Thermal Expansion of Lithium Sulphate

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The thermal expansion of the α and β phases of lithium sulphate has been studied using dilatometric and X-ray diffraction techniques. In the α-phase the coefficient of linear thermal expansion is $4.6 \cdot 10^{-5}\,\mathrm{K}^{-1}$ while in the β-phase the coefficient of linear thermal expansion increases from $0.9 \cdot 10^{-5}\,\mathrm{K}^{-1}$ at room temperature up to $3.4 \cdot 10^{-5}\,\mathrm{K}^{-1}$ close to the first order phase transition at 575 °C. The volume expansion at the phase transition is 3.2%. In the α-phase the thermal Grüneisen parameter has been calculated to be 0.63 at 705 °C.

Introduction

In lithium sulphate a solid electrolyte phase is stable for temperatures between a first order phase transition at 575 °C and the melting point at 860 °C. This phase, α-Li_2SO_4, has attracted much attention due to its high ionic conductivity, up to $3\,\mathrm{ohm}^{-1}\,\mathrm{cm}^{-1}$ close to the melting point [1]. The charge carrier is the highly mobile lithium ion [2], while the sulphate ions form a translationally fixed lattice. The structure is face-centered cubic (space lattice Fm3m) with the sulphate ion situated at the origin and the oxygen ions rotationally disordered about the sulphur atom. The lithium ions occupy the ± (1/4, 1/4, 1/4) positions in the lattice [3]. The β-phase, stable for temperatures below 575 °C is monoclinic, space group $P2_1/a$ [4, 5]. The electrical conductivity in this phase is considerably lower than in the α-phase. In the temperature region just below the phase transition an increase relative to the expected value from extrapolating from lower temperatures has been reported for the heat capacity and the electrical conductivity [6]. Due to the need for accurate values of the thermal expansion coefficient for the calculation of thermodynamic parameters such as, e.g., the Grüneisen parameter, the thermal expansion of α and β-Li_2SO_4 has been reexamined. In the present work both powder X-ray diffraction and an improved dilatometric technique have been used since in earlier dilatometric studies [7, 8] difficulties due to sample plasticity were reported.

Experimental

A horizontally mounted pushrod type dilatometer (Theta Dilatronic, Port Washington, USA) was used for the macroscopic measurements of the thermal expansion. Since the pushrod and the sample holder were made of fused silica only a small correction had to be introduced to compensate for the expansion of the sample holder. The temperature was measured using a Platinel II thermocouple in contact with the sample. The reference thermocouple as well as the differential transformer for the length measurement were kept at a constant temperature of 40.0 °C. The accuracy of the temperature measurement is estimated to be ± 2 K. The sample temperature and length were recorded using a digital voltmeter and a data transfer unit (Solartron). A temperature control unit was used to give a continuous increase (decrease) of temperature. The rate of temperature change was $20\,\mathrm{K\,h}^{-1}$ or lower. The cylindrical samples, 8 – 10 mm in diameter and 10 – 30 mm long, were cast in a quartz mould or pressed in a die using 0.5 GPa pressure. The pressed pellets were then kept at 450 °C for at least 24 h. Suprapure Li_2SO_4 (Merck, Darmstadt, Germany) dried at 200 °C for not less than 72 h, was used for both the dilatometric and the X-ray measurements.

The X-ray diffraction measurements were made with a Philips powder diffractometer using a conventional goniometer constructed for a flat surface powder sample and equipped with a high temperature attachment. The dried Li_2SO_4 powder was melted at 900 °C and was allowed to crystallize under slow cooling and was thereafter ground. In order to avoid temperature errors a very thin

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sample layer (< 0.1 mm) was used. It was applied to the sample holder in the form of a suspension of the Li_2SO_4 powder in ethyl alcohol. The temperature was measured by a Platinel II or a chromel-alumel thermocouple inside a 0.5 mm hole in the platinum sample holder. A Frigistor zero-point reference chamber was used for the cold thermocouple junction. The accuracy of the temperature measurement is estimated to be better than ± 5 K. Silicon powder and in some cases annealed gold powder was mixed into the sample for use as an internal reference for the angular measurement. The lattice constants were determined from a number of well separated diffraction lines in the monoclinic phase using the cell parameter refinement program POWDER. In the case of the α-phase only the (311) reflection was used for the cell determination. This reflection was well resolved in its $CuK\alpha_1$ and $CuK\alpha_2$ components so that the angular errors due to the partial overlapping of these were small. All measured angles were corrected for 2θ-offset and eccentricity errors with the aid of the internal reference diffraction lines before cell calculations.

Results and Discussion

The cell parameters determined from the X-ray diffraction measurements are summarized in Table 1, and the thermal expansion along the a, b, and c axes in the β-phase is plotted as a function of temperature in Figure 1. The expansion is anisotropic with the main expansion in the a and c directions. In order to obtain the equivalent isotropic linear thermal expansion, the (cell volume)$^{1/3}$ from the X-ray measurements was used to calculate the $\Delta l/l_0$ of Table 1 which, in turn, was least squares fitted to a second degree polynomial temperature relation. The dilatometric measurements in the β-phase were performed mainly for temperatures up to 500 °C, and for each run the $\Delta l/l_0$ versus temperature values, where l_0 is the length at 20 °C, were least squares fitted to a second degree polynomial. The results of both least squares fits for temperatures below 500 °C are shown in Table 2. The linear thermal expansion coefficient α was obtained from differentiating $\Delta l/l_0$ as a function of temperature. In Fig. 2 $\Delta l/l_0$ versus temperature is shown for the X-ray diffraction and the dilatometric measurements. In all cases the differences between the dilatometric and the X-ray measurements are within

Table 1. Unit cell data for Li_2SO_4 as a function of temperature.

Temperature °C	a Å	b Å	c Å	β °	Volume Å^3	$\Delta l/l_0$ %
20	8.244	4.951	8.471	107.96	328.897	0.000
50	8.245	4.952	8.478	107.98	329.237	0.035
100	8.254	4.953	8.472	107.98	329.433	0.055
150	8.258	4.958	8.485	108.01	330.388	0.151
200	8.262	4.959	8.498	108.00	331.129	0.226
250	8.276	4.962	8.498	108.11	331.691	0.282
300	8.294	4.966	8.504	108.03	333.069	0.422
350	8.300	4.969	8.519	108.08	333.998	0.514
400	8.317	4.975	8.518	108.15	334.922	0.607
425	8.322	4.975	8.532	108.14	335.680	0.682
450	8.328	4.976	8.537	108.11	336.242	0.739
475	8.334	4.981	8.546	108.23	336.954	0.810
500	8.345	4.981	8.544	108.36	337.061	0.821
525	8.356	4.988	8.561	108.30	338.768	0.994
560	8.367	4.995	8.572	108.35	340.026	1.116
570	8.370	4.997	8.573	108.38	340.271	1.140
600	7.063				352.345	2.322
650	7.078				354.594	2.540
700	7.093				356.853	2.757
750	7.111				359.577	3.018
800	7.126				361.857	3.235

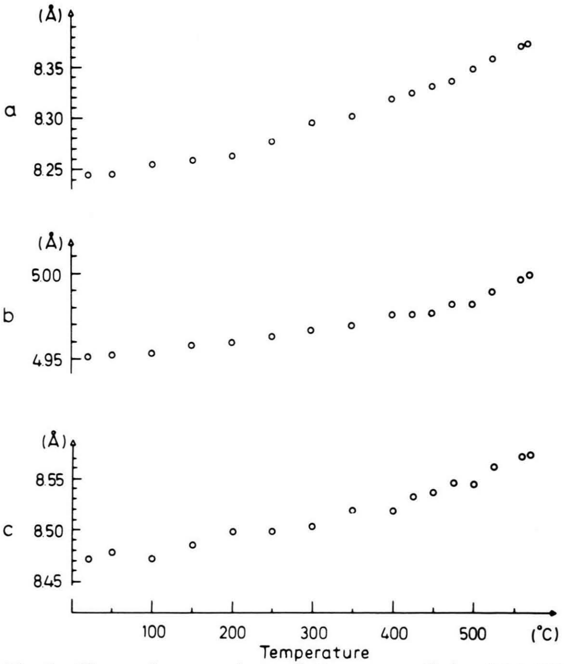

Fig. 1. Thermal expansion of the monoclinic β-Li_2SO_4 lattice. The choice of the scalefactors for the lattice axes permits a direct comparison of the relative length changes through the appearance of the respective slopes.

Table 2. Thermal expansion for β-Li_2SO_4. The values shown are the results of least squares fits for temperatures below 500 °C. The values for 570 °C are obtained from an extended least squares fit.

Temper-ature	X-ray measurements		Dilatometric measurements	
°C	$\Delta l/l_0$ %	α K^{-1}	$\Delta l/l_0$ %	α K^{-1}
20	0.00	$0.9 \cdot 10^{-5}$	−0.01	$1.0 \cdot 10^{-5}$
100	0.08	$1.2 \cdot 10^{-5}$	0.08	$1.3 \cdot 10^{-5}$
200	0.22	$1.6 \cdot 10^{-5}$	0.23	$1.7 \cdot 10^{-5}$
300	0.40	$2.0 \cdot 10^{-5}$	0.42	$2.0 \cdot 10^{-5}$
400	0.62	$2.4 \cdot 10^{-5}$	0.64	$2.4 \cdot 10^{-5}$
500	0.88	$2.8 \cdot 10^{-5}$	0.90	$2.7 \cdot 10^{-5}$
570	1.15	$3.4 \cdot 10^{-5}$		

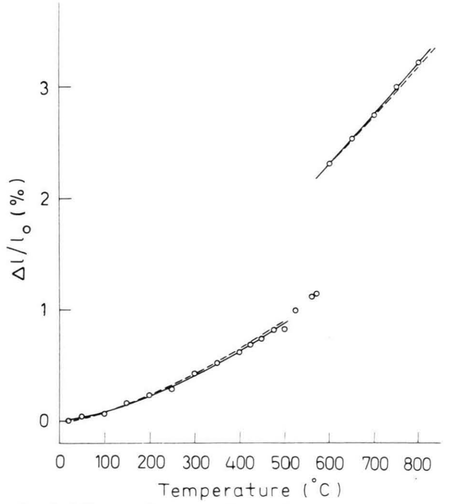

Fig. 2. Thermal expansion of Li_2SO_4. The values from the X-ray diffraction measurements are shown together with the fitted curves for the X-ray (solid line) and dilatometric measurements (dashed line). The expansion at the phase transition is taken from the X-ray measurements.

the limits of error. In the temperature range 500 to 575 °C the thermal expansion coefficient increases further to a value of $3.4 \cdot 10^{-5}\,K^{-1}$ just below the phase transition. In contrast to this finding two earlier dilatometric studies [7, 8] reported a temperature independent linear thermal expansion coefficient of $2.2 \cdot 10^{-5}\,K^{-1}$ for the β-phase. An increase in the heat capacity is typical for the temperature region below transitions to plastic phases [9] and α-Li_2SO_4 has been shown to have characteristics of a plastic phase [10]. Furthermore, a neutron powder diffraction study of β-Li_2SO_4 at 550 °C has shown that strong torsional vibrations of the SO_4 groups of the order of 20° exist slightly below the transition temperature [11].

In the α-phase the X-ray measurements give a temperature independent linear thermal expansion coefficient of $(4.6 \pm 0.1) \cdot 10^{-5}\,K^{-1}$. Dilatometric measurements in α-Li_2SO_4 are difficult due to the plasticity in this phase, and reproducible results could be obtained only for decreasing temperature runs. At least squares fit to a straight line was calculated for each run giving an average value of $(4.5 \pm 0.3) \cdot 10^{-5}\,K^{-1}$, in good agreement with the result above. These values are somewhat higher than the thermal expansion coefficients reported in the earlier dilatometric studies [7, 8], both giving a value of $4.3 \cdot 10^{-5}\,K^{-1}$.

The volume expansion at the phase transition determined from the X-ray measurements is $\Delta V/V_0 = (3.2 \pm 0.2)\%$, where V_0 is the volume at 20 °C. The accuracy of the dilatometric measurements was unsatisfactory due to the creation of cracks in the sample when going through the phase transition. The average value $\Delta V/V_0$ was $(4.6 \pm 1.4)\%$ if all dilatometric measurements were included, and $(3.5 \pm 1.4)\%$ counting only measurements where a sample went through the transition for the first time. The two earlier dilatometric studies also reported high values for $\Delta V/V_0$, 4.2% and 4.7%, respectively [7, 8]. The slope of the phase boundary dp/dT for the $\alpha \leftrightarrow \beta$ transition can be calculated from the Clausius-Clapeyron equation. Inserting the transition enthalpy [12] $2.35 \cdot 10^4\,J\,mol^{-1}$ and our X-ray value of ΔV we get $dp/dT = 1.8 \cdot 10^7\,Pa\,K^{-1}$, which is in fair agreement with the value of Pistorius [13], $1.4 \cdot 10^7\,Pa\,K^{-1}$.

The Grüneisen parameter γ was calculated for α-Li_2SO_4 at 705 °C using

$$\gamma = 3\alpha V_m/\varkappa C_v\,, \tag{1}$$

where V_m is the molar volume, $\varkappa$ the isothermal compressibility and C_v the molar specific heat at constant volume. $\varkappa$ and C_v were calculated from

$$\varkappa = \varkappa_s + 9\alpha^2 T V_m/C_p \tag{2}$$

and

$$C_v = C_p - 9\alpha^2 T V_m/\varkappa\,, \tag{3}$$

where $\varkappa_s$ is the adiabatic compressibility, C_p the molar specific heat at constant pressure and T the absolute temperature. Using the results from this study for $\alpha = 4.6 \cdot 10^{-5}\,\mathrm{K}^{-1}$ and $V_m = 53.8\,\mathrm{cm}^3$ and inserting literature data [14, 15] for $C_p = 221\,\mathrm{J\,mol^{-1}\,K^{-1}}$ and $\varkappa_s = 5.37 \cdot 10^{-11}\,\mathrm{m^2\,N^{-1}}$ we get $\gamma = 0.63$. This value is lower than the Grüneisen parameters reported for most ionic crystals in this temperature range.

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