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INVESTIGATION OF PHASE EQUILIBRIA IN THE SYSTEMS K_2SO_4—$Sc_2(SO_4)_3$, Rb_2SO_4—$Sc_2(SO_4)_3$ AND Cs_2SO_4—$Sc_2(SO_4)_3$

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ABSTRACT

Phase diagrams of the systems K_2SO_4—$Sc_2(SO_4)_3$, Rb_2SO_4—$Sc_2(SO_4)_3$ and Cs_2SO_4—$Sc_2(SO_4)_3$ have been investigated by X-ray diffraction phase analysis and differential thermal analysis techniques. A salient feature of all the systems is the formation of $M_3Sc(SO_4)_3$, which melt incongruently, and $MSc(SO_4)_2$, which on heating decompose in the solid state.

INTRODUCTION

At present, there are numerous data in the literature on the thermal stability of nonaqueous double sulfates of scandium with potassium, rubidium and cesium of different compositions. However, the results obtained by different authors for the same compounds are conflicting. Thermograms of the double sulfates $M_3Sc(SO_4)_3$ and $MSc(SO_4)_2$ (M = K, Rb, Cs; see Table 1) differ both in the number of phase transitions and in the transition temperatures. Such disagreements may, in our opinion, be explained by different synthesis conditions of the compounds under investigation. For instance, some workers [1,4] synthesized their samples from solutions in accordance with solubility data for the triple systems M_2SO_4—$Sc_2(SO_4)_3$—H_2O; others [2,5] prepared samples by a solid-phase synthesis technique by heating at different temperatures for 2—3 h. while Remizov et al. [3] report no data concerning their preparation technique. It should be taken into account that the phase composition of high-temperature calcination products may also depend on the calcination conditions because of the decomposition of scandium sulfate.

In this work we studied the phase diagrams of the systems K_2SO_4—$Sc_2(SO_4)_3$, Rb_2SO_4—$Sc_2(SO_4)_3$ and Cs_2SO_4—$Sc_2(SO_4)_3$ synthesized by the technique used to obtain double sulfates of alkali and rare-earth elements (see, for instance, refs. 6—8).

EXPERIMENTAL

Sulfates of the alkali metals and a nonaqueous sulfate of chemically pure scandium were used as starting materials. The initial sulfates were precal-

TABLE 1

Results of the thermographic investigation of the double sulfates $M_3Sc(SO_4)_3$ and $MSc(SO_4)_2$ (M = K, Rb, Cs)

Compound	Temperature (°C)	Type of transformation	Ref.
$KSc(SO_4)_2$	180— 240	Removal of crystallization water	1
	440— 450	Reversible phase transition	
	800—1200	Incongruent melting	
	410	Solid-phase decomposition	2
$K_3Sc(SO_4)_3$	826	Phase transition	3
	976	Incongruent melting	
	180— 240	Removal of crystallization water	1
	610— 620	Reversible phase transition	
	800—1200	Incongruent melting	
	650	Formation of the compound	2
	935	Congruent melting	
$RbSc(SO_4)_2$	1062	Incongruent melting	3
	>800	Decomposition into Rb_2SO_4 and Sc_2O_3	4
	924	Congruent melting	2
$Rb_3Sc(SO_4)_3$	950	Incongruent melting	4
		Compound was not found	2
$CsSc(SO_4)_2$	1114	Incongruent melting	3
	>800	Decomposition into Cs_2SO_4 and Sc_2O_3	4
		Compound was not found	5
$Cs_3Sc(SO_4)_3$	900	Incongruent melting	4
	600	Incongruent melting	5

cinated at 440°C to remove the adsorbed water. The samples were prepared in steps of 5 mole % (near individual compounds, and for refining the eutectic the step was 1—2.5 mole %). The synthesis was performed by annealing mixtures of the original sulfates in alundum crucibles at 600°C for 250—300 h; the oven temperature was then gradually lowered to room temperature. The samples were repeatedly washed with acetone to ensure better mixing.

The phase composition of the samples was determined by X-ray diffraction analysis in a Guiner—De Wolf camera-monochromator (Cu*K*α radiation).

The thermograms were recorded by a Kurnakov FRU-64 pyrometer at a heating rate of 10—15°C $\min^{-1}$. A Pt—PtRh thermocouple was used to measure the temperature to an accuracy of ±10°C.

To elucidate the nature of the thermal effects the samples were placed in ampoules and tempered in water starting at different temperatures.

RESULTS AND DISCUSSION

The phase diagrams of the M_2SO_4—$Sc_2(SO_4)_3$ (M = K, Rb, Cs) systems are presented in Figs. 1—3. The formation of two compounds, $M_3Sc(SO_4)_3$ and $MSc(SO_4)_2$, is typical for all three systems.

The double sulfates $M_3Sc(SO_4)_3$ (M = K, Rb, Cs) form eutectics containing 85, 88 and 86.5 mole % M_2SO_4 with an alkali metal sulfate. Their melting temperatures are 850, 830 and 780°C, respectively. Compounds $K_3Sc(SO_4)_3$, $Rb_3Sc(SO_4)_3$ and $Cs_3Sc(SO_4)_3$ melt incongruently at 950, 940 and 880°C with the formation of scandium sulfate, which at these temperatures decomposes into scandium oxide, sulfur dioxide and oxygen [9], as was established in a previous derivatographic investigation [10] of these compounds. Diffused thermal effects at 1000°C correspond to this decomposition process. These effects are not presented in Figs. 1—3, since this region is not quasibinary and is not considered in the present work.

The endothermal effect observed at 350°C on the heating curves of samples containing $K_3Sc(SO_4)_3$ is considered to be a polymorphous transformation of this salt. However, rapid cooling of the samples containing 95—55 mole % K_2SO_4 from 400°C did not reveal phases with other structures, prob-

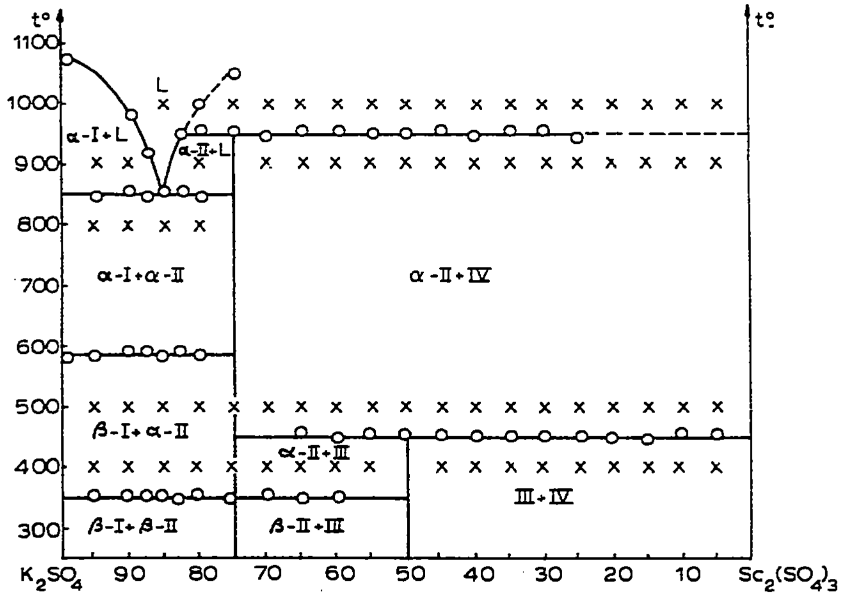

Fig. 1. Phase equilibrium diagram of the K_2SO_4—$Sc_2(SO_4)_3$ system. I, K_2SO_4; II, $K_3Sc(SO_4)_3$; III, $KSc(SO_4)_2$; IV, $Sc_2(SO_4)_3$; ×, points of rapid cooling.

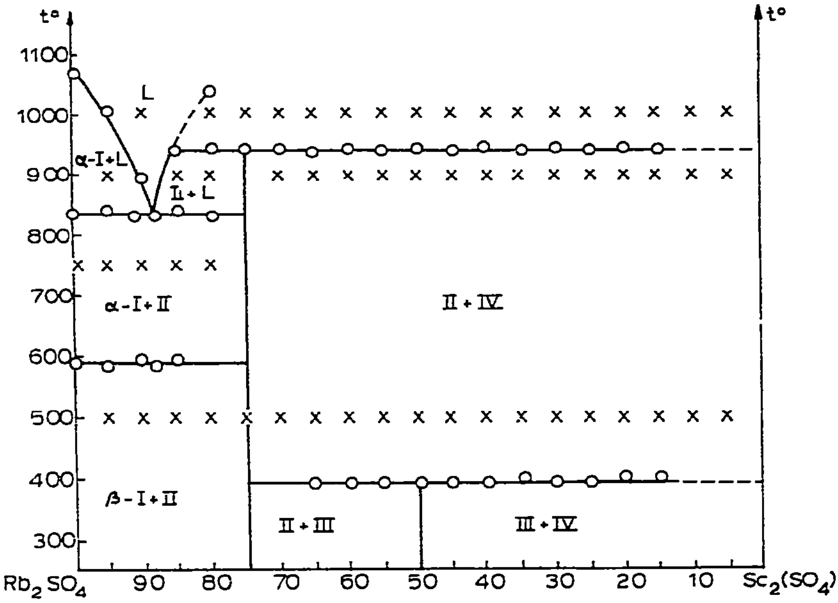

Fig. 2. Phase equilibrium diagram of the Rb_2SO_4—$Sc_2(SO_4)_3$ system. I, Rb_2SO_4; II, $Rb_3Sc(SO_4)_3$; III, $RbSc(SO_4)_2$; IV, $Sc_2(SO_4)_3$; ×, points of rapid cooling.

ably due to the high inverse transformation rate.

The double sulfates $KSc(SO_4)_2$, $RbSc(SO_4)_2$ and $CsSc(SO_4)_2$ decompose, while remaining in the solid state, at 450, 390 and 350° C, respectively. However, X-ray patterns of samples containing between 70 and 5 mole % M_2SO_4, cooled rapidly from 500° C, exhibit lines of double sulfates $MSc(SO_4)_2$ which may be explained by the high formation rates of these compounds.

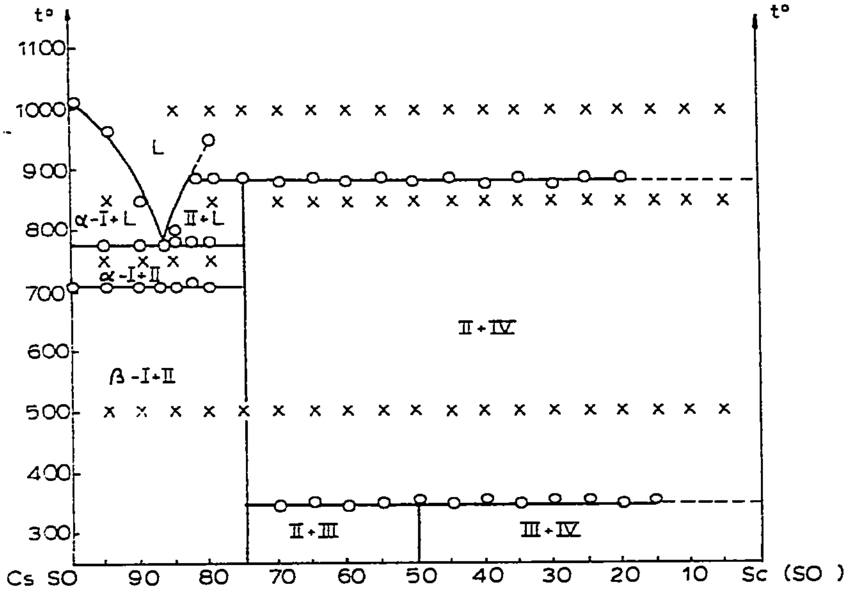

Fig. 3. Phase equilibrium diagram of the Cs_2SO_4—$Sc_2(SO_4)_3$ system. I, Cs_2SO_4; II, $Cs_3Sc(SO_4)_3$; III, $CsSc(SO_4)_2$; IV, $Sc_2(SO_4)_3$; ×, points of rapid cooling.

Although double sulfates of 1 : 1 composition decompose below 600° C, the phase composition of samples annealed at 300 and 600° C was found to be the same, due to the reversibility of decomposition and to the high rate of formation. The samples were therefore synthesized at 600° C to achieve the equilibrium more rapidly.

Thus, there is satisfactory agreement between the data on $M_3Sc(SO_4)_3$ double sulfates obtained in our work and those of other workers [1,4] the discrepancy in incongruent melting temperatures being 10—20° C, but in the case of compounds with 1 : 1 composition, our results for $MSc(SO_4)_2$ are not in agreement, in principle, with those of refs. [1—5].

On the whole, the phase equilibrium diagrams of M_2SO_4--$Sc_2(SO_4)_3$ (M = K, Rb, Cs) are very similar, in appearance, number and composition of the compounds formed, thermal stability, compositions and temperatures of the eutectics, to phase diagrams of Cs_2SO_4—$R_2(SO_4)_3$ (R = La, Nd, Gd, Yb) [8,11] and Rb_2SO_4—$Yb_2(SO_4)_3$ [7].

The systems K_2SO_4—$R_2(SO_4)_3$ (R = Nd, Gd, Yb, Y) [6,12] and Rb_2SO_4—$R_2(SO_4)_3$ (R = La, Nd, Gd) [7] are more complicated, but they are also characterized by the formation of individual phases of $M_3R(SO_4)_3$ (except Rb_2SO_4—$La_2(SO_4)_3$) and $MR(SO_4)_2$; compounds $K_3Gd(SO_4)_3$, $K_3Y(SO_4)_3$, $K_3Yb(SO_4)_3$ and $Rb_3Gd(SO_4)_3$, like scandium double sulfates of a given composition, melt incongruently under heating. A certain analogy can be detected in the thermal stability of potassium double sulfates of $MR(SO_4)_2$ composition with rare-earth elements (at the end of the group) [13] and double sulfates $MSc(SO_4)_2$ investigated in this work. The salient features of both composition groups are the absence of polymorphous modifications, and the solid-phase decomposition at temperatures much lower than the eutectic melting point. This can possibly be attributed to the closeness of the ionic radii of scandium and rare-earth elements (Tm—Lu).

A comparative analysis of the phase equilibrium diagrams for the systems studied in our work and for the systems K_2SO_4—$Sc_2(SO_4)_3$, Rb_2SO_4—$Sc_2(SO_4)_3$ and Cs_2SO_4—$Sc_2(SO_4)_3$ described previously [2,5], reveals serious disagreements in the results. According to Korataeva et al. [2], $K_3Sc(SO_4)_3$ exists only in a narrow temperature interval; the phase diagram of the Rb_2SO_4—$Sc_2(SO_4)_3$ system [2] does not exhibit $Rb_3Sc(SO_4)_3$ and the diagram of Cs_2SO_4—$Sc_2(SO_4)_3$ [5] does not show $CsSc(SO_4)_2$, while in refs. 1 and 4 it was asserted that all these compounds can easily be obtained by solid-phase synthesis at 550—600° C; this has been corroborated by our experiments. On the other hand, we did not observe the existence of $KSc_3(SO_4)_5$ [2] and $CsSc_3(SO_4)_5$ [5]. X-Ray diffraction phase analysis of samples containing 25 mole % M_2SO_4 (M = K, Cs) cooled rapidly from different temperatures shows the presence of a two-phase mixture of $MSc(SO_4)_2$ and $Sc_2(SO_4)_3$. To elucidate these and many other disagreements, we synthesized individual compounds over a period of 2—3 h (as recommended in refs. 2 and 5). The X-ray patterns of annealed samples exhibited lines corresponding to two, three and even four phases. We may therefore conclude that such a synthesis is in no way a satisfactory technique and that Korotaeva et al. [2] and Remizov et al. [5] investigated nonequilibrium samples.

REFERENCES

1 B.I. Bashkov, L.N. Komissarova and V.M. Shatsky, Zh. Neorg. Khim., 15 (5) (1970) 1362.

2 L.G. Korotaeva, V.G. Remizov, A.G. Dudareva and H. Alekhandro Aragon, Zh. Neorg. Khim., 20 (8) (1975) 2197.

3 V.G. Remizov, B.N. Ivanov-Emin and L.G. Korotaeva, Zh. Neorg. Khim., 14 (9) (1969) 2362.

4 L.N. Komissarova, B.I. Bashkov and V.M. Shatsky, Zh. Neorg. Khim., 15 (6) (1970) 1507.

5 V.G. Remizov, L.G. Korotaeva, A.G. Dudareva and B.N. Ivanov-Emin, Zh. Prikl. Khim. (Leningrad), 44 (10) (1971) 2319.

6 P.A. Degtyarev, A.N. Pokrovsky and L.M. Kovba, Vestn. Mosk. Univ., 19 (1) (1978) 95.

7 M.V. Prokofyev, A.N. Pokrovsky and L.M. Kovba, Zh. Neorg. Khim., 24 (8) (1979) 2114.

8 B.G. Samartsev, A.N. Pokrovsky and L.M. Kovba, Zh. Neorg. Khim., 22 (10) (1977) 2721.

9 A.N. Pokrovsky and L.M. Kovba, Zh. Neorg. Khim., 21 (2) (1976) 567.

10 F.M. Korytnaya and A.N. Pokrovsky, Vestn. Mosk. Univ., Khim., 21 (4) (1980) 390.

11 B.G. Samartsev, A.N. Pokrovsky and L.M. Kovba, Vestn. Mosk. Univ., 19 (6) (1978) 727.

12 P.A. Degtyarev, A.N. Pokrovsky and L.M. Kovba, Ann. Chim., 3 (1978) 187.

13 P.A. Degtyarev, A.N. Pokrovsky, L.M. Kovba and F.M. Korytnaya, J. Solid State Chem., 22 (1977) 419.