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THE Li_2CrO_4—$CaCrO_4$ BINARY PHASE DIAGRAM *

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ABSTRACT

Phase equilibria in the Li_2CrO_4—$CaCrO_4$ system were determined by differential thermal analysis and X-ray powder diffraction. The phase diagram is characterized by a eutectic reaction at 489°C and 5 mole% $CaCrO_4$, and a monotectic reaction at 570°C and 80 mole% $CaCrO_4$. The solubility of Li_2CrO_4 in $CaCrO_4$ was ≈15 mole% at the eutectic temperature and declined to <5 mole% at the monotectic temperature. No double salt was formed between the end members. The immiscibility observed in the system is rationalized in terms of the cation coordination polyhedra.

Thermal events indicative of a solid state phase change in Li_2CrO_4 as reported in some references are judged to be the result of a Li_2CO_3 impurity.

INTRODUCTION

The report of phase equilibria in the Li_2CrO_4—$CaCrO_4$ system is the third in a series of studies of binary interactions among constituents of thermal voltaic cell electrolytes [1,2]. The previous studies of the Li_2CrO_4—K_2CrO_4 [1] and K_2CrO_4—$CaCrO_4$ [2] systems have shown that these systems are characterized by the formation of one-to-one double salts of the end members. Study of the Li_2CrO_4—$CaCrO_4$ system was undertaken in a search for similar compound formation and to complete the elucidation of binary limits of the above Ca—K—Li chromate ternary system.

The study also afforded an opportunity to resolve the possibility of solid state phase changes in Li_2CrO_4. Reports of such phase changes [3,4] have been questioned as a result of previous work in this series [1].

EXPERIMENTAL

Materials

High purity $CaCrO_4$ (assay 99.85%) was prepared from reagent grade $CaCO_3$ and Na_2CrO_4, using a method previously described [5]. Suppliers of

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Li_2CrO_4 included Ventron Corporation (Alfa Products), Research Organic/ Inorganic Chemical Corporation, Apache Chemicals, Inc. and ICN K and K Laboratories, Inc. Samples were assayed and only those with purity >99% were used to obtain phase diagram data.

Apparatus and procedures

The Li_2CrO_4—$CaCrO_4$ system was studied by differential thermal analysis (DTA) and X-ray powder diffraction using equipment and techniques described elsewhere [2]. Sample mixtures weighing 15 g were prepared in a dry room (atmospheric water content <50 ppm) and loaded in quartz tubes. The samples were heated to temperatures about 100°C above the liquidus determined in previous survey experiments. Thermal events were observed as the samples cooled in air at 1—2°C min^{-1}.

Some discoloring was observed at the quartz—sample interface of the cooled samples. X-Ray diffraction of the discolored material and thermal analysis of samples deliberately contaminated with powdered SiO_2 showed that any reaction between the quartz and the sample had little effect on the experimental results.

Thermal events observed in selected samples were confirmed by obtaining independent DTA curves with a DuPont Model 990 Thermal Analysis System equipped with a 1600°C High Temperature DTA cell. Samples of 20 mg contained in platinum cups were thermally cycled at 10—20°C min^{-1}. The calibration of the temperature axis of this device was checked with the melting points and phase changes of $AgNO_3$, KNO_3, and LiBr. Event temperatures obtained using this device agreed within ±2°C with those obtained for the larger samples in quartz tubes. This agreement is further evidence that any reaction of the sample with the quartz container during DTA had little effect on results reported here.

Thermogravimetric analysis (TGA) of some of the samples was conducted with a DuPont Model 950 TGA. Interpretation of weight-loss events observed during TGA was confirmed by heating samples in a vacuum system equipped with a UTI Model 100C Precision Gas Analyzer.

TGA and gas analysis results showed that Li_2CrO_4—$CaCrO_4$ mixtures were dehydrated without decomposition in two distinct steps. When samples were heated at 1°C min^{-1} in dry helium, maximum rates of weight loss occurred at 37 and 58°C, respectively. Dehydration was complete at 72°C. These results show that any water adsorbed by the samples in spite of the dry room precautions was vaporized during the heating cycles of the DTA experiments.

RESULTS

The results of DTA and X-ray powder diffraction of Li_2CrO_4—$CaCrO_4$ mixtures are summarized in the phase diagram shown in Fig. 1. Two three-phase equilibria develop in the system; a eutectic reaction occurs at 489°C and 5 mole% $CaCrO_4$, and a monotectic reaction occurs at 570°C and 80

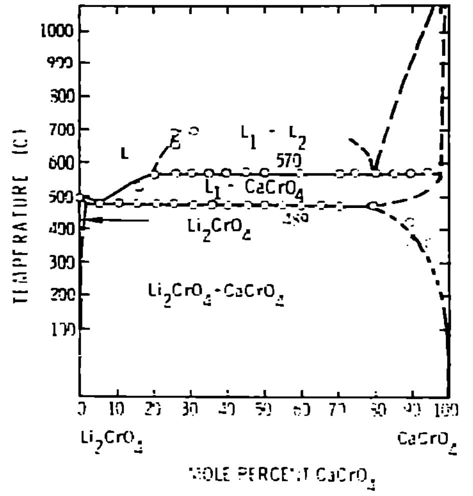

Fig. 1. Phase diagram for the Li_2CrO_4—$CaCrO_4$ system.

mole% $CaCrO_4$. The solubility of Li_2CrO_4 in $CaCrO_4$ reached a maximum of ≈15 mole% at 489°C, the eutectic temperature, and declined rapidly to <5 mole% at the monotectic temperature, 570°C.

The location of the monotectic composition for the reaction

$$L_1 \rightleftharpoons L_2 + \beta_{CaCrO_4}$$

was difficult because the energy change for the reaction was small. A careful comparison of the areas under the differential curves indicated that the composition of 80 mole % was the most likely composition for the monotectic point.

No indication of double salt formation between the system end members could be detected. Shifts in line spacing in diffraction patterns of the samples were within the 0.1% uncertainty of film techniques and indicated that any solid solubility that did occur had little effect on unit cell parameters of the end members.

Repeated attempts to quench or to observe directly the interface in the two-liquid mixture formed by the monotectic reaction failed. However, the monotectic reaction is the only valid means of accounting for the thermal events observed during DTA of the samples.

The phase diagram depicted in Fig. 1 is applicable only for conditions when $CaCrO_4$ is stable. A recent review of the decomposition of $CaCrO_4$ has shown that the stability of this compound is still controversial [6]. During this study, significant evolution of oxygen from $CaCrO_4$ was detected at 930°C and 570°C at oxygen partial pressures of 0.17 and 5×10^{-6} atm, respectively. The observed stoichiometry of the decomposition was 1 mole oxygen per mole of calcium chromate.

The decomposition of $CaCrO_4$ made it difficult to assure that calcium-rich mixtures were equilibrated during DTA and at the same time not badly decomposed. For this reason, data points for samples containing more than 85% $CaCrO_4$ are connected by dotted lines in Fig. 1.

TABLE 1

Assays of commercially prepared Li_2CrO_4

Supplier		Assay	Solid state phase change (°C)	M.p. (°C)
A	Lot 1	99.7	None	502
A	Lot 2	96.7	413	471
A	Lot 3	96.1	413	448
A	Lot 4	96.1	414	477
A	Lot 5	99.5	None	503
B	Lot 1	99.3	None	503
C	Lot 1	99.5	None	500
D	Lot 1	99.7	None	503

Differential thermal analyses of "as received" Li_2CrO_4 samples from various suppliers are listed in Table 1, along with assays as obtained by the indirect iodide method. Samples whose assays are greater than 99 wt.% Li_2CrO_4 yield only a single thermal event and exhibit a mean temperature of melting of 502 ± 1°C as determined by two DTA instruments. Melting points of Li_2CrO_4 samples of purity less than 97 wt.% are substantially depressed and more variable. The low assay samples also produce a second thermal event at about 413°C. Similar events at about 440°C have been reported by others [3,4] and have been attributed to an $\alpha \rightleftharpoons \beta$ equilibrium in Li_2CrO_4. High temperature X-ray diffraction of high purity Li_2CrO_4 did not reveal any phase change up to the melting point. The conclusion is that the second thermal event is likely to be due to impurities.

Infrared spectra of the Li_2CrO_4 samples of purity less than 97% had moderately intense absorptions at 1430 and 1490 cm^{-1}. These absorptions may be assigned to the carbonate chromophore in Li_2CO_3 [7]. No such absorptions were observed in spectra of high purity Li_2CrO_4 samples.

DISCUSSION

Results presented here show that no thermal event occurs in high-purity Li_2CrO_4 that may be assigned to a solid-state phase transformation. Such transformations reported elsewhere may have been due to impurities in the Li_2CrO_4 [3,4]. A very likely impurity is Li_2CO_3, which is quite stable under the conditions typically used to synthesize Li_2CrO_4. Carbonate contamination would be unavoidable if syntheses were conducted in ambient laboratory air. The phase stability data for a limited number of samples run in this laboratory on the Li_2CrO_4—Li_2CO_3 system show extensive solid solubility of Li_2CO_3 in Li_2CrO_4; consequently, recrystallization of Li_2CrO_4 would not necessarily eliminate carbonate impurities. The substantial influence of modest amounts of lithium carbonate on the thermal properties of nominally pure lithium salts have been observed by others [8].

The Li_2CrO_4—$CaCrO_4$ system does not produce a double salt in contrast to both the Li_2CrO_4—K_2CrO_4 and K_2CrO_4—$CaCrO_4$ systems. The Li_2CrO_4—$CaCrO_4$ system is characterized by immiscibility of the end members at the monotectic. The reluctance of Li_2CrO_4 and $CaCrO_4$ to solvate one another is carried over into the liquid phase as evidenced by the formation of a two-liquid region.

Observation of a two-liquid region and the failure to detect a one-to-one double salt are empirically consistent findings. The ThO_2—B_2O_3 system [9] is the only case known to the authors in which a compound decomposes into two liquids.

The marked immiscibility of lithium chromate and calcium chromate may be rationalized by considering the coordination polyhedra about the cations. The calcium chromate structure [10] is similar to that of zircon in which calcium ions are eight-fold coordinated by chromate oxygens [10]. Lithium chromate has the phenacite structure [11] in which lithium ions are coordinated tetrahedrally by chromate oxygens in the "A" configuration [12]. The oxygen atoms are three-fold coordinated in both structures.

For solubility to occur, there must be some similarity of structure between solvent and solute. When this similarity is not present in the pure species, it must be developed in the mixture. The energy necessary to achieve structural similarity in the mixture must, however, not be so great that it overcomes the entropy advantages of solubility.

"Structural field maps" have been shown to be useful devices for determining whether structural alterations exist that may be accomplished at low energy cost [13]. Inspection of such maps shows that the zircon structure may be thermally transformed to the M-fergusonite and the scheelite structures. In both of these structures, eight-fold coordination of the cation is retained. Maps for the phenacite structure show that transformation can occur only to structures in which the cation coordination is no greater than octahedral. Apparently, structural similarity cannot be achieved by either Li_2CrO_4 or $CaCrO_4$ through a low-energy transformation and solid-state immiscibility occurs.

The limits of the liquid phase immiscibility may also be rationalized in terms of the cation coordination polyhedra if it is assumed that liquid structures are not too different from the solid structures at temperatures near the solidus of the system. The rationalization is based on concepts introduced by Levin and Block to explain immiscibility in silicate and borate systems [12].

The chromate ion carries a —2 formal charge distributed over its four oxygens. The —1/2 charge on each oxygen is neutralized when coordinated to cations such that the sum of the ionic bond strengths of these cations equals +1/2. If the lithium and calcium ions retain their solid-state coordination geometries, each will have a bond strength of 1/4 in the liquid state. A chromate oxygen may be saturated by bonding to two cations of either the same or different types in addition to the Cr(IV) ion.

The geometry of the associated cation—anion combination will, however, be quite dependent on the cation type. Miscelles of four-fold coordinated lithium and eight-fold coordinated calcium will occur as separate entities in the liquid whenever the concentration of one exceeds the limiting composition for homogenization by the other [12]. The limiting composition in

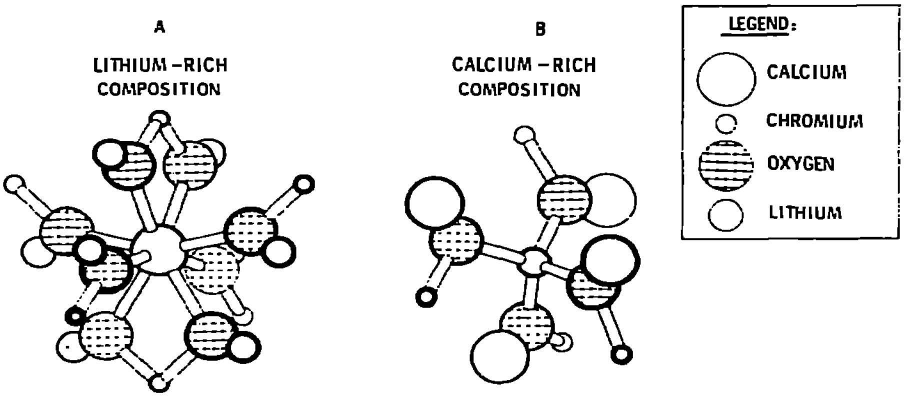

Fig. 2. Coordination configurations of (A) the lithium-rich and (B) the calcium-rich homogenizing compositions in the Li_2CrO_4—Ca_2CrO_4 system. Atomic radii and bond distances have been altered to clarify the coordination geometry. Thicker outlines for the atoms indicate the atoms which are closer to the reader.

lithium-rich solutions occurs when the calcium ions are coordinated to eight oxygens, each of which is also coordinated to a lithium ion. Additional calcium chromate in such a system will occur as a separate phase until the limiting composition for homogenization in the calcium-rich liquid is reached. The second limiting composition involves lithium ion coordinated to four oxygens, each bound to a calcium ion. The limiting compositions liquid structures are schematically represented in Fig. 2. The limiting compositions are 20 mole % Li_2CrO_4 (80 mole % $CaCrO_4$) and 88.9 mole % Li_2CrO_4 (11.1 mole % $CaCrO_4$).

These conodes of the liquid miscibility gap are in good agreement with the experimental results. The above argument, in truth, applies only at 0 K. At higher temperatures, thermal energy will promote a fraction of the species to higher energy, soluble structures. One would expect, as is observed, that the predicted conodes could be shifted toward the end members relative to the experimental data for the system at elevated temperatures.

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