

05.1-30 POLYMORPHISM IN K_2SO_4 . By Y.A. Badr, G. Said, F. El-Kabbany and S. Taha, Faculty of Science, Cairo University, Cairo, Egypt.

An anomalous sharp decrease in D.C. resistivity associated with an increase in both dielectric constant and dielectric loss values and the values of the pyrocurrent for both mono- and polycrystalline potassium sulphate samples were detected in the high temperature region. The pyroelectric behaviour of the high temperature K_2SO_4 phase I suggested that this phase belongs to a polar class having a resultant vector in the crystal. Such polar nature might explain the excessive increase in the dielectric constant ϵ' and dielectric loss ϵ'' with temperature.

Differential thermal analysis (DTA) showed a pronounced peak at 558°C, indicating that the endothermic phase transition II - I of K_2SO_4 was of the order - disorder type. The area under the DTA peak was found to be greater in the case of single crystals than that obtained for polycrystalline samples. Also, the rate of increase of the expansion coefficient during the phase transition II-I, as obtained by thermomechanical analysis (TMA), was found to be higher for single crystals due to the ordering and unique orientation of unit cells (summation rather than averaging).

The decrease of D.C. resistivity associated with the increase of dielectric constant might be attributed to an orientational motion of the tetrahedral ions SO_4^{2-} . Such orientational motion occurring with high frequency $\sim 10^{12}$ Hz at high temperatures seemed to cause rupture in the ionic bonds.

05.1-31 X-RAY AND NEUTRON STUDY OF $LiKSO_4$ AT ROOM TEMPERATURE - SEARCH FOR DISORDER. By Sandhya Bhakay-Tamhane, A. Sequeira and R. Chidambaram, Neutron Physics Division, Bhabha Atomic Research Centre, Trombay, Bombay 400085, India.

The Raman scattering study of $LiKSO_4$ indicates a phase transition at 201 K which appears to be associated with a cooperative reorientation of the sulphate ions in the crystal (Bansal, Deb, Roy & Sahni; Solid State Comm. (1980) 36, 1047). The existing structural information is incomplete and ambiguous as to the choice of a and b axes. In order to understand the nature of the reorientations associated with the phase transition, a combined single-crystal X-ray and neutron diffraction study at room temperature has been carried out. The space group is $P6_3$ with $a = 5.127(2)$, $c = 8.618(3)$ Å and $Z = 2$.

The X-ray data set consisting of 855 independent reflections within $\sin\theta/\lambda = 1.1 \text{ \AA}^{-1}$ ($MoK\alpha$) was recorded using the on-line TDC-312 computer-controlled diffractometer at Trombay. Anisotropic least-squares refinement of the structure using this data set converged to a conventional $R(\text{on } F)$ value of 0.077 and indicated partial disorder for the sulphate groups (~15%). The second minimum corresponded to a rotation of the sulphate ion by 60° about the S-O bond along the 3-fold axis, but the S-O bond distances for this position were somewhat less reasonable.

The refinement based on the neutron data set

(181 independent reflections within $\sin\theta/\lambda = 0.6 \text{ \AA}^{-1}$) which converged to a $R(\text{on } F)$ value of 0.068 does not, however, seem to confirm the disorder in the structure at this stage of the investigation. The tetrahedrally coordinated Li ion is tightly bound with an average Li-O distance of 1.90(2) Å. The detailed results of the two refinements will be compared and the difficulties encountered in searching for possible disorder in this structure will be discussed. Both the X-ray and neutron data suffered from severe extinction (minimum F_o^2/F_c^2 values being 0.095 and 0.25 respectively).

05.1-32 THE ELECTRICAL PROPERTIES OF SINGLE-CRYSTAL $KLiSO_4$. By Zhu Yong, Zhang Dao-fan, Xu Zheng-yi, Institute of Physics, Chinese Academy of Sciences, Beijing, China.

It was found that after applying a dc field along the direction of the c axis or the a axis of a $KLiSO_4$ single crystal the apparent dielectric constants ϵ'_c or ϵ'_a would increase when the temperature was higher than the transition point (438°C). After switching off the dc field, the relaxation of ϵ'_c and ϵ'_a can be expressed by

$$\Delta\epsilon'_c(\text{or } \Delta\epsilon'_a) = \Delta\epsilon' (t/t_0)^{-\beta} \quad (1 \text{ min} \leq t < t_k) \quad (1)$$

$$\Delta\epsilon'_c(\text{or } \Delta\epsilon'_a) = \widetilde{\Delta\epsilon'} (t/t_0)^{-\beta} \ln(t/t_0) \quad (t > t_k) \quad (2)$$

Here t_k is a time region, t_0 is a time parameter, β and β' are relaxation parameters. The current relaxation satisfies Eqs. (1) and (2) at temperatures both above and below the transition point. It was experimentally verified that single-crystal $KLiSO_4$ is an ionic conductor. By using the same method as that described by Zhan An-dung, et al., ((1980), Acta Physica Sinica, 29, 1158), it has been found that single-crystal $KLiSO_4$ has two types of carriers, Li interstitial ions and Li vacancies.

The relaxation behaviours of the apparent dielectric constants and current in single-crystal $KLiSO_4$ are similar to that in $\alpha\text{-LiIO}_3$. Therefore it may be concluded that these relaxation processes in $KLiSO_4$ are also due to an ionic conduction process, as reported in previous papers by the present authors ((1977), Acta Physica Sinica, 26, 115; (1977), 26, 500; (1980), 29, 454). In addition, we have measured the dielectric dispersion of $KLiSO_4$ at different temperatures. The results are analogous to those obtained in $LiIO_3$ by the present authors (to be published).