Determination of the Phase Diagram $Li_2SO_4-Na_2SO_4$ from Differential Thermal Analysis

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The phase diagram of $Li_2SO_4-Na_2SO_4$ has been determined be means of differential thermal analysis. The obtained phase diagram is only in faint agreement with the previous one by NACKEN [1]. The investigation confirms the existence of a b.c.c. phase in nearly equimolar $Li_2SO_4-Na_2SO_4$.

In our investigations of diffusion coefficients [2, 3] and mechanical properties [4, 5] of cubic high temperature modifications, we have found that no reliable phase diagram is available in the literature for the system $Li_2SO_4-Na_2SO_4$. ØYE [6, 7] has reported the existence of a b.c.c. phase in $LiNaSO_4$ at high temperatures, but no such modification is indicated in the phase diagram given by NACKEN [1]. Since it was necessary for our planned diffusion experiments to know the exact extension of the different phases, we decided to investigate the system by means of differential thermal analysis.

Experimental

The experimental equipment, which has been described previously [8] was used with some modifications. The salt was placed in a small beaker of pure quartz with direct contact between the thermocouple (Platinel II) and the salt. The precision of the measurements has been estimated to about ± 2 °C. Quartz powder was used as reference. No disturbances from transitions in the quartz have been observed.

The salts were of reagent grade and all measurements were performed in air. The $(Li, Na)_2SO_4$ samples were obtained from well dried salts, which were weighed, mixed, molten and ground. For each concentration all transition points were measured at least three times with increasing and decreasing temperatures. The heating and cooling rate was between 6 and 10 °C/min.

Results and Discussion

Two typical DTA curves, one cooling and one heating curve, are shown in Fig. 1.

The calculations of some of the transition points must first be discussed. When the temperature interval between two transitions was small, which often is the case in this system, a double peak was obtained. The lower transition point was then calculated from the heating curve and the higher one from the cooling curve.

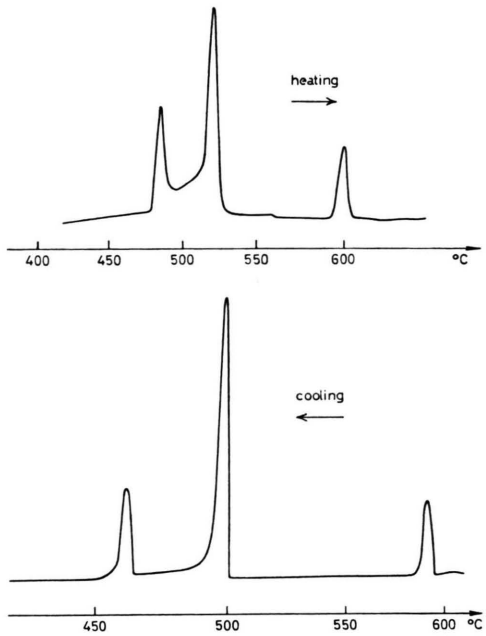

Fig. 1. Typical DTA curves. The heating rate is about 8 °C/min, and the cooling rate about 6 °C/min.

The obtained transitions are tabulated in Table 1.

mole% Na_2SO_4	Liquidus	Solidus	Other transitions 1	2	3	4	5
0	860	860			575		
5	816	804			548	472	
10	785	768			529	472	
15	739	714			501	472	
20	715	689			482	473	
25	674	650			472	472	
30	645	622			480	473	
35	602	587			493	471	
40	595	595	562		502	474	
45	606	606			510	474	
50	610	610			511	475	
55	616	616	557	539	506	474	234
60	628	628	604	564	499	473	238
65	651	632		608	490	473	236
70	689	646			480	471	237
75	724	670			475		237
80	764	709			467		235
85	790	735			459		234
90	824	778			425		234
95	859	835			237		232
100	884	884			241		

Table 1. The transition points in $Li_2SO_4-Na_2SO_4$ in °C.

[1] R. NACKEN, Neues Jahrb. Mineral. Geol., Beilageband **24**, 32 [1907].
[2] A. KVIST and U. TROLLE, Z. Naturforsch. **22 a**, 213 [1967].
[3] A. KVIST and A. BENGTZELIUS, Z. Naturforsch. **23 a**, 679 [1968].
[4] A. LUNDÉN, B. JONSON, and B. AUGUSTSSON, Z. Naturforsch. **21 a**, 593 [1966].
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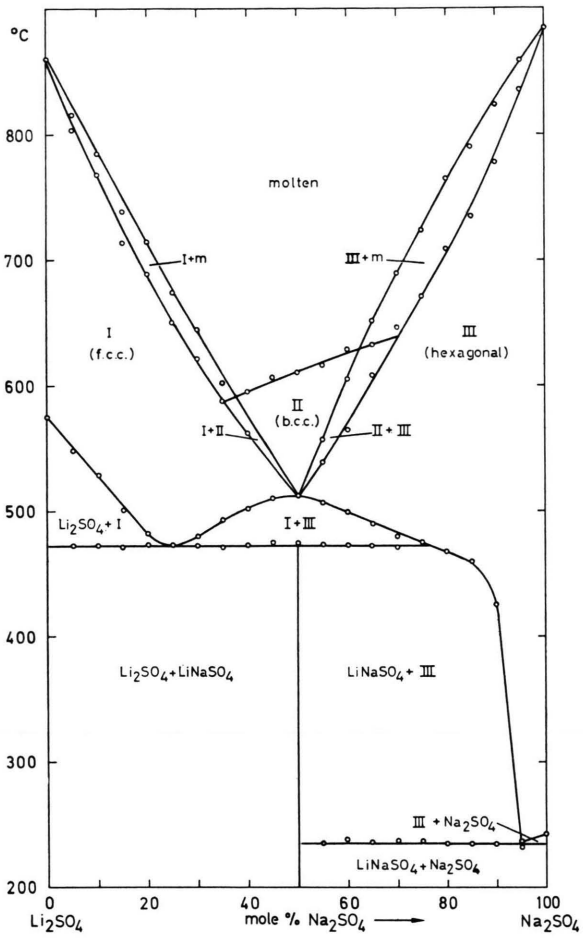

Fig. 2. The phase diagram of $Li_2SO_4-Na_2SO_4$.

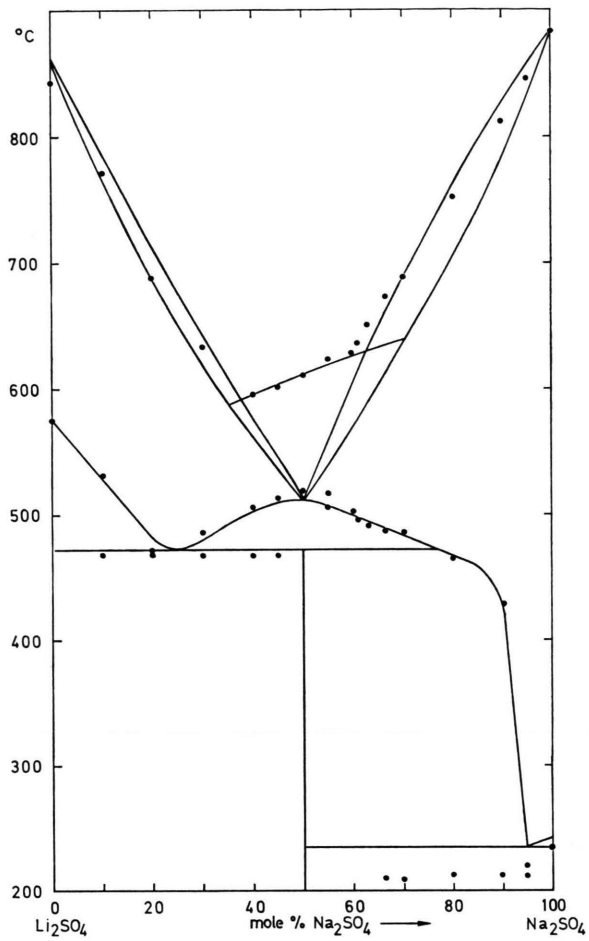

Fig. 3. The phase diagram of $Li_2SO_4-Na_2SO_4$ compared with the transitions found by NACKEN [1].

The phase diagram constructed from this investigation is shown in Fig. 2. Both the transition points (Fig. 3) and the phase diagram differ considerably from the results obtained by NACKEN [1]. For the concentration range 0 – 10 mole% Na_2SO_4 the results agree with those obtained by AUGUSTSSON and GUSTAFSSON [9].

Two transitions were comparably difficult to detect; the transition between phase II and phase I and the transition in equimolar and early equimolar $Li_2SO_4-Na_2SO_4$ at about 473 °C. NACKEN [1] obtained 520 °C as the demixing point of $LiNaSO_4$, but the transition point at 473 °C can hardly be detected by means of ordinary thermal analysis.

The transition at about 235 °C is much less reproducible then the other transitions and there is also a considerable difference for decreasing and increasing temperature.

The phase diagram of $Li_2SO_4-Na_2SO_4$ resembles that of $Li_2SO_4-Ag_2SO_4$, which recently has been investigated by means of concentration cells [6, 7], and where a b.c.c. phase also has been found. This leads for both systems to unusually complicated phase diagrams.

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[9] B. AUGUSTSSON and J. GUSTAFSSON, Z. Naturforsch. **22 a**, 1634 [1967].