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Phase transition in potassium lithium sulphate*

T RANGA PRASAD, Y C VENUDHAR, LEELA IYENGAR and K V KRISHNA RAO
Department of Physics, Osmania University, Hyderabad 500 007

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Abstract. Phase transition and lattice parameter variation with temperature of potassium lithium sulphate have been studied. Precision lattice parameters have been determined at various temperatures, ranging 30°C to 400°C. The diffraction pattern obtained above 435°C differs from that taken at room temperature suggesting a structural change, contrary to the reports of Fischmeister and others.

Keywords. Phase transition; thermal expansion; potassium lithium sulphate.

1. Introduction

Potassium lithium sulphate ($KLiSO_4$) crystallizes in the space group $P6_3$. The structure of the substance was determined by Bradley (1925). A phase transition in $KLiSO_4$ at 435° C was first reported by Blittersdolf (1929). Fischmeister *et al* (1960) determined the lattice parameters of $KLiSO_4$ at different temperatures by x-ray method. According to them, the phase transition in $KLiSO_4$ does not involve any major structural changes except for slight increase in lattice parameters at the transition point. The lattice parameters at different temperatures were measured by them using a one-sided Debye-Scherrer camera of 4·55 cm film radius. The uncertainty in the measurement of their cell constants was $\pm 0{\cdot}01$ Å. As the accuracy of the determination of lattice parameters was low, an attempt was made to study the variation of the lattice parameters with temperature and the nature of phase transition in this substance.

2. Preparation of the sample

Crystals were grown by aqueous solution method from the following equation

$$2KHSO_4 + Li_2CO_3 \rightarrow 2KLiSO_4 + H_2O + CO_2.$$

Potassium bisulphate used for this reaction was obtained by the following reaction.

$$K_2SO_4 + H_2SO_4 \rightarrow 2KHSO_4.$$

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The crystals obtained were hexagonal plates or pillars and colourless. A preliminary examination of the Debye-Scherrer photographs confirmed that the grown crystals were $KLiSO_4$.

3. Experimental procedure and results

Powder photographs were taken at different temperatures using a Unicam 19 cm high temperature powder camera and CuK_α radiation. The experimental set up and other details were given in our earlier paper (Krishna Rao *et al* 1973). The precision lattice parameters were evaluated using the reflections recorded in the Bragg angle

Table 1. Comparison of the lattice parameters of $KLiSO_4$ at room temperature.

Source	Lattice parameters	
	a Å	*c* Å
Bradley (1925)	5·13	8·60
Fischmeister *et al* (1960)	5·147	8·634
NBS	5·1457	8·6298
Present study	5·1455	8·6363
	±0·0001	±0·0001

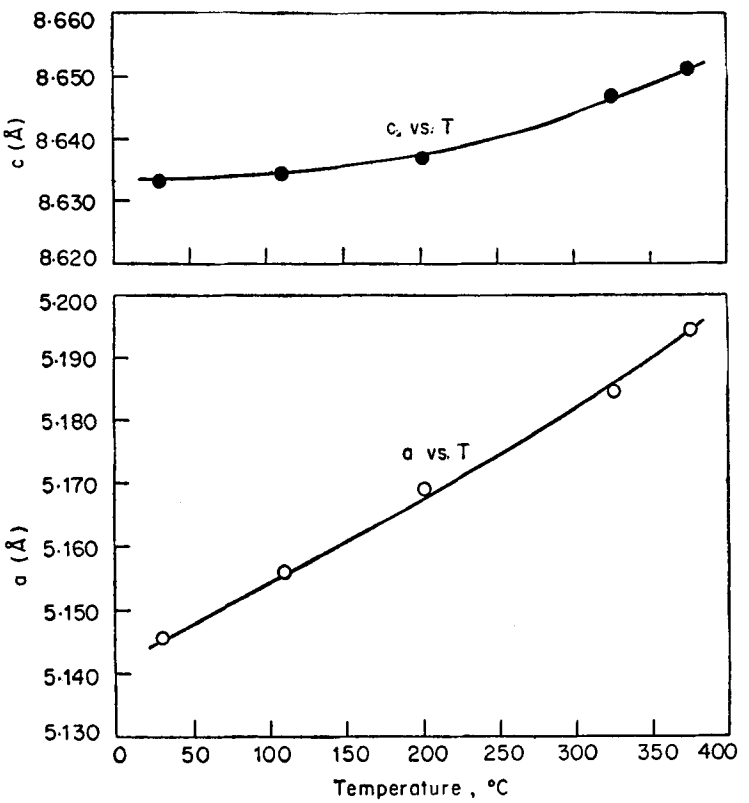

Figure 1. Variation of lattice parameters of $KLiSO_4$ with temperature.

region 50° to 78° by the Cohen's (1935) least squares method. The lattice parameters obtained in the present work were in good agreement with values reported by Fischmeister *et al* (1960) (see table 1).

Figure 1 shows the variation of lattice parameters a and c with temperature. It can be seen that the change in a parameter was more when compared to that in c parameter and this agreed with the results reported by Fischmeister *et al* (1960).

Using the lattice parameters obtained at different temperatures, the coefficients of thermal expansion at different temperatures were evaluated by a graphical method reported in an earlier paper by Krishna Rao *et al* (1962). The temperature dependance of coefficient of thermal expansion $\alpha_{\perp}$ and $\alpha_{\parallel}$ are represented by the following equations.

$$\alpha_{\perp} = 27{\cdot}574 \times 10^{-6} - 3{\cdot}456 \times 10^{-8}\,T + 1{\cdot}349 \times 10^{-10}\,T^2 \qquad (1)$$

$$\alpha_{\parallel} = 1{\cdot}108 \times 10^{-6} + 4{\cdot}737 \times 10^{-9}\,T + 7{\cdot}8657 \times 10^{-11}\,T^2. \qquad (2)$$

The diffraction pattern obtained at 435°C was completely different from that taken at room temperature. The number of reflections increased and there was a sudden drop in the intensities of higher angle reflections, suggesting a structural change, contrary to the reports of Fischmeister *et al* (1960). Because of the limited measurable lines indexing of the diffraction pattern was not possible. The new phase persisted up to 650°C. Further attempts are being made to identify the phase by single crystal techniques.

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