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Investigation of Double Sulfates of Lithium and Rare Earth Elements*

S. P. SIROTINKIN, A. N. POKROVSKII, AND L. M. KOVBA

Department of Inorganic Chemistry, Moscow State University, Moscow, USSR

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Compounds in the system Li_2SO_4–$R_2(SO_4)_3$, where R is a rare earth element, have been investigated. Only compounds of the type $LiR(SO_4)_2$ are formed. The existence of three structural types has been established. X-Ray parameters from Nd to Er have been determined. The thermal stability of the compounds has been investigated.

The purpose of this work was to study the possibility of obtaining chemical compounds in the Li_2SO_4–$R_2(SO_4)_3$ systems where R is a rare earth element. Anhydrous sulfates of lithium and the rare earth elements were used. All the sulfates were carefully heated in air at a temperature of 500–600°C for a period of 2–3 hr to remove any absorbed water.

Thermographic and thermogravimetric studies were conducted on the differential graph of the OD-103 system of F. Paulik, I. Paulik, and L. Erdey. Heating curves were also recorded on a FRU-64 pyrometer. Each specimen was heated in air to a temperature of 1050°C for 100 min by using a special heating oven. X-rays of the specimens were taken on a Guinier–Wolf monochromator camera.

Mixtures of stoichiometric amounts of the anhydrous sulfates of lithium and the rare earth elements were annealed at a temperature of 500°C for 100 hr. X-ray analysis of the specimens indicated that in the Li_2SO_4–$R_2(SO_4)_3$ systems only one compound of the composition $LiR(SO_4)_2$ is formed, which is also substantiated by chemical analysis data. The results support reports given by the authors of references (*1*, *2*), which pertain to a study of the Li_2SO_4–$R_2(SO_4)_3$ systems where R = Eu, Gd, Tb. We have established that binary sulfates of the composition $LiR(SO_4)_2$ crystallize in three structural types: $LiPr(SO_4)_2$ belongs to the first; binary sulfates of the rare earth elements from Nd to Er inclusive belong to the second; and binary sulfates from thulium to lutetium belong to the third. We have discovered existence of a high temperature modification α–$LiNd(SO_4)_2$, having a temperature for the β–α conversion of 585°C, which is isostructural with $LiPr(SO_4)_2$. In our opinion, endothermic effects at 584°C for $LiEu(SO_4)_2$, 616°C for $LiEr(SO_4)_2$, 573°C for $LiTm(SO_4)_2$, 600°C for $LiYb(SO_4)_2$ and 573°C for $LiLu(SO_4)_2$ are also related to polymorphism in these compounds. Attempts to anneal the high-temperature modifications, however, proved fruitless, which may be explained by a great speed of the reverse conversion of the high-temperature modification of $LiR(SO_4)_2$ to the low. X-ray data of the compound β–$LiNd(SO_4)_2$ indicate the tetragonal class. The probable space group is $P4_2/mnm$ with cell parameters $a = 7.708 \pm 0.003$ Å, $c = 5.665 \pm 0.005$Å, $Z = 2$, $\rho exp = 3.41$, $\rho calcd = 3.41$.

Results of indexing the powder photograph of β–$LiNd(SO_4)_2$ are shown in Table I, and the parameters of the isostructural compounds, in Table II. As seen in Table II, decrease in the volume of the crystal lattice occurs with an increase in the magnitude of the atomic number of the rare earth element,

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TABLE I

RESULTS OF INDEXING X-RAY DIFFRACTOGRAMS OF β-$LiNd(SO_4)_2$

I	exptl $1/d^2 \times 10^4$	calcd $1/d^2 \times 10^4$	$h\ k\ l$
90	336.3	336.5	1 1 0
90	480.5	480.0	1 0 1
85	649.4	648.2	1 1 1
10	673.6	672.9	2 0 0
20	841.1	841.2	2 1 0
100	1153	1153	2 1 1
15	1247	1247	0 0 2
30	1347	1346	2 2 0
30	1583	1584	2 1 2
25	1685	1682	3 1 0
80	1826	1826	3 0 1
15	1916	1920	2 0 2
10	1993	1994	3 1 1
35	2500	2499	3 2 1
40	2592	2593	2 2 2
10	2690	2692	4 0 0
45	2931	2929	3 1 2
15	2973	2974	1 0 3
10	3032	3028	3 3 0
40	3174	3172	4 1 1
15	3368	3365	4 2 0
30	3642	3647	2 1 3
20	3936	3939	4 0 2
5	4104	4107	4 1 2
10	4277	4275	3 3 2
10	4323	4320	3 0 3
5	4374	4374	5 1 0
20	4523	4518	5 0 1, 4 3 1

which is simply explained by a decrease in the radius of the rare earth element with increasing atomic number. From the powder data we could not determine parameters of the crystal lattices for the compounds $LiPr(SO_4)_2$ and β-$LiR(SO_4)_2$ (R = Tm, Yb, Lu), which can be done only by using single crystal data. In Table III are shown the interplanar spacings for the compounds $LiPr(SO_4)_2$ and β-$LiTm(SO_4)_2$. A partial annealing of the specimen of the $LiEr(SO_4)_2$ compound has established that α-$LiEr(SO_4)_2$ is isostructural with β-$LiTm(SO_4)_2$. Thus, the end members of the (Nd–Er) series which crystallize in the second structure type of compound of the composition $LiR(SO_4)_2$ have high-temperature modifications that are correspondingly isostructural with $LiPr(SO_4)_2$, related to the first structure type, and to β-$LiTm(SO_4)_2$, a representative of the third structure type.

Differential-thermal analysis of the double sulfates of lithium and rare earth elements has shown incongruent melting character for all the compounds with composition $LiR(SO_4)_2$, the first products of dissolution being the starting sulfates, whereas at higher temperatures thermal decomposition of the rare earth element sulfate occurs with formation of oxysulfates and, subsequently, oxides:

$$LiR(SO_4)_2 \rightarrow \text{melt} + R_2(SO_4)_3 \rightarrow \text{melt} + R_2O_2SO_4 \rightarrow \text{melt} + R_2O_3$$

with evolution of SO_2 and oxygen.

TABLE II

LATTICE PARAMETERS OF THE COMPOUNDS $LiR(SO_4)_2$ BELONGING TO STRUCTURE TYPE 2

Compound	a (Å)	c (Å)	V (Å^3)
β-$LiNd(SO_4)_2$	7.708 ± 0.003	5.665 ± 0.005	336.58
$LiSm(SO_4)_2$	7.682 ± 0.003	5.666 ± 0.005	334.37
β-$LiEu(SO_4)_2$	7.652 ± 0.003	5.567 ± 0.006	325.96
β-$LiGd(SO_4)_2$	7.648 ± 0.002	5.565 ± 0.004	325.50
$LiTb(SO_4)_2$	7.613 ± 0.002	5.530 ± 0.003	320.51
$LiDy(SO_4)_2$	7.597 ± 0.003	5.506 ± 0.004	317.17
$LiHo(SO_4)_2$	7.580 ± 0.002	5.486 ± 0.004	315.21
β-$LiEr(SO_4)_2$	7.573 ± 0.003	5.472 ± 0.006	313.82

TABLE III

X-RAY DATA FOR THE COMPOUNDS $LiPr(SO_4)_2$ AND β-$LiTm(SO_4)_2$

$LiPr(SO_4)_2$				β-$LiTm(SO_4)_2$			
I	*d*	I	*d*	I	*d*	I	*d*
50	13.310	10	2.817	5	6.202	60	2.597
25	6.657	35	2.749	30	5.852	30	2.549
100	6.001	15	2.632	20	4.918	15	2.467
10	4.777	10	2.547	100	4.534	5	2.409
20	4.562	8	2.528	20	4.077	20	2.312
30	4.431	10	2.505	10	4.029	45	2.264
35	4.251	12	2.352	15	3.997	10	2.243
5	3.811	8	2.273	20	3.877	5	2.221
10	3.579	25	2.208	20	3.757	30	2.162
40	3.515	8	2.180	5	3.633	8	2.142
60	3.398	8	2.134	35	3.539	20	2.122
3	3.361	25	2.123	15	3.506	30	2.079
15	3.321	8	2.062	95	3.309	25	2.039
15	3.276	8	2.000	35	3.200	25	2.012
10	3.102	45	1.916	5	3.162	15	1.985
70	3.035	10	1.901	40	3.099	45	1.972
80	3.007	10	1.883	45	2.984	10	1.946
5	2.976	15	1.857	5	2.921	15	1.930
10	2.955	10	1.831	50	2.754	20	1.909
3	2.864	10	1.763	35	2.622		

TABLE IV

TEMPERATURES OF INCONGRUENT MELTING OF $LiR(SO_4)_2$

Compound	*T*°C	Compound	*T*°C
$LiPr(SO_4)_2$	720	$LiDy(SO_4)_2$	710
$LiNd(SO_4)_2$	710	$LiHo(SO_4)_2$	681
$LiSm(SO_4)_2$	760	$LiEr(SO_4)_2$	630
$LiEu(SO_4)_2$	780	$LiTm(SO_4)_2$	608
$LiGd(SO_4)_2$	788	$LiYb(SO_4)_2$	660
$LiTb(SO_4)_2$	739	$LiLu(SO_4)_2$	655

The fusion temperatures of the compounds of composition $LiR(SO_4)_2$ are presented in Table IV.

Results

1. In Li_2SO_4–$R_2(SO_4)_3$ systems where *R* is a rare earth element, only compounds of the composition $LiR(SO_4)_2$ are formed. The existence of three structural types of $LiR(SO_4)_2$ compounds has been established.

2. The parameters of the crystal lattices of the $LiR(SO_4)_2$ compounds from Nd to Er have been determined.

3. The thermal stability of the double sulfates of lithium and rare earth elements has been investigated.

References

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