

## THERMAL DIFFUSIVITY OF LITHIUM HYDRAZINIUM SULFATE (LHzS) CRYSTALS\*

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Angstroem's temperature wave method is applied for measuring the thermal diffusivity of lithium hydrazinium sulfate (LHzS) crystals in the crystallographical directions [100], [010] and [001], in the temperature range from +20°C to 70°C. The highest diffusivity was found in the [001] and the lowest in the [100] direction. The high thermal diffusivity is probably related with the large electrical conductivity of LHzS crystals in the [001] direction. The thermal diffusivity coefficients of LHzS crystals grown from aqueous solutions containing 0.5 per cent weight of p-nitroaniline were found to decrease in the [100], [010] and [001] directions by, respectively, 8, 20 and 10 per cent of the numerical values measured at room temperature.

### Introduction

The apparent ferroelectric nature of lithium hydrazinium sulfate,  $\text{Li}(\text{N}_2\text{H}_5)\text{SO}_4$  (LHzS), was first reported by Pepinsky, Vedam, Okaya and Hoshino [1]. They observed good hysteresis loops from about  $-15^\circ\text{C}$  to  $+80^\circ\text{C}$ , but found no dielectric anomaly between  $-196^\circ\text{C}$  and  $+140^\circ\text{C}$  or specific heat anomaly between  $-120^\circ\text{C}$  and  $+205^\circ\text{C}$ . They drew the conclusion that the crystal was ferroelectric, with its ferroelectric axis along [001] direction. The crystal structure has been investigated by X-ray diffraction (Niizeki and Koizumi [2], Brown [3], Van den Hende and Boutin [4]), and by neutron diffraction (Padmanabhan and Balasubramanian [5]). The structure is orthorhombic (point group 2 mm), with space group  $Pbn2_1$ . The structure is composed of a  $\text{LiSO}_4$  — framework of corner-sharing oxygen tetrahedra with channels which run along the [001] direction and contain the hydrazinium ions. The  $\text{NH}_3^+$  group of the hydrazinium ion forms three hydrogen bonds to the framework and the  $\text{NH}_2$  groups forms one hydrogen bond to the framework and one to the next  $\text{NH}_2$  group related by the [001] direction to give an ordered  $\text{N}-\text{H}\cdots\text{N}-\text{H}$  chain directed along the negative [001] direction. There are two mechanisms

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able to produce a change in configuration of the chain, the one consisting in rotation of the  $\text{NH}_2$  groups and the other in a transfer of the proton along the hydrogen bond from one nitrogen atom to the next. A combination of both effects would allow the protons to migrate along the chain, and this could explain the large electrical conductivity in the [001] direction (Vanderkooy, Cuthbert and Petch [6]). Schmidt, Drumheller and Howell [7] published the results of their extensive investigation of the dielectric properties of LHzS which, they conclude, is not ferroelectric. They interpreted the hysteresis loops by a mechanism of partially blocked conduction along the hydrogen bond chains.

The thermal diffusivity of LHzS crystal has not been studied hitherto. We present the results of our investigation of this property. For thermal diffusivity measurements, we applied Angstroem's temperature wave method [8-10].

### *1. Preparation of the crystals and measuring method*

LHzS crystals for thermal diffusivity studies were grown from aqueous solutions by the isothermal method at  $+49^\circ\text{C}$ . Salts purified by five-fold slow recrystallization from aqueous solutions were used. Some crystals were grown from aqueous solutions containing 0.5 per cent weight of p-nitroaniline. The crystals were all colorless and well formed with excellent faces. The crystals were cut into rods of square cross-section, oriented for thermal diffusivity studies in the three principal crystallographical directions [100], [010] and [001]. In each rod, two holes were bored for the introduction of copper-constantan thermoelements at points fulfilling the optimal conditions with respect to the upper surface of the rod as defined by Green and Cowles [11]. The rods were then processed to cylinders 0.4 cm in diameter, of a length of 2.2 cm. In order to ensure minimal heat outflow from the crystal cylinder through the thermoelement, the latter was made of sufficiently long wires 0.005 cm in diameter. Using Degussa "liquid silver", a micro-heater was glued to the top surface of the cylinder whereas a copper heat-sink of large heat capacity was attached to the other surface. The crystal with micro-heater, thermoelements and heat-sink was then placed inside a modified vacuum holder, the details of which have been published elsewhere [12]. The construction of the heat-sink ensured good thermal contact of the crystal and outer shield of the vacuum holder, the temperature of which was varied continuously by means of a Hoeppler thermostat. The temperature of the crystal at thermal equilibrium was measured with the copper-constantan thermoelement by the compensation method with an accuracy of  $\pm 0.01^\circ\text{C}$ . A block diagram of the measuring device used in the thermal diffusivity studies has been published elsewhere [13].

The thermal diffusivity was measured in the three crystallographical directions [100], [010] and [001] over the temperature range from  $+20^\circ\text{C}$  to  $+70^\circ\text{C}$ .

### *2. Results of measurements, and discussion*

The continuous curves of Fig. 1 show the temperature dependence of the thermal diffusivity coefficients  $k$  of LHzS crystals grown from pure aqueous solutions and of ones grown from aqueous solutions containing 0.5 per cent weight of p-nitroaniline (dashed

curves in Fig. 1), for the three principal directions. From these curves, the thermal diffusivity of LHzS crystals increases almost linearly with increasing temperature in the [001] direction and is larger than for the other directions, though of the same order of magnitude as in the directions [100] and [010]. In the same direction, the electrical conductivity observed

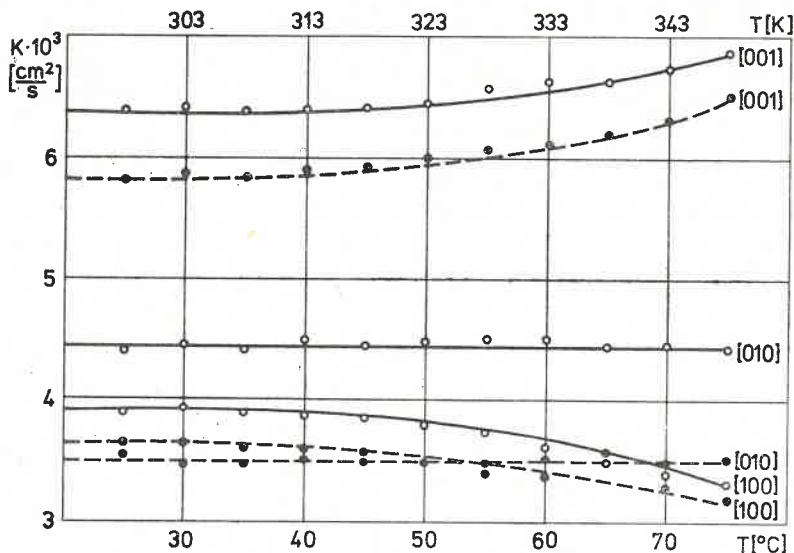


Fig. 1. Temperature variations in thermal diffusivity of LHzS crystals in the directions [100], [010] and [001]. Continuous curves — thermal diffusivity of crystals grown in pure aqueous solutions of LHzS. Dashed curves — thermal diffusivity of ones grown from solutions containing p-nitroaniline

by Vanderkooy [6] is much larger than the conductivity measured perpendicularly to [001] direction. Probably, the increase in thermal diffusivity in the [001] direction is related with the large electrical conductivity, and the scattering of phonons in the channels is low. The thermal diffusivity coefficient in the [010] direction is constant. Microscopic examination of the LHzS crystals showed strations running in the [010] direction but not on all faces of the crystals. Application of a strong electric field did not change the situation. In all cases, the strations appeared on the same side as originally. The thermal diffusivity in the [100] direction decreases with increasing temperature. Probably, for this direction, the dissipation of phonons on the channels is large. Application of an electric field did not affect the values of the thermal diffusivity coefficients. The thermal diffusivity of LHzS crystals grown in the presence of dipolar p-nitroaniline  $C_6H_4NO_2:NH_2$  molecules in aqueous solution decreases for the [001], [010] and [100] directions by 10, 20 and 8 per cent, respectively, with respect to the thermal diffusivity measured at room temperature. The crystals grown from solutions containing p-nitroaniline were found to contain no molecules of the latter compound. Our study shows, that the dipolar molecules of p-nitroaniline have the ability to control the growth process of LHzS crystals. Hence, the possibility exists of modifying the thermal diffusivity of LHzS crystals by the introduction into their lattice of appropriate admixture partially or completely blocking the channels occurring therein.

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