Mechanical Properties, Electrical Conductivity and Differential Thermal Analysis of Lithium Sulphate with Small Quantities of Potassium Sulphate

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Previously obtained conductivity and viscosity results for the system $(Li,K)_2SO_4$ with less than 3 mole% K_2SO_4 show bad agreement with the phase diagram given in the literature. From conductivity, viscosity and differential thermal analysis we have constructed a new phase diagram for these concentrations.

Several investigations of pure cubic lithium sulphate and cubic lithium sulphate with small quantities of impurities have been performed in this institute[1–11].

When a small quantity of potassium sulphate is added to cubic lithium sulphate, there is a considerable change in the mechanical properties[8] and the electrical conductivity[6] of the salt. The results obtained in these investigations indicated that structural changes took place at temperatures which had no correspondence in the phase diagrams given in the literature[12–14].

To obtain more information about the system $(Li,K)_2SO_4$ with small quantities of K_2SO_4, we have measured the electrical conductivity and viscosity at different temperatures and concentrations. The measurements have also been completed with differential thermal analysis.

In all experiments reagent grade salts have been used without further purification.

Conductivity Measurements

The experimental technique of the conductivity measurements is described elsewhere in detail[15].

Measurements were performed both in the melt and in the solid. In the melt, we have previously found that the decrease in conductivity is strictly proportional to the concentration of potassium ions (l. c.[10]) and this was used as a check of the conductivity cells. In Fig. 1 we have plotted the change in electrical conductivity of molten lithium sulphate when small quantities of potassium ions are added. The change per mole percent of potassium ions equals $-0.106\ \Omega^{-1}\ \mathrm{cm}^{-1}$, a value which agrees completely with previous results[10].

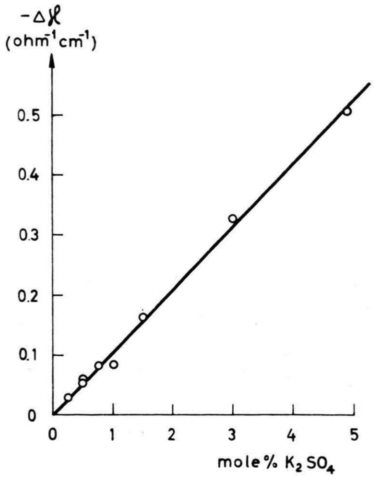

Fig. 1. The change in electrical conductivity of molten Li_2SO_4 when small quantities of K_2SO_4 are added at 890 °C.

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Fig. 2. The electrical conductivity of Li_2SO_4 with 0.5 and 1.5 mole% K_2SO_4 compared with pure Li_2SO_4.

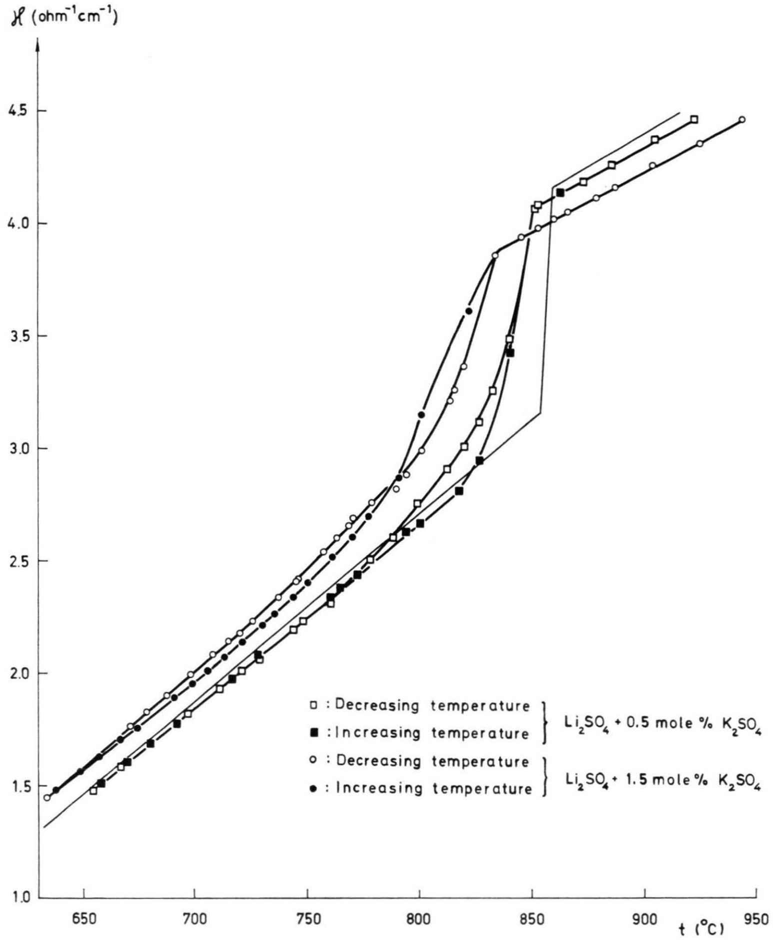

Fig. 2 shows the specific electrical conductivity ($\varkappa$) of lithium sulphate with 0.5 and 1.5 mole percent of potassium sulphate as a function of the temperature compared with $\varkappa$ for the pure salt.

With potassium sulphate concentrations higher than about 1.2 mole% a double curve appears for decreasing and increasing temperature in the solid salt, but at lower concentrations we have found that $\varkappa$ is independent of the thermal pretreatment.

For the solid with 0.5 mole% K_2SO_4 $\varkappa$ is lower than in pure Li_2SO_4. For increasing temperature a transition occurs at about 818 °C and the melting point is reached at about 850 °C.

However, for the solid with 1.5 mole% K_2SO_4, $\varkappa$ is considerably higher than in the pure salt. For increasing temperature there is a change in the slope of the curve at about 722 °C, which also appears with decreasing temperature. At about 790 °C an irregularity occurs and the salt is molten at 833 °C.

Viscosity Measurements

The experimental technique is mainly described elsewhere [8]. The molten salt was allowed to solidify between two concentric cylinders and a constant torque was applied on the inner cylinder, while the outer one was fixed. The angular velocity of the inner cylinder was measured by using a dial gauge, which was registered with a Robot camera. From the angular velocity, the ratio of the shear stress and the velocity gradient was calculated. As this ratio is a function of the shear stress it is here called the apparent viscosity (η) [8, 16]. All measurements were performed with the same torque, which gave a mean shear stress of about $5 \cdot 10^4$ N/m^2.

In Fig. 3 we have plotted some typical values of η for 0.5 and 1.5 mole% K_2SO_4 as a function of the

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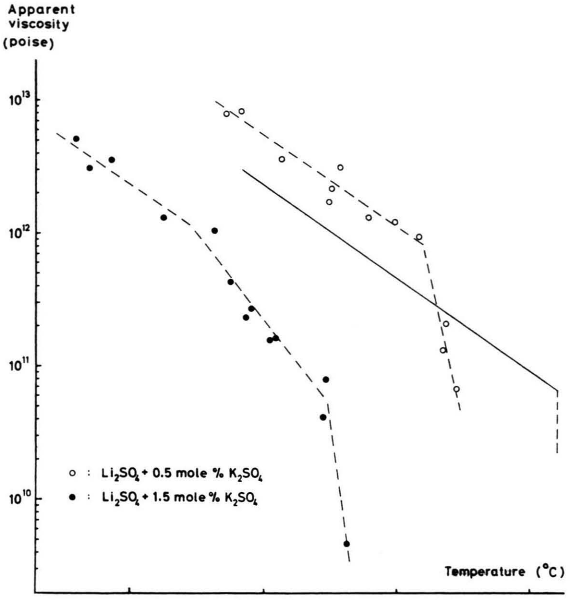

Fig. 3. The apparent viscosity of Li_2SO_4 with 0.5 and 1.5 mole% K_2SO_4 compared with pure Li_2SO_4.

temperature. The continuous line corresponds to the results for the pure salt given in a previous paper [8].

For the solid with 0.5 mole% K_2SO_4 η is higher than for the pure salt. The temperature dependence of η is obviously the same as in the pure salt below 815 °C. At this temperature the slope of the curve changes considerably.

With 1.5 mole% K_2SO_4 η is much lower than in pure Li_2SO_4 and it is possible to distinguish three different regions. Below 730 °C the slope is probably the same as for the pure salt. Between 730 and 775 °C a greater temperature dependence is obtained, which becomes still greater above 775 °C.

Differential Thermal Analysis

Since the temperature dependence of $\varkappa$ and η was in bad agreement with the phase diagram given in the literature [12], we have also made differential thermal analysis of lithium sulphate with 0.5, 1.0, 1.5, 2.0 and 2.5 mole% K_2SO_4, where Al_2O_3 was used as reference.

The two samples were placed in a small steel block in a furnace and the temperature was measured with a chromel-alumel thermocouple. The temperature difference between the two samples was detected by using a potentiometric microvoltmeter (MEDISTOR, model 75 A) as amplifier. Temperature and temperature difference were registered by a recorder. The measurements were performed with increasing temperature, with a temperature change of about ten degrees per minute.

Fig. 4 shows the differential thermal curve for 1.0 mole% K_2SO_4. Four transitions have been found between 400 and 600 °C for all the investigated concentrations. Since the height of the corresponding peaks increases with increasing temperature, a similar behaviour of the heat of transition is to be expected. The highest peak at about 575 °C corresponds to the $\beta-\alpha$ transition in pure lithium sulphate. According to VOSKRENSKAYA and BANASHEK [17], the heat of conversion at 575 °C is about six times the heat of melting for the pure salt.

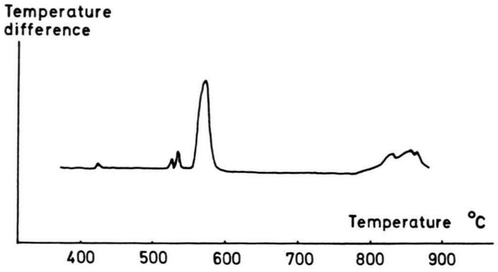

Fig. 4. Differential thermal curve for Li_2SO_4 with 1.0 mole% K_2SO_4.

For 1.0 mole% K_2SO_4 the slope of the curve changes at about 780 °C, which indicates that a second order transition takes place. At about 810 °C another transition appears. Around the melting point the curve is irregular, due to the construction of the experimental equipment.

Summary

In Fig. 5 we have sumarized the results of the different measurements, which give the phase diagram up to 3 mole% K_2SO_4. It is seen that the transition points obtained from viscosity, electrical conductivity and thermal analysis are in good agreement. Some of the points were obtained from our previous papers [6, 8, 11].

Above 575 °C two changes in the structure take place before the melting point is reached. The considerable change in the viscosity indicates that the

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structural changes might be due to the rotation properties of the sulphate ions, which should cause only small changes in the conductivity.

The decrease in $\varkappa$ and increase in η when less than about 1.2 mole% K_2SO_4 is added can be explained by assuming that a small amount of potassium ions can be accomodated in the octahedral positions of the sulphate lattice [6, 11]. At higher concentration of potassium ions there is probably a formation of dislocations.

A further discussion of the different phases must wait until X-ray investigations have been performed.

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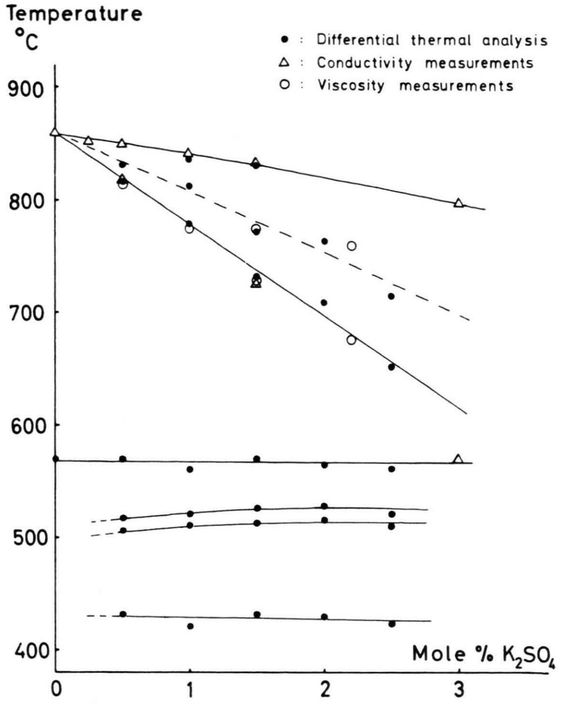

Fig. 5. The phase diagram of Li_2SO_4 with small quantities of K_2SO_4.

Refractive Index Measurements of Molten Salts with Wave-front-shearing Interferometry

I. Test of Apparatus and Procedure

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A wave-front-shearing interferometer has been used for refractive index measurements on liquids. A test series on water gave agreement within $\pm 5 \cdot 10^{-5}$ with earlier data. The refractive index of molten potassium nitrate has been measured between 340 and 460 °C and found to depend linearly on temperature according to the equation

$$n = 1.46478 - 1.579 \cdot 10^{-4} \cdot t$$

at a wavelength of 6330 Å.

I. General Description of the Method

An interferometer with two SAVART plates has previously been used more or less as a refractive index recording instrument [1]. In the present work it is used as a path difference measuring device by utilization of the wellknown technique of rotating a plane parallel glass plate in the light path. The two vertically sheared, partially overlapping wavefronts interfere to give three sets of straight, vertical fringes in the plane where the glass plate immersed in the liquid is imaged. The upper and lower parts of the image consist of light passing only through glass or through liquid, respectively, giving rise to non-moving fringes. In the middle portion, of height equal to the shear distance and representing the vicinity of the edge of the glass plate, the fringes are the result of interference of light passing through glass with light passing through liquid. The position of these fringes is a measure of the path difference

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