

## The Phase Diagram of the System $\text{Li}_2\text{CrO}_4\text{-K}_2\text{CrO}_4$

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The  $\text{Li}_2\text{CrO}_4\text{-K}_2\text{CrO}_4$  phase diagram was determined by using differential thermal analyses with confirmation by high-temperature X-ray diffraction. The outstanding features are the formation of a eutectic composition of ~22.5 mole%  $\text{K}_2\text{CrO}_4$  between  $\text{Li}_2\text{CrO}_4$  and the double salt,  $\delta\text{-Li}_2\text{CrO}_4 \cdot \text{K}_2\text{CrO}_4$ , at  $390^\circ\text{C}$ ; the formation of a congruently melting double salt  $\text{Li}_2\text{CrO}_4 \cdot \text{K}_2\text{CrO}_4$  with three solid state allotropic forms,  $\gamma$ ,  $\delta$ , and  $\epsilon$ , the  $d$  spacings and colors of which are given; and the formation of a eutectic composition at ~54 mole%  $\text{K}_2\text{CrO}_4$  between  $\alpha\text{K}_2\text{CrO}_4$  and the double salt,  $\gamma\text{-Li}_2\text{CrO}_4 \cdot \text{K}_2\text{CrO}_4$ , at  $525^\circ\text{C}$ .

### Introduction

Metal chromates are often used as cathodic depolarizers in thermal voltaic cells. One common thermal cell employs a calcium anode, an iron cathode,  $\text{CaCrO}_4$  as the cathodic depolarizer, and a  $\text{LiCl-KCl}$  eutectic electrolyte (1). The possible ions present in such a molten system can include  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{K}^+$ ,  $\text{Li}^+$ ,  $\text{Cl}^-$ , and  $\text{CrO}_4^{2-}$ .

It is obviously very difficult to enunciate the equilibrium phases present in such a complex system since all of the possible binary pairs have not even been reported. We have undertaken the task of simplification by studying isolated pairs of these reactants. The system  $\text{K}_2\text{CrO}_4\text{-CaCrO}_4$  has been previously reported (2) and this paper reports the equilibrium system  $\text{Li}_2\text{CrO}_4\text{-K}_2\text{CrO}_4$ .

Three prior articles are concerned with this system (3a, 3b, 4). References (3a) and (3b) are tabulated in the same reference source with no critical comment although Ref. (3a) reports a reaction,  $\alpha\text{-Li}_2\text{CrO}_4 \rightleftharpoons \beta\text{-Li}_2\text{CrO}_4$  at  $440^\circ\text{C}$  not substantiated by Ref. (3b). Both references indicate a congruently melting double salt,  $\text{Li}_2\text{CrO}_4 \cdot \text{K}_2\text{CrO}_4$ , and also a eutectic between the double salt and  $\text{K}_2\text{CrO}_4$  at ~55

mole%  $\text{K}_2\text{CrO}_4$ . Reference (3a) consistently reports temperatures 10 to  $15^\circ\text{C}$  higher for every event than Ref. (3b).

Belyaev (4) acknowledges both Refs. (3a) and (3b) but makes no evaluation of them. His data do not note any phase change in solid  $\text{Li}_2\text{CrO}_4$  and indicate a melting point of  $516^\circ\text{C}$  for the salt.

Belyaev also reported the formation of a double salt,  $\text{Li}_2\text{CrO}_4 \cdot \text{K}_2\text{CrO}_4$ , and its existence in two solid state forms,  $\alpha$  and  $\beta$ , presumably with the solid-state phase change at  $437^\circ\text{C}$ . His construction of the diagram, however, exhibits a violation of the phase rule. He shows the following four phases in equilibrium at  $437^\circ\text{C}$  and 50 mole%  $\text{K}_2\text{CrO}_4$ :

- (1) liquid,
- (2)  $\alpha\text{-Li}_2\text{CrO}_4 \cdot \text{K}_2\text{CrO}_4$ ,
- (3)  $\beta\text{-Li}_2\text{CrO}_4 \cdot \text{K}_2\text{CrO}_4$ ,
- (4)  $\alpha\text{-K}_2\text{CrO}_4$ .

Of course, in condensed systems, a maximum of three phases can exist in equilibrium with no degrees of freedom.

It was concluded that valid reason existed to clarify the phase diagram for this system. The plan was to utilize differential thermal analysis

(DTA) to postulate the phases present and then to confirm the diagram with high-temperature X-ray diffraction.

### Experimental

The apparatus was essentially as reported elsewhere (2). A shielded thermocouple was inserted into a well in a quartz tube which contained the sample inside another quartz tube. For this system, because  $\text{Li}_2\text{CrO}_4$  is hygroscopic, the outer container was fitted with a cork stopper. The samples were weighed in a "dry room," and the tubes were then filled and stoppered until placed in the differential thermal holder. The stoppers were removed before the heating cycle was begun and, after the samples were cooled and removed from the apparatus, the stoppers were replaced so that the samples would remain dry or nearly dry for reuse. The initial heating cycle is assumed not to have evolved any water and therefore should have given useful cooling cycle data upon which to base the determination of the diagram.

The starting materials were reagent grade  $\text{K}_2\text{CrO}_4$  from Fisher Scientific Co. and high purity  $\text{Li}_2\text{CrO}_4$  prepared by Research Organic/Inorganic Chemical Corp. Our assay on the dried  $\text{Li}_2\text{CrO}_4$  was 99.7 wt% as measured by the indirect iodide titration method. This value represents a high purity for chromate salts. Supplementing the iodide method, spectrographic analysis of the  $\text{Li}_2\text{CrO}_4$  indicated that estimates of Fe, Mg, Si, Cu, Ag, Al, Na, and K could all be bracketed in the 1- to 50-ppm range with only Ca as high as 100 ppm.

Room temperature X-ray powder diffraction patterns were obtained with a 114.6-mm diameter Philips powder camera and  $\text{CuK}\alpha$  ( $\lambda = 1.54178 \text{ \AA}$ ) Ni-filtered radiation. Both elevated and room temperature X-ray data ( $\text{CuK}\alpha$  radiation) were obtained with a Materials Research Corporation high-temperature camera and platinum heating stage in conjunction with a Norelco powder

diffractometer equipped with a graphite monochromator and a scintillation detector. Silicon powder was used to standardize the high-temperature diffractometer with respect to angle.

### Results

Our initial differential thermal analyses on  $\text{Li}_2\text{CrO}_4$  produced no evidence of any transition except melting at  $498^\circ\text{C}$  as opposed to the reported melting temperature of  $517^\circ\text{C}$  (3a, 3b, 4). To eliminate the question of contamination by the quartz tube which might have lowered the melting point and also might have suppressed a phase change, a similar run was made in a platinum crucible. The same thermal arrest at  $498^\circ\text{C}$  was obtained with no phase changes in the solid state which indicated no effective quartz combination. Very careful calibration of the instrumentation system verified the temperature readings at  $\pm 1^\circ\text{C}$  in this range so that we have no reason to doubt the melting point at  $498^\circ\text{C}$ . High-temperature X-ray diffraction results on the high-purity material indicated only the single solid phase.

A separate determination (5) by differential thermal analysis on  $\text{Li}_2\text{CrO}_4$  in quartz supported the existence of only a single solid phase, and the melting point of  $498^\circ\text{C}$ . When runs were repeated with bare chromel-alumel couples and also with thermocouple wires purposely dissolved, lower-temperature events were found. The authors suggest such a possibility for the one reference (3a) which indicated an  $\alpha$ - $\beta$  solid-state change.

The differential thermal analysis data points and the deductions from them are shown in the phase diagram in Fig. 1. Two eutectics are indicated at  $\sim 22.5$  mole%  $\text{K}_2\text{CrO}_4$  which involves  $\text{Li}_2\text{CrO}_4$  and the double salt,  $\delta\text{-Li}_2\text{CrO}_4 \cdot \text{K}_2\text{CrO}_4$ , and also at 54 mole%  $\text{K}_2\text{CrO}_4$  which involves  $\text{K}_2\text{CrO}_4$  and the double salt,  $\gamma\text{-Li}_2\text{CrO}_4 \cdot \text{K}_2\text{CrO}_4$ , in agreement with Refs. (3a, 3b, 4). The double salt,  $\text{Li}_2\text{CrO}_4 \cdot \text{K}_2\text{CrO}_4$ , is formed and we deduce

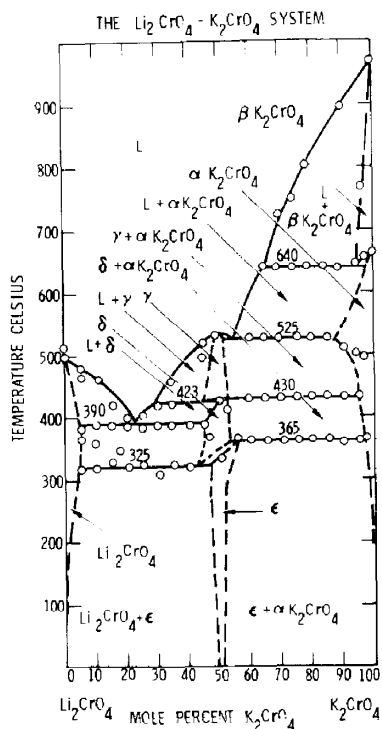


FIG. 1. The phase diagram for the  $\text{Li}_2\text{CrO}_4$ - $\text{K}_2\text{CrO}_4$  system.

that it must have three polymorphs,  $\epsilon$ ,  $\delta$  and  $\gamma$ , in order to produce the thermal arrests noted.<sup>1</sup> The solid-state events are shown as pairs of eutectoids and peritectoids typically so that three phase equilibria are established. These events are all near the 1:1 mole ratio, and since the compositions of the eutectoids and peritectoids are not known with accuracy, the lines are shown "dotted". It is not considered useful to pursue the accuracy further than this level.

Figure 2 is a schematic presentation of the region around the double salt which clarifies the peritectoid-eutectoid pairs of reactions resulting in the  $\gamma$ ,  $\delta$ , and  $\epsilon$  phases.

X-Ray diffraction studies were carried out on samples consisting of 40 and 60 mole%

<sup>1</sup>The three polymorphs of the double salt,  $\text{Li}_2\text{CrO}_4 \cdot \text{K}_2\text{CrO}_4$ , were designated  $\epsilon$ ,  $\delta$ , and  $\gamma$  instead of  $\alpha$ ,  $\beta$ , and  $\gamma$  to avoid confusion with the previously designated  $\alpha$  and  $\beta$  phases of  $\text{K}_2\text{CrO}_4$ .

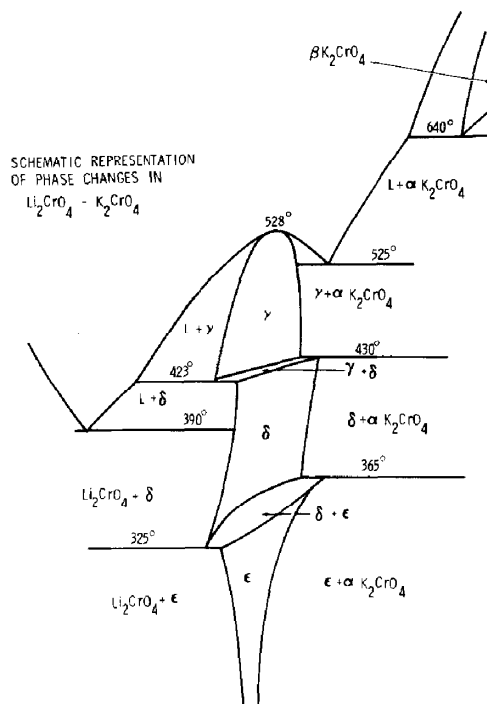


FIG. 2. A schematic representation of the phase changes for the  $\text{Li}_2\text{CrO}_4$ - $\text{K}_2\text{CrO}_4$  system.

$\text{K}_2\text{CrO}_4$  to verify the interpretation of the thermal events observed by DTA. Both room temperature and high-temperature data were collected. It should be stated that the accurate temperatures could not be determined in conjunction with the use of the high-temperature diffractometer attachment; however, the reported temperatures are accurate to within  $25^\circ\text{C}$  based on the observation of melting points.

Diffraction patterns for the three double salt phases were obtained from the investigation of data for the 40 and 60 mole%  $\text{K}_2\text{CrO}_4$  samples, and subtraction of lines due to  $\text{Li}_2\text{CrO}_4$  and  $\text{K}_2\text{CrO}_4$ .

At room temperature the diffraction patterns for the double salt phase,  $\epsilon$ - $\text{Li}_2\text{CrO}_4 \cdot \text{K}_2\text{CrO}_4$ , was observed in both the diffraction patterns of the 40 and 60 mol.%  $\text{K}_2\text{CrO}_4$  samples (Table I). The strongest reflections of the diffraction pattern for  $\text{K}_2\text{CrO}_4$  were observed in the 60 mole%  $\text{K}_2\text{CrO}_4$  sample, and the strongest reflections

TABLE I  
OBSERVED *d*-SPACINGS AND RELATIVE INTENSITIES FOR THE  $\text{Li}_2\text{CrO}_4 \cdot \text{K}_2\text{CrO}_4$  PHASES

$\epsilon$		$\delta$		$\gamma$	
<i>d</i> observed (Å)	<i>I</i> / <i>I</i> <sub>0</sub>	<i>d</i> observed (Å)	<i>I</i> / <i>I</i> <sub>0</sub>	<i>d</i> observed (Å)	<i>I</i> / <i>I</i> <sub>0</sub>
4.28	55	4.29	70	4.39	30
4.17	90	4.21	100	4.12	95
4.07	30	4.10	80	3.90	55
4.03	35	4.06	55	3.19	100
3.63	40	3.20	65	3.13	50
3.26	30	3.12	70	3.02	45
3.20	35	3.09	55	2.70	40
3.16	15	2.91	75	2.60	55
3.11	95	2.60	100	2.24	50
2.90	100	2.31	30	2.18	15
2.59	60	1.62	55	2.12	20
2.50	30	1.61	75	2.07	30
2.43	25	1.53	45	1.77	20
2.29	35			1.76	30
2.26	30			1.65	30
2.20	30			1.62	85
2.15	40			1.53	45
2.09	35				
1.62	65				
1.58	25				
1.52	75				

for  $\text{Li}_2\text{CrO}_4$  in the 40 mole%  $\text{K}_2\text{CrO}_4$  sample. The observation of  $\text{Li}_2\text{CrO}_4$  and  $\text{K}_2\text{CrO}_4$  in the 40 and 60 mole%  $\text{K}_2\text{CrO}_4$  samples, respectively, is evidence that the composition of the  $\epsilon$  phase is ~50 mole%  $\text{K}_2\text{CrO}_4$ . At higher temperatures the intensities of the reflections due to  $\text{Li}_2\text{CrO}_4$  and  $\text{K}_2\text{CrO}_4$  tended to become weaker, which suggests that the solid solution range for the double salt became larger as the temperature was increased.

The X-ray diffraction pattern for  $\delta$ - $\text{Li}_2\text{CrO}_4 \cdot \text{K}_2\text{CrO}_4$  was recorded at ~400°C for the 60 mole%  $\text{K}_2\text{CrO}_4$  sample and at ~350°C for the 40 mole%  $\text{K}_2\text{CrO}_4$  sample (Table I).

For  $\gamma$ - $\text{Li}_2\text{CrO}_4 \cdot \text{K}_2\text{CrO}_4$  the X-ray diffraction pattern was recorded at ~470°C for the 60 mole%  $\text{K}_2\text{CrO}_4$  sample (Table I). No attempt was made to examine the 40 mole%  $\text{K}_2\text{CrO}_4$  sample above 390°C due to the presence of the liquid phase.

The observed *d*-spacings and the relative intensities reported for the three new phases,  $\epsilon$ -,  $\delta$ -, and  $\gamma$ - $\text{Li}_2\text{CrO}_4 \cdot \text{K}_2\text{CrO}_4$ , in Table I are the average of five separate patterns for each phase. Some difficulty was encountered in correctly choosing the reflections for  $\gamma$ - $\text{Li}_2\text{CrO}_4 \cdot \text{K}_2\text{CrO}_4$  due to the lack of reproducibility of some reflections from pattern to pattern. The observation of these three new phases by high-temperature X-ray diffraction verifies the interpretation of the events observed by differential thermal analysis.

During the course of the high-temperature X-ray diffraction experiments, it was possible to observe color changes as a function of temperature. There appears to be a correlation of color with phases present in the  $\epsilon$ ,  $\delta$ , and  $\gamma$  series. A tabulation of temperature versus color was recorded for the 40 mole%  $\text{Li}_2\text{CrO}_4$ -60 mole%  $\text{K}_2\text{CrO}_4$  sample as shown in Table II.

TABLE II

A CORRELATION OF COLORS, TEMPERATURE, AND PHASES FOR 40 mole%  $\text{Li}_2\text{CrO}_4$ -60 mole%  $\text{K}_2\text{CrO}_4$ 

Degree ( $^{\circ}\text{C}$ )	Color	Phase observed or deduced
535	red	Clear liquid
503	red	Solid + liquid
500	red	Solid + liquid
484	red	$\gamma + \alpha\text{-K}_2\text{CrO}_4$
471	red	$\gamma + \alpha\text{-K}_2\text{CrO}_4$
466	red	$\gamma + \alpha\text{-K}_2\text{CrO}_4$
460	red	$\gamma + \alpha\text{-K}_2\text{CrO}_4$
456	red	$\gamma + \alpha\text{-K}_2\text{CrO}_4$
445	red	$\gamma + \alpha\text{-K}_2\text{CrO}_4$
434	red	$\gamma + \alpha\text{-K}_2\text{CrO}_4$
424	red orange	$\delta + \alpha\text{-K}_2\text{CrO}_4$
404	red orange	$\delta + \alpha\text{-K}_2\text{CrO}_4$
388	orange red	$\delta + \alpha\text{-K}_2\text{CrO}_4$
369	orange red	$\delta + \alpha\text{-K}_2\text{CrO}_4$
354	orange	$\epsilon + \alpha\text{-K}_2\text{CrO}_4$
320	orange yellow	$\epsilon + \alpha\text{-K}_2\text{CrO}_4$
275	orange yellow	$\epsilon + \alpha\text{-K}_2\text{CrO}_4$
215	yellow orange	$\epsilon + \alpha\text{-K}_2\text{CrO}_4$
168	yellow	$\epsilon + \alpha\text{-K}_2\text{CrO}_4$
123	yellow	$\epsilon + \alpha\text{-K}_2\text{CrO}_4$
Original at R.T.	yellow green	$\epsilon + \alpha\text{-K}_2\text{CrO}_4$

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