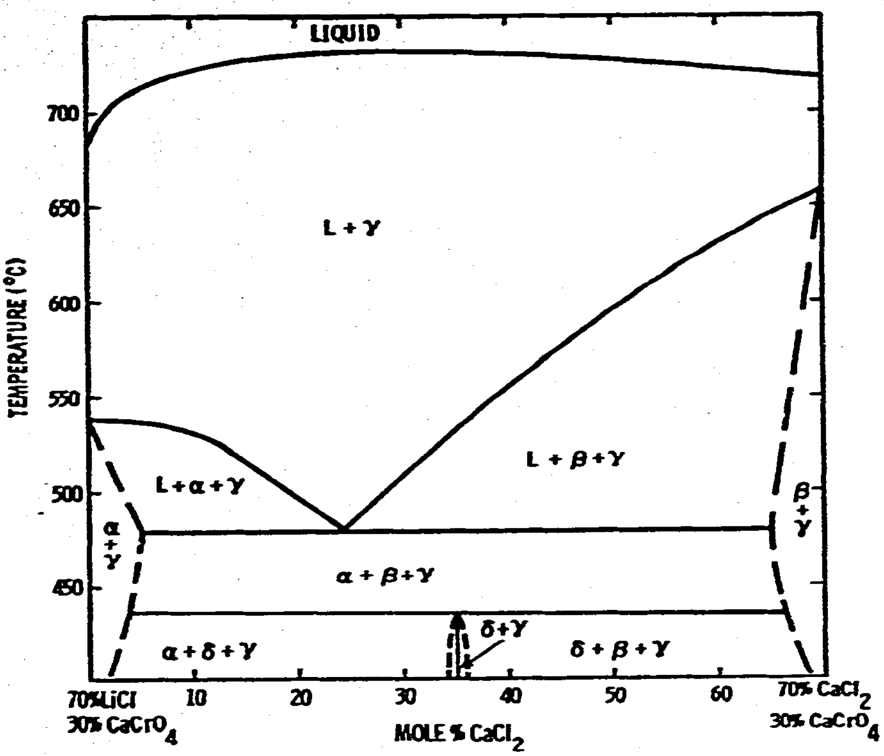


Fig. 13. Constant 30 mole % $CaCrO_4$ vertical section through the $LiCl$–$CaCl_2$–$CaCrO_4$ phase diagram.

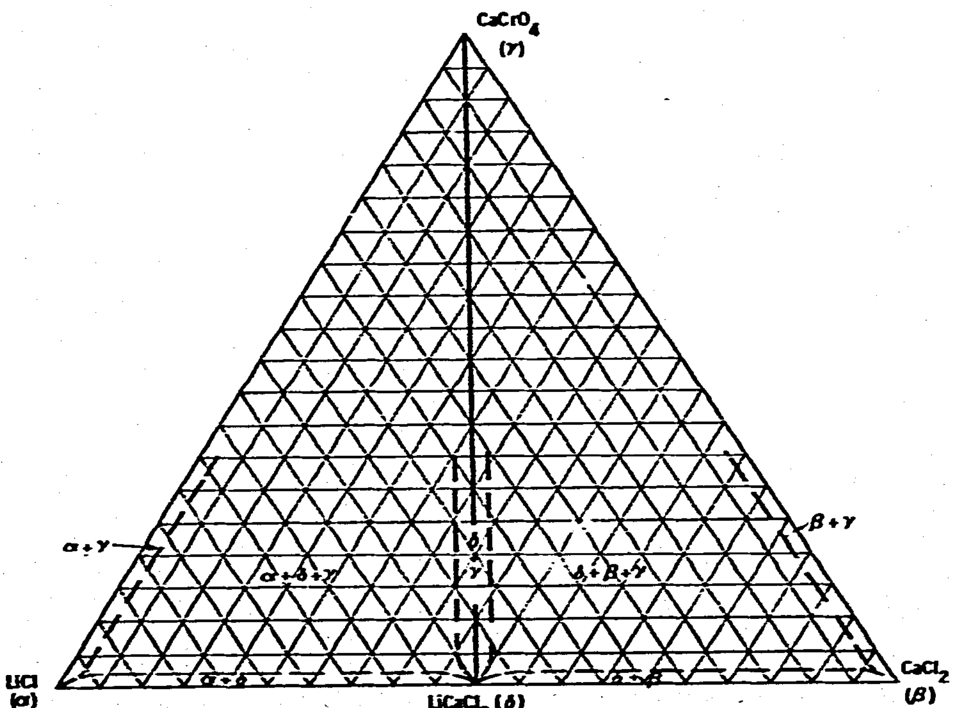


Fig. 14. The 425°C isothermal section through the $LiCl$–$CaCl_2$–$CaCrO_4$ phase diagram.

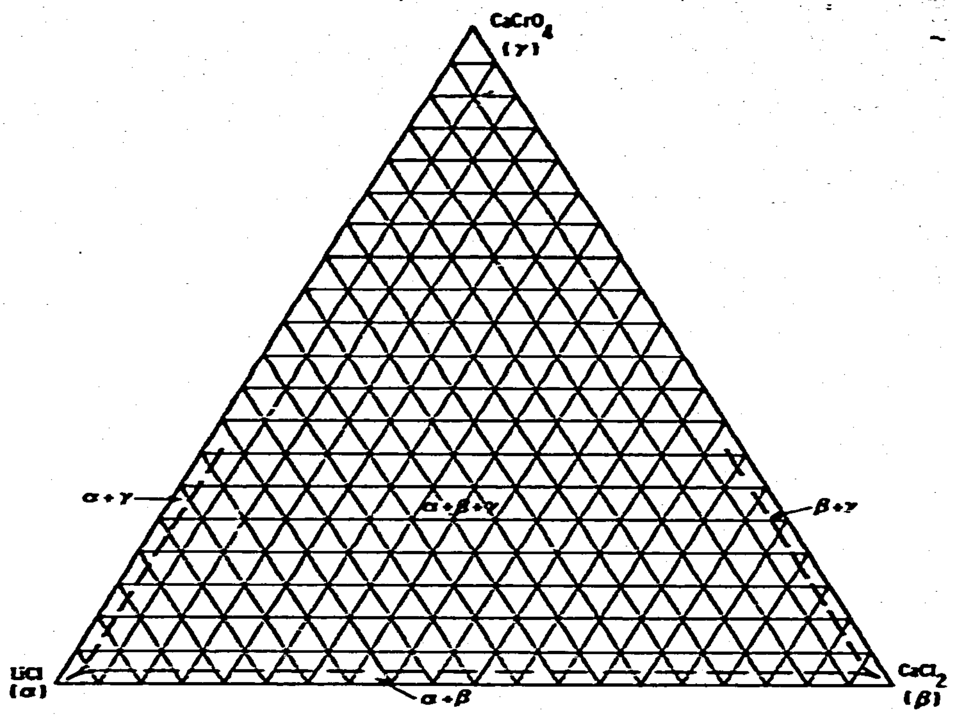


Fig. 15. The 450°C isothermal section through the LiCl–$CaCl_2$–$CaCrO_4$ phase diagram.

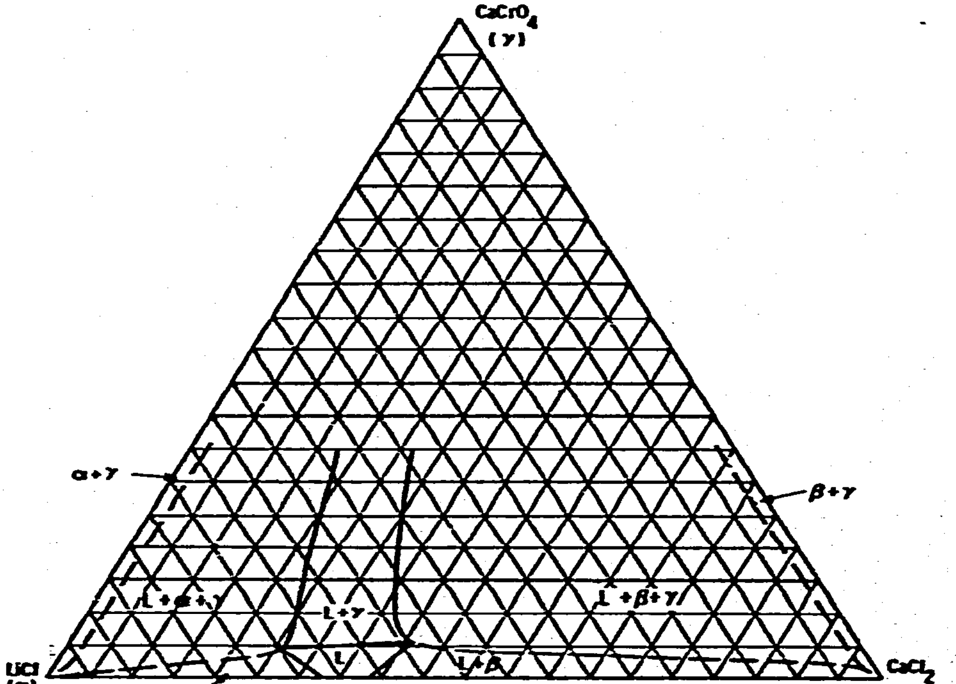


Fig. 16. The 500°C isothermal section through the LiCl–$CaCl_2$–$CaCrO_4$ phase diagram.

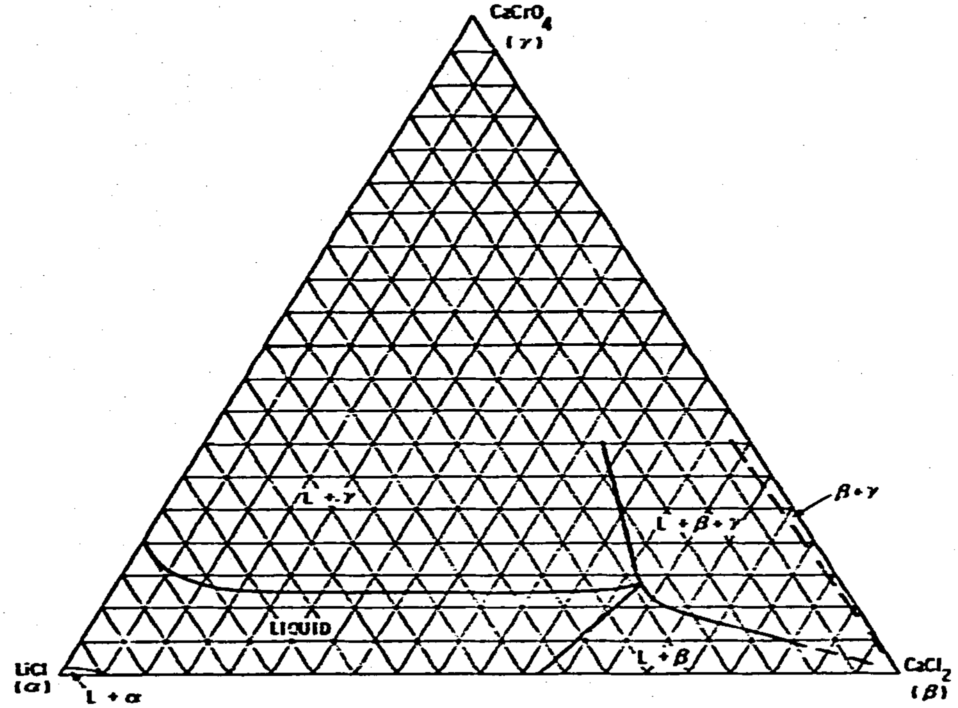
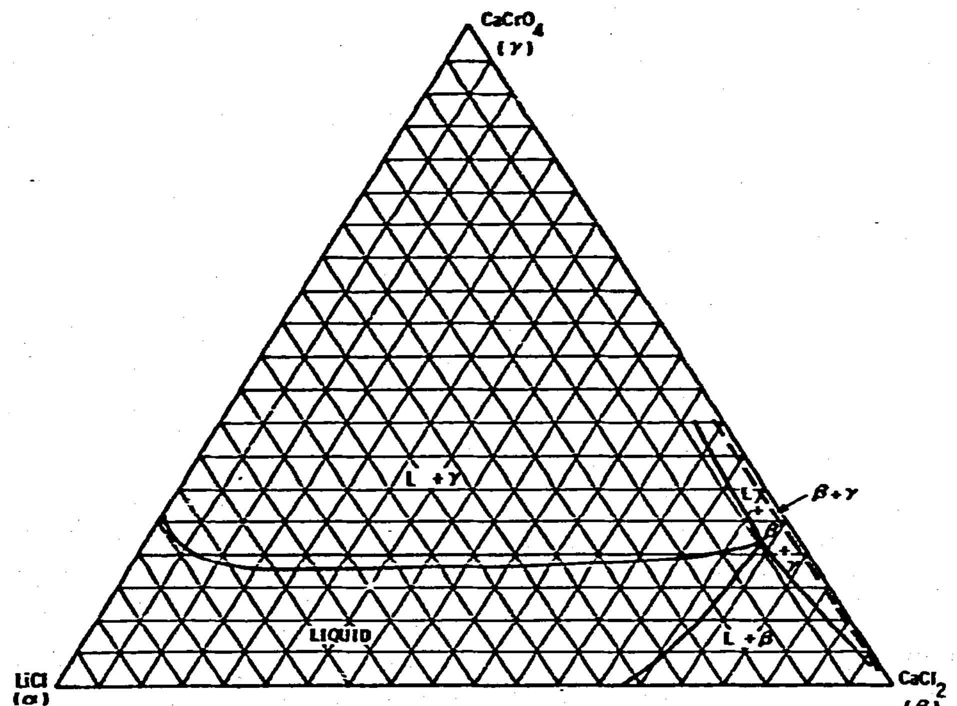


Fig. 17. The 600°C isothermal section through the $LiCl$–$CaCl_2$–$CaCrO_4$ phase diagram.



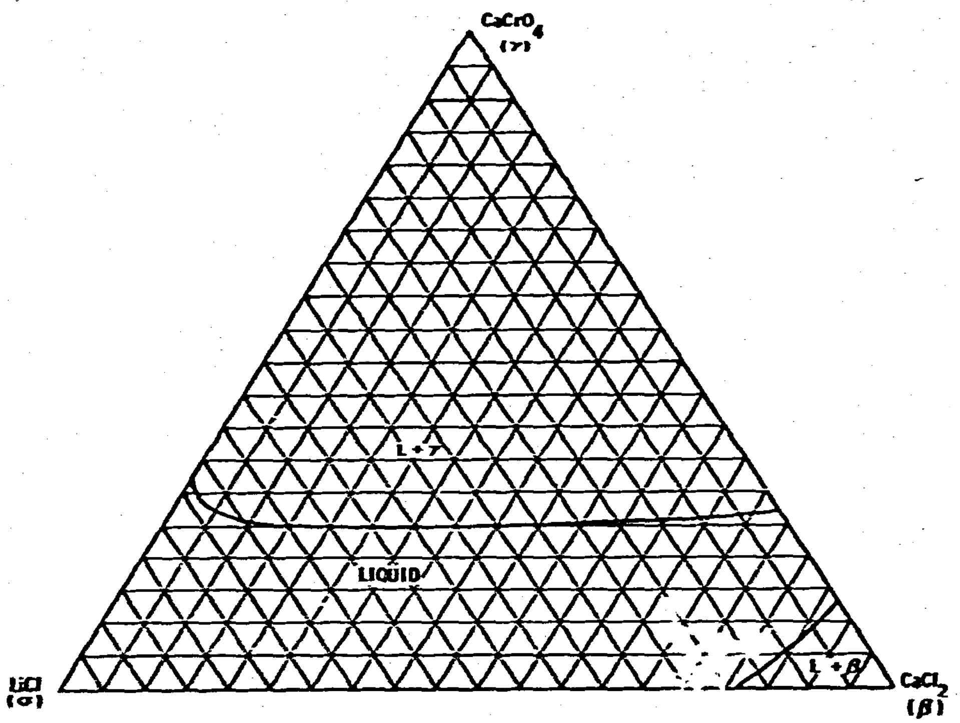


Fig. 19. The 700 °C isothermal section through the $LiCl-CaCl_2-CaCrO_4$ phase diagram.

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