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The Phase Diagram of the System $LiNaSO_4$–$LiKSO_4$ and Crystallographic Parameters and Ionic Conductivity of $Li_2NaK(SO_4)_2$

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The phase diagram of the pseudo-binary system $LiNaSO_4$–$LiKSO_4$ has been investigated by X-ray diffraction and DTA method. The high-temperature phase of $Li_2NaK(SO_4)_2$ is formed by a peritectoid reaction at 500°C. It transforms to an intermediate-temperature phase and a room-temperature phase at 401 and 369°C, respectively. At room temperature $Li_2NaK(SO_4)_2$ crystallizes in an orthorhombic structure with $a = 19.11$, $b = 7.83$, $c = 4.96$ Å. Its high-temperature modification is also orthorhombic with $a = 9.20$, $b = 8.49$, $c = 5.05$ Å. The phase-transition heats and the peritectoid heat of this compound are 447, 27.4, and 32.4 J/g, respectively. The ionic conductivity is very low at room temperature and its activation energy is up to 0.89 eV.

Introduction

The high-temperature modification of Li_2SO_4 with face-center cubic lattice $a = 7.07$ Å (610°C) (*1, 2*) has a very high ionic conductivity (*3*). But since the temperature of the phase transition is as high as 573°C (*4*), Li_2SO_4 has no practical value as a fast ionic conductor. A great deal of work has been undertaken in order to lower the temperature of the phase transition or to stabilize the high-temperature phase at room temperature by adding other components (*5–8*). Schroeder (*8*) investigated the systems Li_2SO_4–Na_2SO_4 and Li_2SO_4–K_2SO_4. We report here our studies of the binary system $LiNaSO_4$–$LiKSO_4$ and of the phase transitions and the ionic conductivity of $Li_2NaK(SO_4)_2$, the only compound within this system.

Experimental

$Li_2SO_4 \cdot H_2O$(A.R.) and Na_2SO_4, K_2SO_4 were used to synthesize $LiNaSO_4$ and $LiKSO_4$, respectively. Samples of $LiNaSO_4$ and $LiKSO_4$ in various ratios were mixed, ground, and pressed into pellets, then sintered below 600°C in a muffle furnace for 15 days.

The DTA measurements were made with a home-made PCR-II-type DTA apparatus.

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Pt crucibles were used as vessels and α-Al_2O_3 powder as a reference material. The temperature was measured and controlled with Pt–PtRh thermocouples. The apparatus was checked by measuring the phase transition of crystalline quartz at 573°C. The precision of the measurement was about ±3°C. The heating and cooling rate was 10°C/min and the experiment was made in the atmosphere.

The phase analyses of the samples at room temperature and at high temperature were made with a Guinier–de Wolff and a Guinier–Lenne monochromatic focusing camera, respectively. Cu$K\alpha$ radiation and silicon or platium as an internal standard were used in both cases.

The specific heat of the compound $Li_2NaK(SO_4)_2$ was measured with a SH-3000-type adiabatic scanning calorimeter made by ULVAC Corp. of Japan. The temperature region measured was from room temperature to 580°C.

For the conductivity measurements a sample $Li_2NaK(SO_4)_2$ was ground and pressed into a pellet, and then sintered at 450°C for 14 days. The sample became a compact thin slice. Electrodes were made by evaporating a layer of gold onto the surface of the sample. The temperature dependence of the dc conductivity was measured with an electrometer, applying a potential of 6 V between the electrodes.

The Phase Diagram of the System $LiNaSO_4$–$LiKSO_4$

The phase diagram of the quasi-binary system $LiNaSO_4$–$LiKSO_4$, as based on the results of phase analyses and DTA measurements, is shown in Fig. 1.

An eutectic reaction $L \rightleftharpoons \alpha' + \beta''$ takes place at 590°C, forming the high-temperature phase α' of $LiNaSO_4$ solid solution and the high-temperature phase β'' of $LiKSO_4$ solid solution. The composition at the eutectic point is 34 mole% $LiKSO_4$. The regions of solid-solution phase α' and β'' were measured with the lattice parameters method.

A eutectoid reaction $\alpha' \rightleftharpoons \alpha + \beta''$ occurs at 485°C, where the phase decomposes into the low-temperature phase α of $LiNaSO_4$ and β''. The composition at the eutectoid point is about 25 mole% $LiKSO_4$. A peritectoid reaction $\beta' + \beta'' \rightleftharpoons \gamma''$ occurs at 500°C, that is β'' solid solution and solid solution β' react to form the phase γ''. Another eutectoid reaction takes place at 474°C. The compound $Li_2NaK(SO_4)_2$ exists in a solid-solution region. It transforms into the intermediate-temperature phase γ' and the low-temperature phase γ when the temperature is lowered to 401 and 369°C, respectively.

Phase α' is the high-temperature phase of $LiNaSO_4$ and crystallizes in a cubic structure with the parameter a = 5.77 Å at 556°C (9). We made X-ray diffraction experiments at 545°C on five samples with compositions of 0, 10, 20, 30, and 35 mole% $LiKSO_4$, respectively. The resulting lattice parameters are plotted in Fig. 2. Based on the "principle" that parameters in single-phase

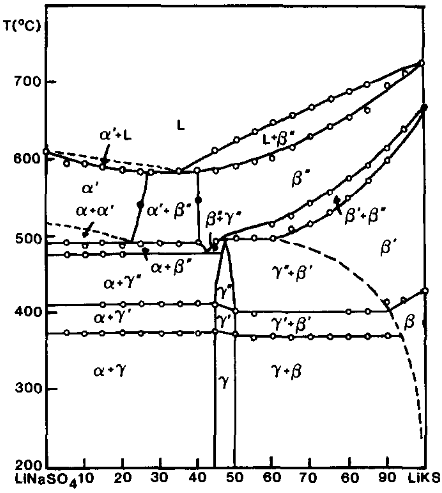

FIG. 1. The pseudo-binary phase diagram of LiNa$SO_4(\alpha)$–$LiKSO_4(\beta)$. ○, From DTA data; ●, from lattice parameters.

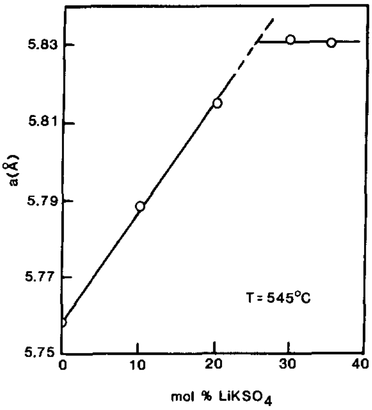

FIG. 2. Variation of lattice parameter *a* with composition in α' solid solution.

regions change with composition while parameters in two-phase regions of binary system do not change with composition, we determined the limit of solid solution at 545°C as 25.5 mole% $LiKSO_4$.

The low-temperature phase α of $LiNaSO_4$ is hexagonal with $a = 7.613$, $c = 9.80$ Å (*10*). A solubility of $LiKSO_4$ in phase α has not been observed.

The structure of the high-temperature phase β'' of $LiKSO_4$ also belongs to the hexagonal system with the lattice parameters $a = 5.31$, $c = 8.82$ Å at 700°C. Its space group is D^4_{6h}-$P6_3/mmc$ (*11*). We also made X-ray diffraction measurements at 563°C on six samples with compositions of 30, 35, 45, 55, 65, and 75 mole% $LiKSO_4$, respectively. The results are shown in Fig. 3. From the composition dependence of the parameters *a* and *c* we determined the limit of solid solution β'' to be 40 mole% $LiKSO_4$ at 563°C.

There is still some dispute about the structure of the intermediate-temperature phase β' of $LiKSO_4$ (*8*, *11*). $LiNaSO_4$ has the highest solubility in the phase β' at 500°C, at the composition 60 mole% $LiKSO_4$. The low-temperature phase β of $LiKSO_4$ also has a hexagonal structure with space group C^6_6-$P6_3$ (*12*, *13*). The solubility of $LiNaSO_4$ in phase β is very small and negligible at room temperature. With rising temperature the solubility increases slowly.

Investigation of $Li_2NaK(SO_4)_2$

1. X-Ray Diffraction Results

Because the intermediate-temperature phase γ' of the compound $Li_2NaK(SO_4)_2$ exists in a narrow temperature region, the pure phase is difficult to obtain. Here we only discuss the structures of the room-temperature phase γ and the high-temperature phase γ''.

X-ray diffraction data of the room-temperature phase were indexed by the TREOR program (*14*) and the indexing results are listed in Table I. The indexing results show that the structure of the room-temperature phase belongs to the orthorhombic system with lattice parameters $a = 19.11$, $b = 7.83$, and $c = 4.96$ Å. Its density was measured to be 2.39 g/cm^3. Assuming $Z = 4$, the X-ray density is calculated as 2.40 g/cm^3, in good agreement with the measured value. According to the indexing results, for *hkl* diffraction no systematic extinction occurs; for 0*k*0 diffraction only diffraction lines with $k = 2n$ exist; and for 00*l* diffraction only those with $l = 2n$ exist. So the possible space group is $P22_12_1$. Because

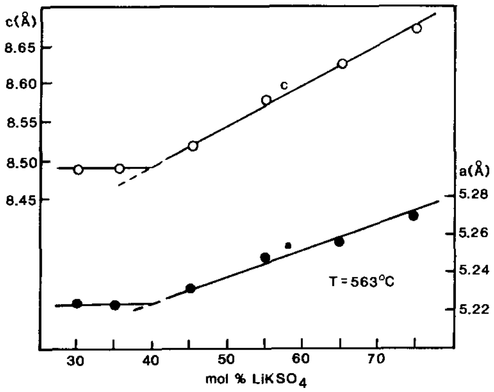

FIG. 3. Variation of the lattice parameters *a* and *c* with composition in β'' solid solution.

TABLE I

X-Ray Diffraction Data of the Room-Temperature Phase γ-$Li_2NaK(SO_4)_2$ and Indexing Based on an Orthorhombic Cell with a = 19.11, b = 7.83, c = 4.96 Å

No.	$h\ k\ l$	d_{calc}	d_{obs}	I/I_0	No.	$h\ k\ l$	d_{calc}	d_{obs}	I/I_0
1	2 0 0	9.555	9.566	m	29	2 3 1	2.245	2.245	w
2	1 1 0	7.244	7.236	m	30	3 1 2	2.217	2.217	m
3	2 1 0	6.055	6.056	m	31	3 3 1	2.171	2.173	w
4	4 0 0	4.778	4.773	m	32	5 3 0	2.155	2.154	w
5	0 1 1	4.190	4.184	w		8 0 1	2.152		
6	4 1 0	4.078	4.081	vs	33	0 2 2	2.095	2.096	w
7	0 2 0	3.914	3.910	vs	34	5 0 2	2.080	2.079	w
	3 0 1	3.914				4 3 1	2.079		
8	2 1 1	3.834	3.834	s	35	9 1 0	2.049	2.047	w
	1 2 0	3.834				2 2 2	2.046		
9	2 2 0	3.622	3.620	m	36	7 2 1	2.041	2.039	m
10	3 1 1	3.501	3.493	w		8 2 0	2.039		
11	3 2 0	3.335	3.332	w	37	3 2 2	1.990	1.991	w
12	6 0 0	3.185	3.184	s	38	5 3 1	1.977	1.975	w
13	4 1 1	3.150	3.149	m	39	10 0 0	1.911	1.914	w
14	0 2 1	3.073	3.071	m	40	7 3 0	1.886	1.886	f
15	4 2 0	3.028	3.027	vs		8 2 1	1.886		
	5 1 0	3.028			41	9 2 0	1.866	1.866	w
16	6 1 0	2.950	2.948	m	42	5 2 2	1.837	1.838	w
17	2 2 1	2.925	2.924	s		7 0 2	1.836		
18	5 1 1	2.824	2.823	s	43	4 4 0	1.811	1.810	w
19	3 2 1	2.768	2.766	vs	44	2 4 1	1.788	1.788	w
20	5 2 0	2.735	2.732	m		7 1 2	1.787		
	7 0 0	2.730			45	5 4 0	1.742	1.741	m
21	1 3 0	2.585	2.584	m	46	8 1 2	1.680	1.681	w
	4 2 1	2.584			47	11 0 1	1.640	1.639	w
22	6 1 1	2.536	2.535	w	48	0 1 3	1.618	1.617	f
23	0 0 2	2.480	2.481	s	49	8 2 2	1.575	1.576	f
24	1 0 2	2.459	2.460	w	50	9 3 1	1.563	1.564	f
25	7 0 1	2.392	2.390	m		4 0 3	1.562		
	8 0 0	2.389			51	11 2 1	1.512	1.512	f
26	1 1 2	2.346	2.347	w	52	2 2 3	1.504	1.504	f
27	3 0 2	2.311	2.311	w	53	9 2 2	1.491	1.491	f
	0 3 1	2.309				5 1 3	1.490		
28	2 1 2	2.295	2.296	w	54	3 2 3	1.481	1.481	f
	1 3 1	2.293							

the $0k0$ and $00l$ diffraction data are scarce, other possible space groups are *Pmmm*, *Pmm*2, or *P*222.

X-ray diffraction data and the indexing results of the high-temperature phase γ'' are listed in Table II. The indexing results show that the high-temperature phase also belongs to the orthorhombic system with parameters a = 9.20, b = 8.49, c = 5.05 Å at 457°C. With the number of formula unit per unit cell Z = 2, the calculated density is 2.25 g/cm^3. Based on the indexing results (for hkl diffraction no systematic extinction occurs; for $h0l$ diffraction only lines with $h + l = 2n$ exist) the possible space group is either *Pmn*2 or *Pmnm*.

TABLE II

X-RAY DATA OF THE HIGH-TEMPERATURE PHASE γ''-$Li_2NaK(SO_4)_2$ AT 457°C AND INDEXING BASED ON AN ORTHORHOMBIC CELL WITH $a = 9.20$, $b = 8.49$, $c = 5.05$ Å

No.	$h\ k\ l$	d_{calc}	d_{obs}	I/I_0	No.	$h\ k\ l$	d_{calc}	d_{obs}	I/I_0
1	1 0 1	4.428	4.423	m	19	3 3 0	2.081	2.082	m
2	0 2 0	4.247	4.241	m	20	4 1 1	2.033	2.035	m
3	2 1 0	4.046	4.043	vs	21	2 4 0	1.928	1.929	f
4	1 1 1	3.926	3.922	vs	22	3 1 2	1.900	1.901	w
5	1 2 0	3.856	3.850	m	23	1 3 2	1.846	1.847	w
6	2 1 1	3.158	3.156	s	24	2 4 1	1.801	1.800	w
7	2 2 0	3.121	3.120	m		5 1 0	1.799		
8	1 2 1	3.065	3.064	vs	25	2 3 2	1.744	1.744	f
9	3 1 0	2.885	2.885	m	26	4 0 2	1.701	1.699	f
10	1 3 0	2.706	2.705	m		0 5 0	1.699		
11	3 0 1	2.622	2.622	s	27	4 3 1	1.683	1.685	w
12	0 0 2	2.526	2.524	m	28	3 4 1	1.650	1.650	w
13	3 1 1	2.505	2.506	w	29	1 1 3	1.626	1.625	w
14	2 3 0	2.411	2.411	m		0 4 2	1.625		
15	1 3 1	2.385	2.388	w	30	1 2 3	1.543	1.544	f
16	2 0 2	2.214	2.214	w	31	3 0 3	1.476	1.477	f
17	2 1 2	2.142	2.142	f		5 3 1	1.476		
18	0 4 0	2.124	2.123	m					

2. *Phase Transitions*

The result of our calorimetric measurements on $Li_2NaK(SO_4)_2$ is shown in Fig. 4.

The specific-heat curve shows three peaks. The first corresponds to the transition from the room-temperature phase γ to the intermediate-temperature phase γ'; the second corresponds to the transition from the intermediate-temperature phase γ' to the high-temperature phase γ''; and the third is the heat effect of the peritectoid decomposition of the phase γ'': $\gamma'' \rightleftharpoons \beta' + \beta''$.

The heats of transformation and the peritectoid heat of the compound were determined from the areas of the phase transition peaks and the decomposition peak, respectively, as 44.7 J/g at 369°C and 27.4 J/g at 401°C and 32.4 J/g at 500°C, respectively.

3. *Ionic Conductivity*

The temperature dependence of the conductivity of $Li_2NaK(SO_4)_2$ is shown in Fig. 5 in a log σ vs $1/T$ plot. The logarithmic increase of the conductivity with temperature means that the conduction of $Li_2NaK(SO_4)_2$ is mainly caused by an ionic transport. According to Arrhenius' equation:

$$\sigma = \sigma_0 \exp(-E/kT),$$

where E is an activation energy and k is the Boltzmann constant. From our plot we derive $E = 0.89$ eV.

It can also be seen from Fig. 5 that the ionic conductivity of $Li_2NaK(SO_4)_2$ at room

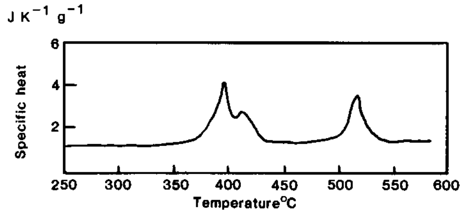

FIG. 4. Variation of the specific heat of $Li_2NaK(SO_4)_2$ with temperature.

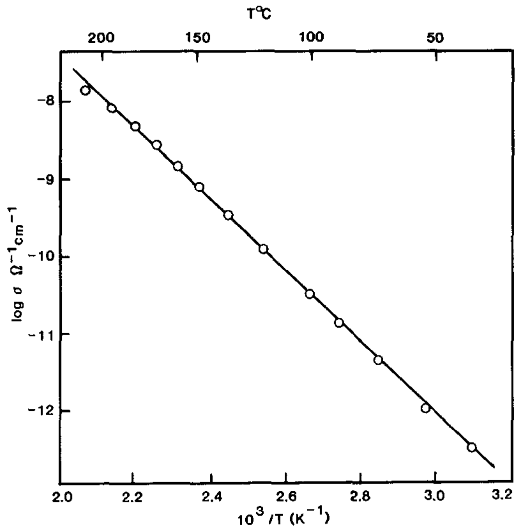

FIG. 5. Variation of the ionic conductivity of $Li_2NaK(SO_4)_2$ with temperature.

temperature is very low (of the order of 10^{-13} $(\Omega\ cm)^{-1}$. Although with rising temperature, the conductivity increases, it is still very small at 200°C ($\sim 10^{-8}$ $(\Omega\text{-cm})^{-1}$) and its activation energy is high: up to 0.89 eV. Thus, the ionic conductivity of $Li_2NaK(SO_4)_2$ around room temperature is not an attractive property for technical application.

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