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ABSTRACT

LiYS₂ with the hexagonal α -NaFeO₂ structure has been prepared from isostructural NaYS₂ by ion-exchange in a molten LiCl/KCl mixture at a relatively low temperature as compared to previous syntheses using high-temperature solid state reactions. The X-ray powder diffraction data from α -NaFeO₂-type LiYS₂ are reported in this paper. This ion-exchange can be completely reversed to form NaYS₂ from LiYS₂ using a molten NaI/KI mixture.

MATERIALS INDEX: Ternary sulfides, lithium, sodium, yttrium

Introduction

Currently, there is interest in the ionic conductivity (1,2) and infrared transmission (3) of compounds derived from the A₂LnS₂ (A = Li, Na, K; Ln = Y, rare earth) family. These compounds adopt two structures featuring six-fold cation coordination—the cubic NaCl and hexagonal α -NaFeO₂ structures—and one structure with eight-fold cation coordination derived from the cubic Th₃P₄ structure. The NaCl and α -NaFeO₂ structures are illustrated in Figure 1; in the former the two cation types are disordered while in the latter they are segregated on alternate (111) rock salt planes, thus lowering the symmetry to hexagonal. A structure field map compiled from previous reports (4-8) of single-phase compounds in the A₂LnS₂ system is shown in Figure 2 and was prepared using six-coordinate crystal radii (9). For certain members of the series with borderline cation radius ratio values, both six-coordinate structure types are known and are interrelated by an order-disorder transition (4). For the sodium and lithium series, the borderline radius ratio values that correlate with the presence of an order-disorder transition between the NaCl and the α -NaFeO₂ forms are 1.03-1.06 and 0.85-0.88 ($r_{A^+}/r_{Ln^{3+}}$), respectively. In the potassium series, only the ordered α -NaFeO₂ structure is observed owing to the large size of K⁺ relative to that of the trivalent metal ions.

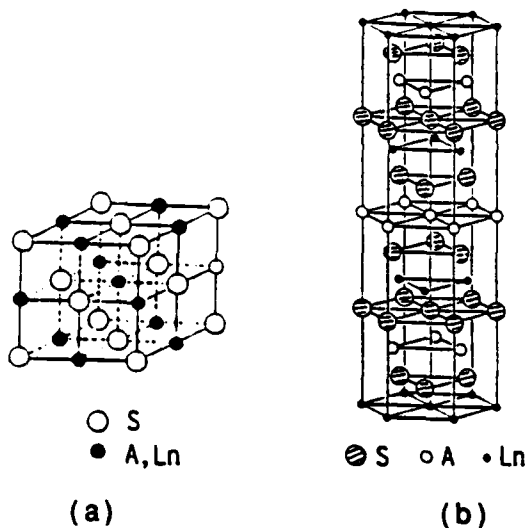


FIG. 1

Six-coordinate structure types adopted by $AlnS_2$ compounds ($A = Li, Na, K; Ln = Y, \text{rare earth}$); (a) cubic NaCl structure with disordered cations and (b) hexagonal $\alpha\text{-NaFeO}_2$ structure with cation types ordered on alternate (111) planes of the parent NaCl structure.

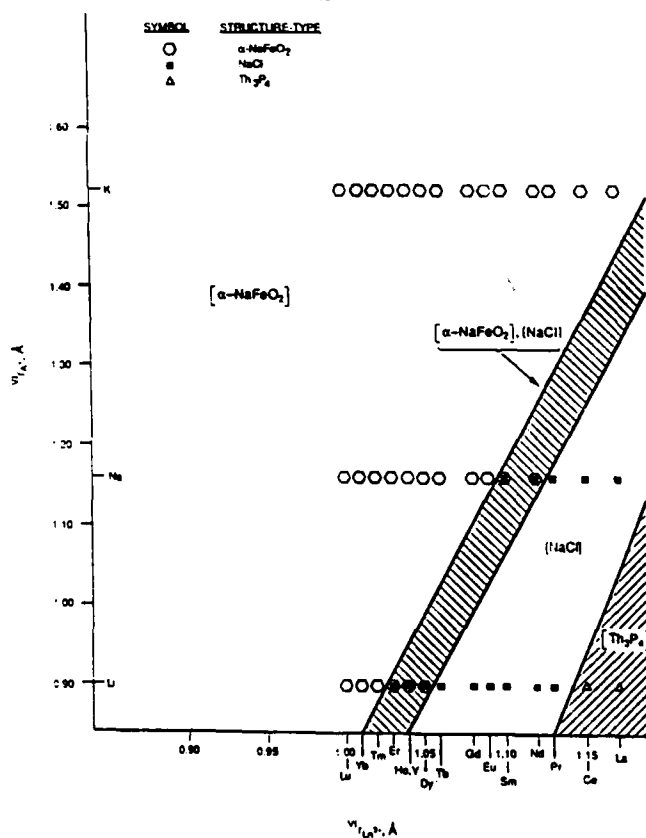


FIG. 2

Structure field map for $AlnS_2$ compounds ($A = Li, Na, K; Ln = Y, \text{rare earth}$) (4-8) using six-coordinate crystal radii (9).

In previous reports, the lithium compounds (LiLnS_2) have been synthesized by high-temperature (900°C) solid state reactions under flowing H_2S starting with Li_2CO_3 and Ln_2O_3 (5,7) or LiCl and LnCl_3 (8), or directly from the elements in evacuated silica ampules (4). These syntheses employ an excess of the alkali metal reagent which can be removed from the relatively stable ternary products with water.

LiYS_2 with the disordered NaCl structure was reported in 1965 (5). Recent work (4) has shown that ordered $\alpha\text{-NaFeO}_2$ -type LiYS_2 can also be prepared by carefully annealing the rock salt form.

The present work describes the facile preparation of LiYS_2 with the ordered $\alpha\text{-NaFeO}_2$ structure at a relatively low temperature (500°C) using a molten salt ion-exchange procedure.

Experimental

NaYS_2 was prepared from Na_2S (Alfa, anhydrous) and Y_2S_3 (Cerac 99.9%) in the mol ratio 1.5:1, respectively (6). The reactants were ground in air with an agate mortar and pestle and reacted in a graphite crucible enclosed in an evacuated silica ampule at 950°C for 15 days. The product was ground, washed with distilled water to remove the excess sodium sulfide, rinsed with acetone, and dried in air.

Ion-exchange reactions were performed in molten LiCl/KCl 46/54 wt % eutectic mixtures (m.p. = 355°C (10)). The NaYS_2 and a 50X (Li) molar excess of the chloride mixture were reacted in graphite crucibles enclosed in evacuated silica ampules. The chlorides were removed from the sulfide product by quickly washing with distilled water, followed by an acetone rinse and drying in air. Reverse-exchange reactions of the resulting LiYS_2 were performed with a 40X (Na) molar excess of a NaI/KI 56/44 wt % eutectic mixture (m.p. = 583°C (11)) in a like manner.

X-ray powder diffraction patterns were obtained with a Scintag PAD V diffractometer using $\text{CuK}\alpha$ radiation. Unit cell parameters were obtained by a least-squares refinement program. Elemental analysis was carried out by Schwarzkopf Microanalytical Laboratory.

Results and Discussion

The X-ray powder diffraction data, given in Table 1, from the light-beige platelets of NaYS_2 were indexed on a hexagonal unit cell ($a = 3.9635(3)$, $c = 19.893(2)$ Å) in good agreement with literature values (4,6,7).

Essentially single-phase LiYS_2 with the $\alpha\text{-NaFeO}_2$ structure was obtained, as described above, by ion-exchange of NaYS_2 at 500°C for 24 hours; elemental analysis indicated that at least 97% of the Na had been exchanged. The LiYS_2 produced in this manner is very similar in color and morphology to the NaYS_2 . The X-ray powder diffraction data, given in Table 1, were indexed on a hexagonal unit cell ($a = 3.9033(7)$, $c = 18.522(5)$ Å) in good agreement with that reported for $\alpha\text{-NaFeO}_2$ -type LiYS_2 (4).

In contrast, heating the $\text{NaYS}_2/\text{LiCl/KCl}$ reaction mixture at 370°C for 3 hours produced no reaction; only the starting material NaYS_2 was observed by X-ray powder diffraction. Reaction times of 4 and 8 hours at 500°C resulted in incomplete ion-exchange; mixtures of NaYS_2 and LiYS_2 were observed by X-ray powder diffraction. No shifts in unit cell parameters, arising from possible mixing of Na and Li in one phase, were observed in any of these samples.

The $\text{NaYS}_2\text{-Li}^+$ ion-exchange reaction is reversible: NaYS_2 was obtained from the $\alpha\text{-NaFeO}_2$ -type LiYS_2 by ion-exchange in a NaI/KI mixture, as described above, at 595°C for 16 hours. The unit cell obtained by refinement of the X-ray powder diffraction data indicated

single-phase NaYS₂. This reversibility is surprising in consideration of the larger ionic size of Na⁺ versus Li⁺ and the larger unit cell volume of NaYS₂ versus LiYS₂ (270.64 vs. 244.39 Å³). In the present study, the larger K⁺ ion was not found to exchange into these compounds to form KYS₂.

TABLE 1
Indexed X-Ray Powder Diffraction Data.

NaYS ₂						LiYS ₂					
h	k	l	d _{obs}	d _{calc}	I	h	k	l	d _{obs}	d _{calc}	I
0	0	3	6.67	6.6311	100	0	0	3	6.21	6.1741	100
1	0	1	3.387	3.3825	9	1	0	1	3.329	3.3254	20
0	0	6	3.321	3.3156	10	0	1	2	3.181	3.1754	3
0	1	2	3.250	3.2447	7	0	0	6	3.095	3.0871	3
1	0	4	2.828	2.8250	49	1	0	4	2.732	2.7303	58
0	1	5	2.601	2.5990	4	0	1	5	2.499	2.4970	16
0	0	9	2.212	2.2104	2	1	0	7	2.0845	2.0836	9
1	0	7	2.1896	2.1890	8	0	0	9	2.0592	2.0580	9
0	1	8	2.0142	2.0138	21	1	1	0	1.9525	1.9516	15
1	1	0	1.9826	1.9818	7	0	1	8	1.9108	1.9102	25
1	1	3	1.8994	1.8988	5	1	1	3	1.8616	1.8609	8
1	0	10	1.7216	1.7212	2	0	2	1	1.6848	1.6832	3
0	2	1	1.7101	1.7099	1	0	2	4	1.5866	1.5877	10
1	1	6	1.7014	1.7010	1	0	0	12	1.5436	1.5435	8
0	0	12	1.6583	1.6578	16	0	1	11	1.5066	1.5072	3
0	2	4	1.6228	1.6224	12	0	2	7	1.4239	1.4244	3
0	1	11	1.6001	1.6000	5	1	1	9	1.4160	1.4161	3
2	0	5	1.5761	1.5759	1	2	0	8	1.3649	1.3651	5
1	1	9	1.4758	1.4755	1	1	0	13	1.3127	1.3129	2
0	2	7	1.4694	1.4691	2	2	1	1	1.2742	1.2746	2
2	0	8	1.4128	1.4125	4	0	1	14	1.2320	1.2320	4
0	0	15	1.3260	1.3262	3	1	1	12	1.2102	1.2107	7
0	1	14	1.3126	1.3129	1	3	0	0	1.1271	1.1268	2
2	1	1	1.2943	1.2946	1	1	2	8	1.1183	1.1186	3
1	1	12	1.2712	1.2715	6						
2	1	4	1.2551	1.2554	3						
2	0	11	1.2447	1.2449	1						
1	2	5	1.2332	1.2334	1						
2	1	7	1.1800	1.1802	1						
1	0	16	1.1689	1.1690	3						
1	2	8	1.1501	1.1502	2						
3	0	0	1.1441	1.1442	2						
0	0	18	1.1051	1.1052	1						
1	1	15	1.1020	1.1022	2						

Hexagonal, R $\bar{3}m$ a = 3.9635(3) Å c = 19.893(2) Å	Hexagonal, R $\bar{3}m$ a = 3.9033(7) Å c = 18.522(5) Å
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The mechanism of these NaYS₂-LiYS₂ reactions is likely related to the ionic mobility associated with ionic conductivity (1,2); in the α -NaFeO₂ structure, the monovalent cations are segregated into planes (see Fig. 1b) comprising continuous potential pathways for diffusion. Other examples of bulk ion-exchange in solids with this structure include Ag⁺ for Li⁺ (12) and H⁺ for Li⁺ (13) in α -LiAlO₂ and H₃O⁺ for Na⁺ (14) in α -NaCrO₂.

Conclusions

An ion-exchange reaction has been used to prepare phase-pure α -NaFeO₂-type LiYS₂ from isostructural NaYS₂. This represents an alternative low-temperature synthetic route to compounds prepared only with difficulty, or not at all, by conventional high-temperature solid state reactions. This reaction can be reversed, despite the larger size of the Na⁺ ion—a result consistent with the layered structures and ionic mobilities of the compounds. The present results demonstrate the applicability of this low-temperature method to ternary sulfide systems.

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