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BINARY SYSTEMS WITH Li_2SO_4 AS ONE OF THE COMPONENTS

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Six binary systems were studied using DTA with supplementary XRD. In Li_2SO_4–MSO_4 systems (M = Mg, Co, Ni), a primary solid solution with α-Li_2SO_4 structure (high-temperature form) and an incongruent melting compound $Li_2M_y(SO_4)_{1+y}$ exist: $y = 2$ with Mg and $y = 1$ with Co and Ni. In Li_2SO_4–Li_3XO_4 systems (X = P, V), which are very different from one another, only primary solid solutions exist. In the Li_2SO_4–$Li_2B_4O_7$ system there is neither a solid solution nor an intermediate compound. Comparisons with previous investigations are made.

Keywords: binary systems, DTA, Li_2SO_4, solid solution, XRD

Introduction

Li_2SO_4 is dimorph and its melting point is 860°C. It is an interesting compound for several reasons. The β→α transition, at 572°C, is coupled with a considerable change of enthalpy, 24.2 $kJ \cdot mol^{-1}$, which is three times stronger than the melting enthalpy [1]. The ionic conductivity increases from 1.26×10^{-7} $S \cdot cm^{-1}$ at 300°C [2] to 1.08 $S \cdot cm^{-1}$ at 600°C [3]. These two properties are probably connected. In order to obtain a good ionic conductor material at a temperature lower than 600°C, many mixtures with Li_2SO_4 as one of the components have been examined. The study of binary systems is of interest in this connection because homogeneous and heterogeneous solid regions are clearly bounded. Moreover, the presence or absence of intermediate compounds and boundaries of primary or intermediate solid solutions can also be determined. We present here six binary systems, which have been studied in the last few years and make some comments on the techniques used, mainly DTA and XRD, and the results obtained. Generally, the entire binary system was examined except in the MSO_4 (M = Mg, Co, Ni)-rich ends due to decomposition of these sulphates.

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Experimental

Reagent grade salts were used when available; this was the case for Li_3PO_4 and for hydrated sulphates – $Li_2SO_4 \cdot H_2O$, $MgSO_4 \cdot 7H_2O$, $CoSO_4 \cdot 7H_2O$ and $NiSO_4 \cdot 7H_2O$ – which were carefully dehydrated. Li_3VO_4 and $Li_2B_4O_7 \cdot 3H_2O$ were synthesised from $LiOH \cdot H_2O$, V_2O_5 and H_3BO_3 [4, 5]. Several DTA and XRD instruments were successively used; details of procedures are reported elsewhere [6, 7, 8].

Results and discussion

Li_2SO_4–MSO_4 systems

Though MSO_4 (M = Mg, Co, Ni) compounds are isostructural [9], the binary systems are slightly different (Figs 1, 2 and 3). These sulphates are not soluble in β-Li_2SO_4 and slightly soluble in α-Li_2SO_4. The main difference arises from the intermediate compounds, which melt incongruently. With Mg[8], $Li_2Mg_2(SO_4)_3$ exists: its structure has been described [10]. The diagram (Fig. 1) agrees closely

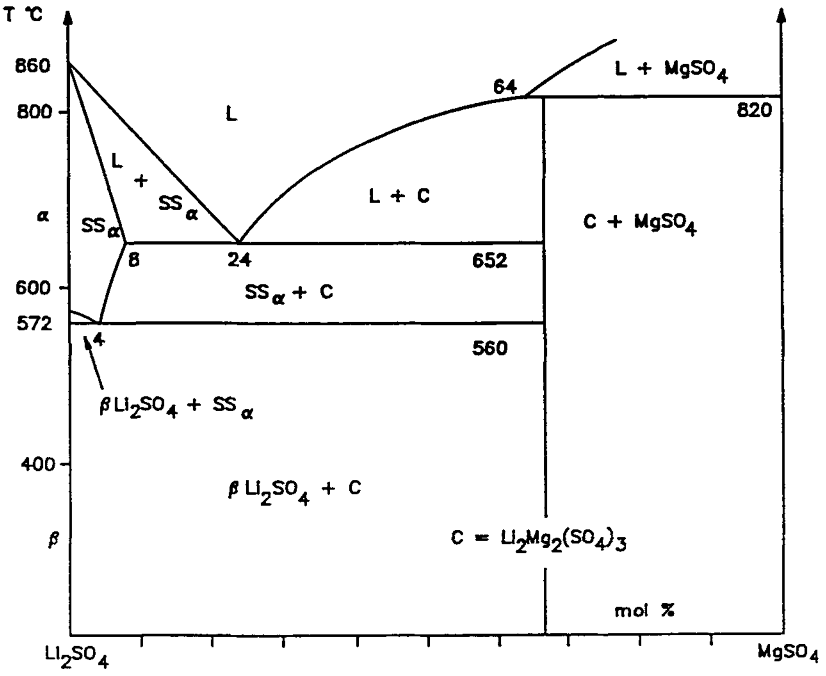

Fig. 1 Phase diagram of the Li_2SO_4–$MgSO_4$ system. SS_α is a primary solid solution of $MgSO_4$ in α-Li_2SO_4

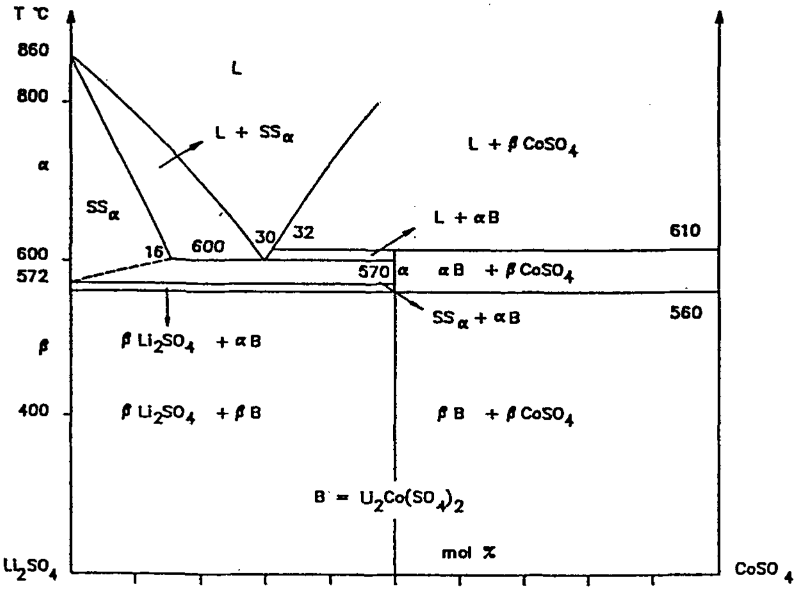

Fig. 2 Phase diagram of the Li_2SO_4–$CoSO_4$ system. SS_α is a primary solid solution of $CoSO_4$ in α-Li_2SO_4

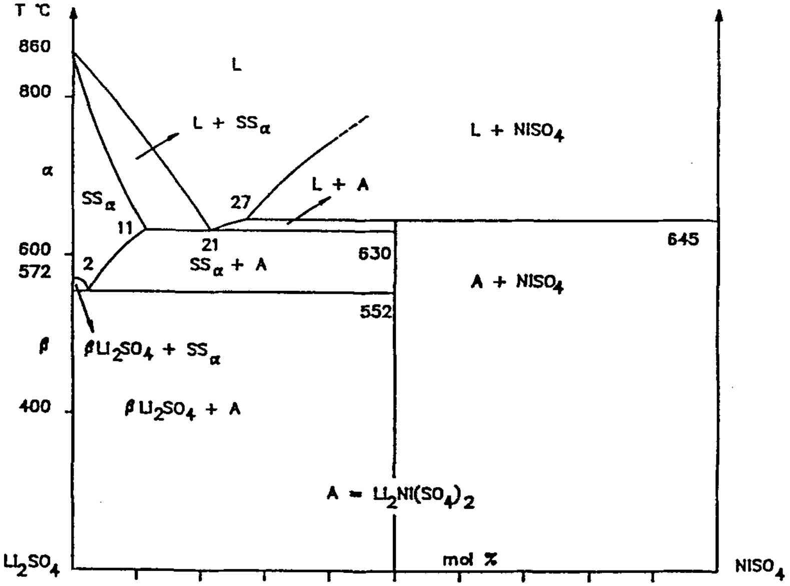

Fig. 3 Phase diagram of the Li_2SO_4–$NiSO_4$ system. SS_α is a primary solid solution of $NiSO_4$ in α-Li_2SO_4

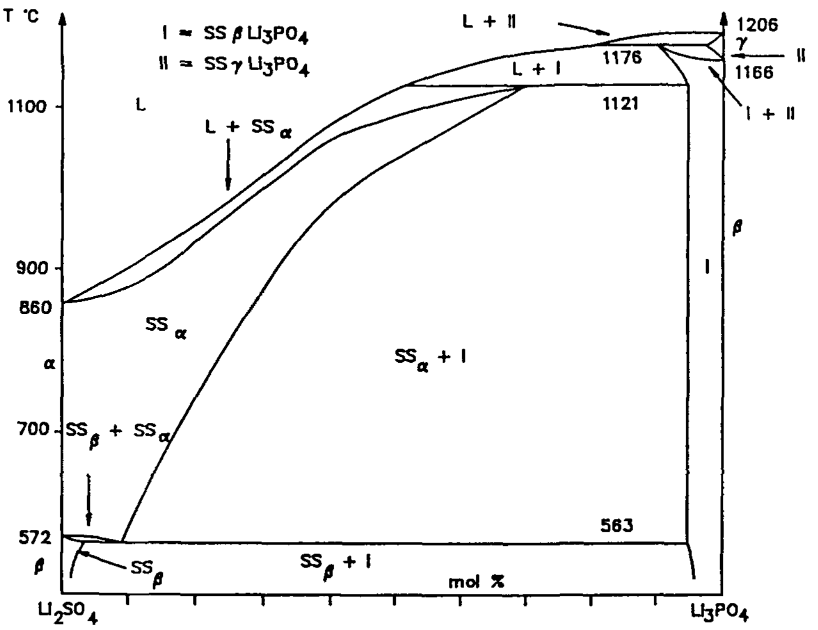

Fig. 4 Phase diagram of the Li_2SO_4–Li_3PO_4 system. SS_α and SS_β are primary solid solutions of Li_3PO_4 in respectively α-Li_2SO_4 and β-Li_2SO_4

with previous studies except for two where either another form of Li_2SO_4 is found [11] or an intermediate compound, $Li_2Mg_4(SO_4)_5$, has been described [12]. Two forms of $Li_2Co(SO_4)_2$ were found with a transition at 560°C (Fig. 2); this phenomenon is clearly distinct from that of the β-Li_2SO_4 → α-Li_2SO_4 transition and has been pointed out only in the 50–90 $CoSO_4$ mol% composition range [6]. With Ni, the compound $Li_2Ni(SO_4)_2$ exists [6] (Fig. 3). $Li_2Ni(SO_4)_2$ and β-$Li_2Co(SO_4)_2$ were identified by X-ray powder diffraction but were never obtained alone; they are always accompanied by components arising from partial reversibility of the peritectic reactions [6]. This phenomenon is often observed when a substance melts incongruently [13]. Previous investigations also indicated a compound, $Li_4Ni(SO_4)_3$, with a congruent melting point [14].

Li_2SO_4–Li_3XO_4 systems

Three forms of Li_3PO_4 exist and Li_2SO_4 is slightly soluble in each (Fig. 4); on the other hand, solubility of Li_3PO_4 in α-Li_2SO_4 increases with temperature: a large region of $Li_{2+z}S_{1-z}P_zO_4$ solid solution is found, until z equals 0.7. No intermediate phase exists in the system [7]. This last result was recently questioned by Wijayasekera and Mellander [15], who suggested, on the basis of poorly defined DSC peaks, that an intermediate phase, Li_5PSO_8, exists within the temperature range 556° to 566°C. This interpretation clashes with our observations and especially the Tammann graph of the 563°C phenomena inferred from DTA experiments. The reason for this divergence may be the fact that, in DSC-mode, the samples were heated only up to 850°C [15], which does not permit attainment of the liquid phase (Fig. 4) and good homogeneity of the mixture. Our first results on the Li_3VO_4-Li_2SO_4 phase diagram almost agree with the previous study of Liang *et al.* [16]: there is no intermediate compound in this system as found with Li_3PO_4, but the boundaries of primary solid solution were slightly different especially on the Li_3VO_4 side. The complete diagram will be published later, following further experimentation.

Li_2SO_4–$Li_2B_4O_7$ *system*

This system has never been studied before. The aim was to find a possible intermediate compound and to specify at which temperature the liquid phase appears before undertaking conductivity measurements. Results of a few DTA experiments led to the diagram presented in Fig. 5. In this system there is neither a solid solution nor an intermediate compound.

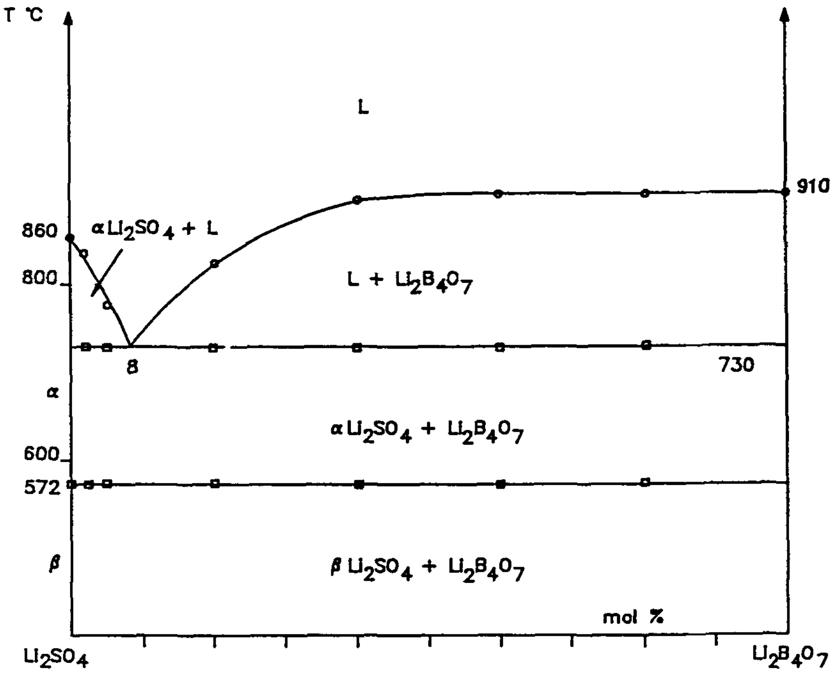

Fig. 5 Phase diagram of the Li_2SO_4–$Li_2B_4O_7$ system

Conclusion

DTA is the best method to establish a phase diagram although other techniques such as XRD are also useful [13]. However, sometimes results obtained by XRD measurements are not convincing, such as those conducted at several temperatures on Li_2SO_4–Li_3PO_4 mixtures in order to delimit the boundaries of solid solutions [15]. These investigators [15] found a lower solid solubility of Li_3PO_4 in α-Li_2SO_4, especially at temperatures approaching the eutectoid point, which is, according to them, situated at about 1 mol% Li_3PO_4 instead of about 10 mol% Li_3PO_4 in our DTA measurements (Fig. 4).

We can see that the solid solubility of MSO_4 in α-Li_2SO_4 is low; the main reason is the difference of environment of Li^+ which is tetrahedral and of M^{2+} which is octahedral [6]. The considerable solubility of Li_3PO_4 in α-Li_2SO_4 may be explained by the structural analogy between these two compounds where the cations have the same tetrahedral environment and almost the same size: r_{S6+} = 0.12 Å and r_{P5+} = 0.17 Å [17]. As r_{V5+} = 0.36 Å [17], the difference in size with S6+ may explain the low solubility of Li_3VO_4 in Li_2SO_4. On the other hand, no reason can be given for the presence or absence of the intermediate compounds and to justify their different formulae; these may be found only after experiments.

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Zusammenfassung — Mittels DTA und ergänzender Röntgendiffraktion wurden sechs binäre Systeme untersucht. In den Systemen Li_2SO_4–MSO_4 (M = Mg, Co, Ni) existiert ein primäres Mischkristall mit α-Li_2SO_4-Struktur (Hochtemperaturform) und eine inkongruent schmelzende Verbindung $Li_2M_y(SO_4)_{1+y}$: y=2 für Mg und y=1 für Co und Ni. In den Systemen Li_2SO_4–Li_3XO_4 (X=P, V), die sich sehr voneinander unterscheiden, existieren nur primäre Mischkristalle. Im System Li_2SO_4–$Li_2B_4O_7$ gibt es weder ein Mischkristall noch eine Zwischenverbindung. Vergleiche zu früheren Untersuchungen wurden angestellt.