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STUDY ON THE PHASE TRANSITION IN POTASSIUM HYDROGEN SULPHATE CRYSTALS

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ABSTRACT

The electrical and thermal properties of potassium hydrogen sulphate ($KHSO_4$) crystals were measured within the temperature range 300-500 K. A phase transition at 648 K was observed. The phase transition is discussed on the basis of the geometry and properties of hydrogen bonds, using correlation curves to illustrate the role of the hydrogen bond.

INTRODUCTION

There is great interest in the nature of the phase transition of hydrogen bonded ferroelectrics [1]. However the molecular mechanism of this phenomena is not completely clear.

Potassium hydrogen sulphate is a member of a family with the general formula $MeHBX_4$ ($Me = Na, K, Rb, Cs, N_2H_5, NH_4$; $BX_4 = BeF_4, SO_4$ or SeO_4). The growing interest in this family was stimulated by the results of Baranov et al. [2]. They found that some bisulphate groups show anomalous high ionic conductivity. These $KHSO_4$ crystals possess orthorhombic symmetry with space group D_{2n}^{15} and 16 molecules per unit cell [3,4]. The unit cell dimensions are $a = 8.4$, $b = 9.19$ and $c = 18.93$ Å. Using an electron spin resonance technique Sunandana [5] detected the existence of two types of sulphate ions, type I forming HSO_4 dimers, which were joined through two hydrogen bonds and type II forming a polymeric chain along the a axis by means of a ladder type hydrogen bond.

The present work deals with the study of the phase transition taking place in the range 300-500 K for prepared $KHSO_4$ crystals using differential thermal analysis (DTA), thermal mechanical analysis (TMA) and electrical conductivity measurements along the three crystallographic axes.

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EXPERIMENTAL

Single crystals of potassium hydrogen sulphate $KHSO_4$ were grown by a slow evaporation method from aqueous solution containing the initial salt at 298 K. Samples for electrical conductivity measurements were made in the form of a thin slab ($1 \times 1 \times 0.15$ cm^3) cut from large single crystals with the edge parallel to the crystallographic axes. For the thermal mechanical analysis, rectangular rods ($3 \times 3 \times 20$ mm^3) with their longer part oriented along the crystallographic axes under investigation were prepared.

Differential thermal analysis curves were recorded on a Shimadsu differential thermal analysis system DTA 30 at constant heating rate of 2 K min^{-1} using Al_2O_3 as inert standard reference. Thermal mechanical analysis TMA was performed using a Heraeus TMA 500 S dilatometer. Electrical conductivity measurements were carried out using a special holder [6]. The method is described elsewhere [7].

RESULTS AND DISCUSSION

The differential thermal analysis curve for $KHSO_4$ is given in Fig. 1, which shows a sharp peak at 468 K indicating a phase transition for $KHSO_4$. The transition occuring at 468 K were not observed when the sample was cooled and reheated. This indicates that this transition is irreversible. The heat of transition, ΔQ, was estimated from the area of the peak. The existence of such a large thermal hystersis as well as the magnitude of the heat of transition suggests that the transition of $KHSO_4$ at 468 K is likely to be first order [8].

The temperature dependence of strain and elongation of the $KHSO_4$ crystal are shown in Fig. 2(a, b and c) where $\Delta L/L_0$ showed an increase with temperature interrupted by the contracted region at (468–483 K). The straight lines were resumed with different slopes.

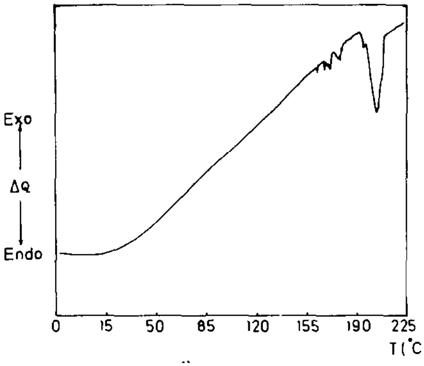

Fig. 1. Differential thermal analysis curve of the $KHSO_4$ crystal.

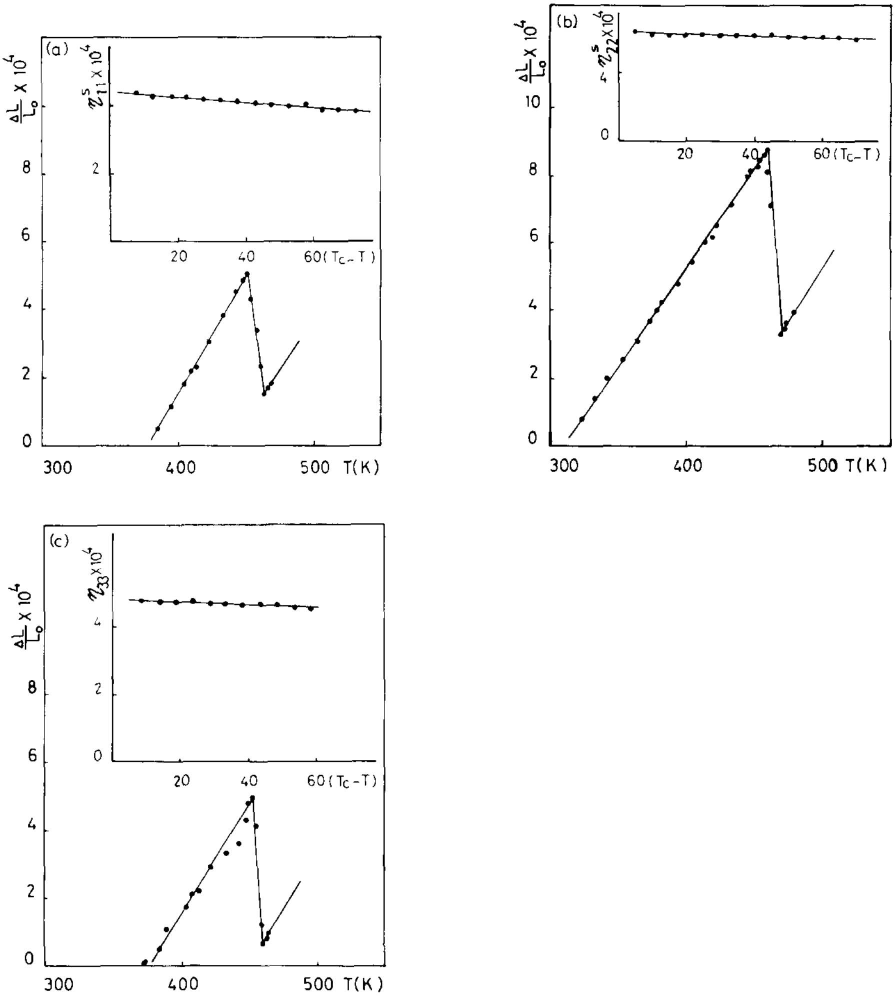

Fig. 2. Lattice constant and spontaneous tensile strains as a function of temperature measured along different crystallographic axes.

The linear thermal expansion coefficient of $KHSO_4$ crystals measured along the three crystallographic axes a, b and c appeared to be anisotropic. The difference between the observed value of $\Delta L/L_0$ in the high temperature phase and that obtained by the extrapolation from the low temperature phase is believed to come from the spontaneous strain induced by the phase transition [9]. Figure 3 illustrates that the spontaneous strain η_{ij} with $i = j = 1$, 2 or 3 shows linear temperature dependence. Figure 3 shows the temperature dependence of the volume change $\Delta V/V$ calculated from the linear thermal expansion data produced from Fig. 2. The presence of a chain structure consisting of HSO_4 dimer ions may provide an explanation for the anomaly in the thermal expansion of $KHSO_4$ crystals. The change of the

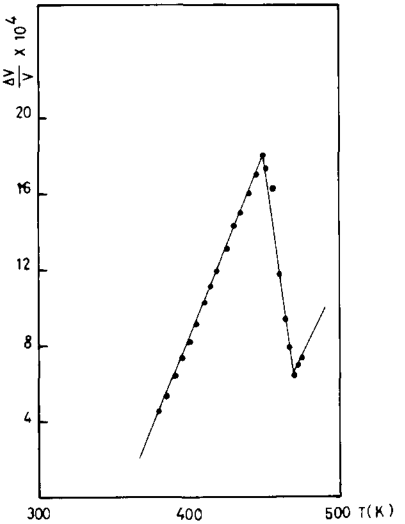

Fig. 3. Molar volume of unit cell as a function of temperature.

chain structure due to dimerization induces an anomaly in the expansions along *a*, *b* and *c* as they affect each other.

The conductivity of the $KHSO_4$ crystal represented in Fig. 4 shows linear behaviour in the relation of log σT versus $1/T$ in the temperature range 300–500 K. The electrical conductivity of $KHSO_4$ increased with rising temperature. Such increase may come partially from the lattice distortion as revealed by anomalous trends in the lattice constant and molar volume, at 468 K. The other factor causing the increase of electrical conductivity may

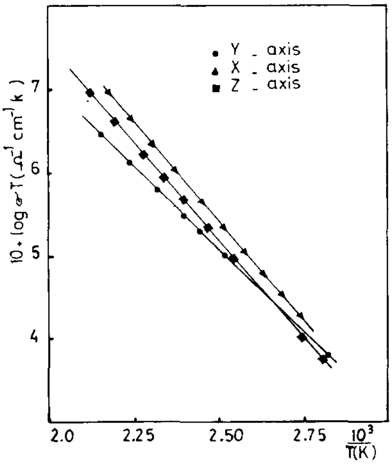

Fig. 4. Temperature dependence of electrical conductivity measured along different crystallographic axes.

be attributed to the sulphate groups of $KHSO_4$ which are connected to each other by hydrogen bonds in two different ways, forming cyclic dimers and open chains. This indicates that the hydrogen bond arrangement may be broken leading to protonic conduction.

It is concluded that both the electrical conductivity and the thermal expansion of $KHSO_4$ along different axes showed anisotropic behaviour due to structure transformation within the crystals.

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