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POLYMORPHOUS TRANSFORMATIONS OF RUBIDIUM-LITHIUM AND CESIUM-LITHIUM DOUBLE SULPHATES

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Anhydrous double salts of rubidium sulphate and cesium sulphate with lithium sulphate have been prepared, and polymorphous transformations at +60° and +200° for $Rb_2SO_4 \cdot Li_2SO_4$ and at —75° for $Cs_2SO_4 \cdot Li_2SO_4$ have been disclosed by means of differential thermal analysis. These findings were confirmed by dilatometric measurements and X-ray phase analysis at various temperatures.

Differential thermal analysis of the double sulphates $Rb_2SO_4 \cdot Li_2SO_4$ and $Cs_2SO_4 \cdot Li_2SO_4$ indicated the presence of solid state phase-transitions which are presumably due to polymorphous transformations. To confirm this assumption, additional methods, *viz.* dilatometry and high-temperature X-ray phase analysis, were employed to investigate the compounds in question.

The double salt $Rb_2SO_4 \cdot Li_2SO_4$ was obtained by fusion of the corresponding sulphates, or by crystallization from an aqueous solution containing both sulphates in equimolar quantities. The crystals of this compound are biaxial and slightly birefringent ($N_p = 1.482$, $N_m = 1.483$, $N_g = 1.485$). The density $d_{25}^4 = 2.940$ g/cm^3 [1]. DTA curves with a heating rate of 9—10 °/min. were recorded on a Kurnakov DTA apparatus. The sample was placed in a corundum crucible. A Pt—Pt/Rh thermocouple was used to measure temperatures. The reference material was calcined alumina.

On the DTA curves of the double salt obtained by fusion, endothermic peaks were observed at 200° and 740° corresponding to a polymorphous transformation and to the fusion of the compound, respectively. On the DTA curves of the double salt obtained by crystallization, a third, less distinct endothermic peak appears at ~60°, indicating another transformation (Fig. 1).

To confirm the existence of these phase transitions, coefficients of linear thermal expansion were calculated for various temperatures from linear extention measurements performed during the heating of $Rb_2SO_4 \cdot Li_2SO_4$. For these measurements, three polycrystalline samples were used which were pressed into cylindrical shapes (diameter 4.08 mm, length 5.73, 7.88 and 8.2 mm) employing a pressure of 4500 g/cm^2. The experimental results are presented in Table 1.

Fig. 2 shows the dependence of the coefficient of linear thermal expansion, α, on temperature. The curve has two peaks, at ~60° and ~200°. The change in the curve at ~60° confirms that the endothermic peak observed at this temperature

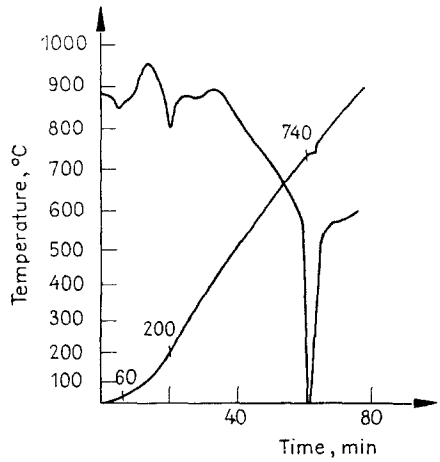

Fig. 1. DTA curve of $Rb_2SO_4 \cdot Li_2SO_4$

Table 1

Coefficients of linear expansion, α, of $Rb_2SO_4 \cdot Li_2SO_4$ at different temperatures

t °C	$\alpha \times 10^{-5}$	Sample	t °C	$\alpha \times 10^{-5}$	Sample
17.5	1.95	I	167.5	2.20	III
19.8	2.01	II	179.4	2.20	II
26.0	1.95	III	186.8	2.48	III
29.0	2.45	I	191.8	2.90	I
52.8	2.78	III	192.6	3.93	II
60.0	4.25	II	194.2	3.98	I
61.4	4.00	I	196.5	4.15	III
69.4	2.78	II	198.5	4.85	III
72.8	2.04	III	200.0	4.30	I
86.1	2.25	III	200.3	3.50	III
90.6	2.16	II	202.2	3.41	I
111.4	2.10	III	204.1	3.52	II
113.0	2.10	I	207.0	3.46	III
122.1	2.05	I	209.3	3.44	I
131.9	1.95	II	215.5	3.40	II
149.5	2.30	I	216.6	3.35	III
155.6	2.20	I	225.5	3.29	I
162.4	1.95	II	236.9	3.25	II

is not accidental but obviously due to a polymorphous transformation. The nature of the peaks on the curve (α vs. t) shows that an expansion of the sample occurs at both transformations.

The polymorphous transformation at 200° is also clearly indicated by a study of X-ray diffraction patterns of $Rb_2SO_4 \cdot Li_2SO_4$ at various temperatures. Diffrac-

tion patterns were obtained with CuKα radiation. A device was applied to the diffractometer to heat the sample and to keep it at a definite temperature [2].

Diffraction patterns were recorded at 25°, 100°, 200°, 300° and again at 25° after cooling. These patterns (Fig. 3) show that the intensities of the lines which characterize the compound at 25° gradually decrease with increasing temperature.

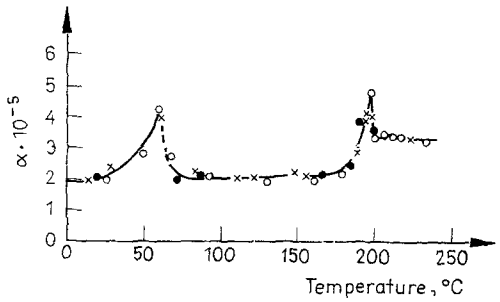

Fig. 2. Temperature dependence of coefficients of linear expansion, α, for $Rb_2SO_4 \cdot Li_2SO_4$. × sample I, ○ sample II, ● sample III

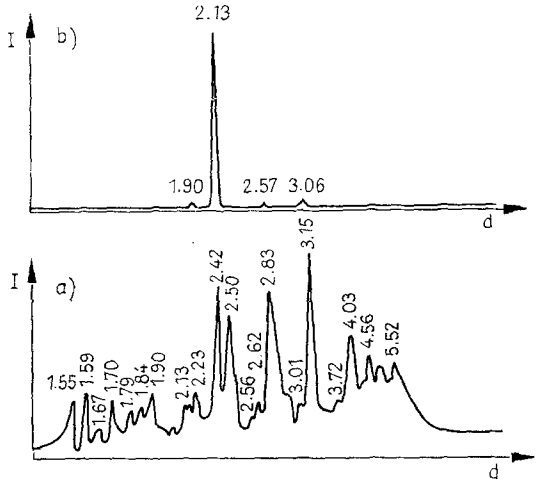

Fig. 3. Diffraction patterns of $Rb_2SO_4 \cdot Li_2SO_4$. a) at 25°C; b) at 300°C

and a new line corresponding to $d = 2.13$ Å begins to appear, indicating that a new phase is being formed. This line becomes very intense at 200° and remains at higher temperatures. Fig. 3, clearly showing the difference between the diffraction patterns at 25° and 300°, confirms that two modifications of $Rb_2SO_4 \cdot Li_2SO_4$ exist. The fact that the diffraction patterns at 25° obtained before and after heating are identical indicates that the transformations are enantiomorphous.

The double salt $Cs_2SO_4 \cdot Li_2SO_4$ was investigated in an analogous manner. The double salt was obtained by fusion of the anhydrous sulphates and by crystallization of their aqueous solution, respectively. The crystals are biaxial and slightly birefringent ($N_p = 1.525$, $N_m = 1.526$, $N_g = 1.528$). The density $d_{25}^4 = 3.467$ g/cm^3 [3].

On the DTA curves of the double salt $Cs_2SO_4 \cdot Li_2SO_4$, an endothermic peak at ~730° corresponds to the fusion of the compound. Mention is made in the literature [4] of a polymorphous transformation of this compound at 35°. In repeated tests, however, we did not succeed in finding such an effect.

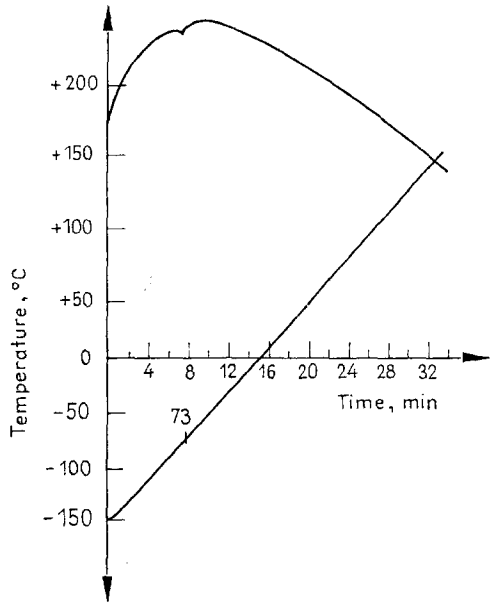

Fig. 4. DTA curve of $Cs_2SO_4 \cdot Li_2SO_4$

X-ray phase analysis performed at various temperatures also showed that no such transformation exists. Diffraction patterns were taken at 25°, 120°, 450° and again at 25°. No new lines could be detected in the diffraction patterns within the investigated temperature range. Slight variations in the values of interplanar spacings and insignificant intensity changes of the lines are presumably due to the temperature increase.

Thermal analysis at sub-zero temperatures, however, disclosed a phase transition of the compound at —75°. In Fig. 4, a slight endothermic peak is clearly visible. Cooling curves and repeated heating curves have shown that the effect is reproducible [3].

The existence of a transformation at —75° was also confirmed by thermal expansion measurements of $Cs_2SO_4 \cdot Li_2SO_4$ in the temperature range of —180° to 250°. Coefficients of linear thermal expansion are presented in Table 2. A peak is clearly seen on the temperature dependence α curve. As the Fig. 5 shows the transition

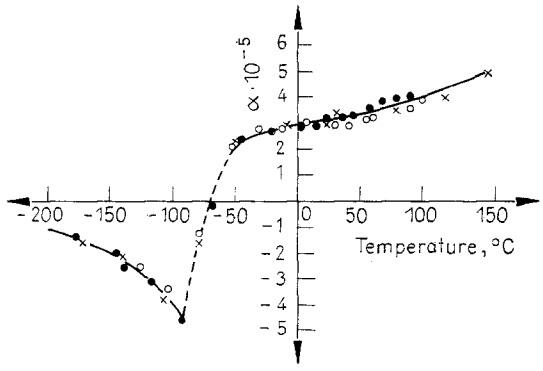

Fig. 5. Temperature dependence of coefficients of linear expansion, α, for $Cs_2SO_4 \cdot Li_2SO_4$. × sample I, ○ sample II, ● sample III

Table 2

Coefficients of linear expansion, α, of $Cs_2SO_4 \cdot Li_2SO_4$ at different temperatures

t °C	$\alpha \times 10^{-5}$	Sample	t °C	$\alpha \times 10^{-5}$	Sample
—178.0	—1.5	III	7.5	+3.0	II
—175.0	—1.6	I	16.0	+2.9	III
—144.0	—2.0	II	25.5	+3.1	II
—140.0	—2.6	III	26.5	+3.0	III
—140.0	—2.2	I	30.5	+2.9	II
—126.0	—2.6	III	33.0	+3.4	I
—117.0	—3.1	III	37.5	+3.2	II
—106.0	—3.8	I	43.0	+2.9	II
—104.5	—3.5	II	48.0	+3.3	III
— 93.5	—4.6	III	56.0	+3.1	II
— 79.5	—1.7	I	59.0	+3.6	III
— 79.0	—1.3	II	60.5	+3.2	II
— 54.0	+2.0	II	70.0	+3.8	III
— 48.0	+2.2	I	81.0	+3.9	III
— 46.0	+2.3	III	82.5	+3.5	I
— 32.0	+2.8	II	92.0	+4.2	III
— 21.0	+2.6	III	94.5	+3.6	II
— 12.5	+2.8	II	102.0	+3.9	II
— 10.6	+2.8	I	122.5	+4.0	I
+ 3.5	+2.8	III	157.0	+5.0	I

takes place in temperature interval of —93° to —54° (the dotted line). Therefore the transformation temperature can be determined in this case as a mean one, i.e. about —73°. No change in the curve can be detected in the temperature range of +20 . . . +50°.

The results of dilatometric tests indicate that, in contrast to those of $Rb_2SO_4 \cdot Li_2SO_4$, the polymorphous transformation of $Cs_2SO_4 \cdot Li_2SO_4$ is accompanied by contraction.

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RÉSUMÉ — On a observé, lors de l'examen par ATD de $Rb_2SO_4 \cdot Li_2SO_4$ et $Cs_2SO_4 \cdot Li_2SO_4$ anhydres, des transformations polymorphiques à + 60° et à +200° dans le cas de la première combinaison et à —75° dans le cas de la seconde. Ces observations ont été confimées par les résultats dilatométriques et d'analyse de phase par rayons X.

ZUSAMMENFASSUNG — Mit Hilfe differentialthermoanalytischer Untersuchungen konnten polymorphe Umwandlungen in den wasserfreien Doppelsalzen Rubidiumsulfat-Lithiumsulfat bzw. Cäsiumsulfat-Lithiumsulfat festgestellt werden. Die entsprechenden Temperaturen betragen bei $Rb_2SO_4 \cdot Li_2SO_4$ +60° und +200°, bei $Cs_2SO_4 \cdot Li_2SO_4$ —75°. Diese Befunde wurden durch dilatometrische Messungen und weiterhin durch röntgenographische Phasenanalyse bei verschiedenen Temperaturen bekräftigt.

Резюме — Синтезированы безводные двойные сульфаты рубидия и цезия с сульфатом лития. С помощью дифференциального термического анализа выявлено наличие полиморфных превращений при +60° и +200° С у $Rb_2SO_4 . Li_2SO_4$ и при —75° С у $Cs_2SO_4 . Li_2SO_4$. Эти данные подтверждаются результатами дилатометрических измерений и рентгенофазового анализа при разных температурах.