

MEASUREMENT OF THERMOPHYSICAL PROPERTIES OF KNO_3

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ABSTRACT

The thermal properties, specific heat capacity C_p , thermal conductivity λ and thermal diffusivity a of KNO_3 were measured in the temperature range 300–500 K. Specific heat capacity measurements indicate the presence of a structural phase transition from orthorhombic to rhombohedral at 408 K. The mechanism of heat transfer is due to phonons, whereas the effects due to electrons and bipolars are negligible in the measured temperature range.

INTRODUCTION

The thermophysical properties of nitrates have recently received considerable attention because of the many technical and scientific applications of the nitrates. Among these nitrates we have studied KNO_3 .

The specific heat capacity was used to follow the phase transition. A clear variation in the specific heat was noticed during the phase transition. The investigation of the thermal conductivity at different temperatures helps in the understanding of the mechanisms of heat conduction in this material.

Seven modifications of KNO_3 were found under varying conditions of temperature and pressure [1,2]. The first three modifications, I, II and III, occurred between room temperature and the melting point at atmospheric

pressure. KNO_3 has an orthorhombic aragonite-type structure at room temperature, with the space group D_{2h}^{16} [3]. The crystal structure changes from orthorhombic to trigonal at about 408 K. The three phases, I, II and III, were detected at atmospheric pressure; only one structure-type has previously been recognized for NaNO_3 which has a rigid calcite-type structure [4] and therefore is isostructural with the high temperature phase, I, of KNO_3 .

MEASURING METHOD

The pulse method was used to measure the thermal diffusivity a and specific heat capacity C_p [5]. The thermal diffusivity can be calculated using

$$a = 0.139 \frac{l^2}{t_{0.5}} (\text{m}^2 \text{ s}^{-1}) \quad (1)$$

where $t_{0.5}$ is the time required for the lower surface of the sample to reach half-maximum in its small temperature rise, and l is the thickness of the sample.

The specific heat capacity C_p can be measured by the relationship

$$C_p = q/MT_m \quad (2)$$

where q is the power dissipated through the sample, M is the mass of the sample and T_m is the maximum temperature rise.

The power dissipated through the sample can be measured by using a standard material of known specific heat.

The thermal conductivity λ can be calculated from the relationship

$$\lambda = dC_p a \quad (3)$$

where d is the density of the sample.

The heat losses due to radiation from the boundaries of the sample were taken into consideration. The ratio between the diameter of the sample and the thickness can be selected [5]. The experimental errors of these measurements did not exceed 2% for the heat capacity C_p , 3% for the thermal diffusivity and 5% for the thermal conductivity.

RESULTS AND DISCUSSION

Figure 1 shows the variation of specific heat capacity C_p with temperature. It was found that a transition occurs at 408 K. The transition region extended over the temperature interval 403–411 K. Before transition, the structure of KNO_3 is orthorhombic aragonite (phase II) with the space group D_{2h}^{16} and four molecules per unit cell [6]. After the transition, the

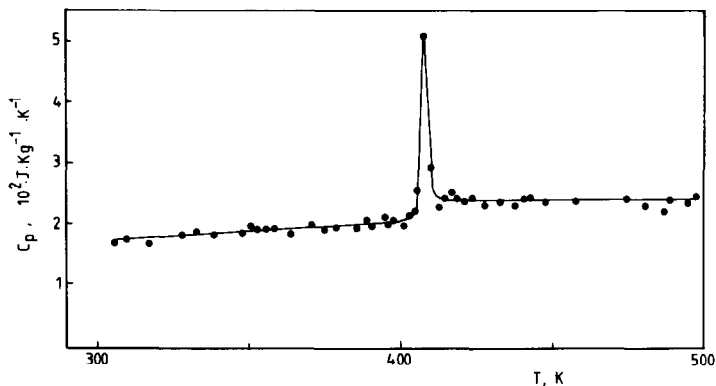


Fig. 1. The variation of specific heat capacity with temperature for KNO_3 .

structure changes to rhombohedral with the space group $C_{3v}^5 - R_{3m}$ and one molecule per unit cell. Before and after the transition the specific heat capacity obeys the Debye theory of specific heat. After the transition, it was found that C_p slightly increases with increasing temperature. The increase in C_p with temperature could be attributed to the anharmonicity of lattice vibration.

The dependence of $\ln \sigma$ on $1/T$ for KNO_3 is shown in Fig. 2. The energy gap was calculated and was found to be 0.984 eV for the orthorhombic structure and 0.285 eV for the rhombohedral.

The thermal conductivity of KNO_3 was found to decrease with temperature as shown in Fig. 3. In addition to the phonon thermal conductivity there can be an electronic contribution due to thermal motion of free electrons, λ_e , and to thermal electron-hole pairs (bipolar), λ_{bj} .

The electronic thermal conductivity λ_e was calculated in terms of the electrical conductivity σ from the Wiedemann-Franz law [7]:

$$\lambda_e = L\sigma T \quad (4)$$

where L is the Lorenz number and T is absolute temperature. The calculated

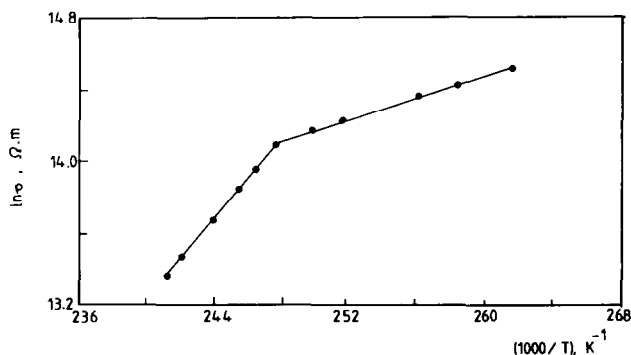


Fig. 2. The variation of $\ln \sigma$ with $1/T$ for KNO_3 .

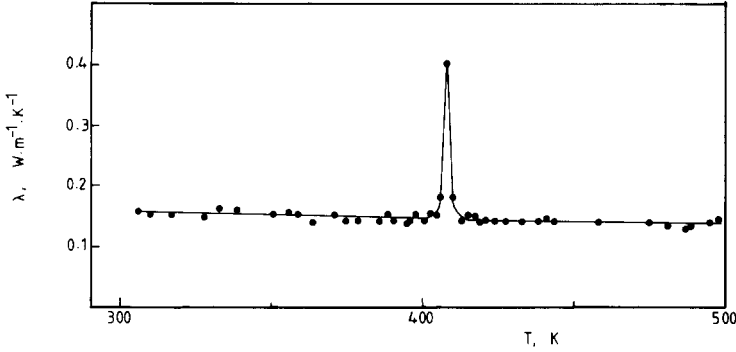


Fig. 3. The variation of thermal conductivity with temperature for KNO_3 .

values of λ_e for KNO_3 changed from $6.2 \times 10^{-15} \text{ W m}^{-1} \text{ K}^{-1}$ at 373 K to $1.04 \times 10^{-14} \text{ W m}^{-1} \text{ K}^{-1}$ at 453 K.

The electron-hole thermal conductivity λ_{bi} can be calculated according to

$$\lambda_{bi} = \frac{3L\sigma T}{3\pi^2} \left(\frac{E_g}{KT} + 4 \right)^2 \quad (5)$$

The calculated values of λ_{bi} for KNO_3 were found to be 6.9×10^{-13} respectively and $8.9 \times 10^{-14} \text{ W m}^{-1} \text{ K}^{-1}$ at 373 K and 453 K. From the above-mentioned results we found that the role of both electrons and bipolars was very small and negligible; therefore we conclude that the main mechanism of heat transfer in the investigated sample is due to phonons.

Figure 4 shows the variation in thermal diffusivity of KNO_3 with temperature: it was found to decrease with increasing temperature. The transition point was also observed at 408 K. The values for a indicate that KNO_3 behaves as an insulator in the measured temperature range.

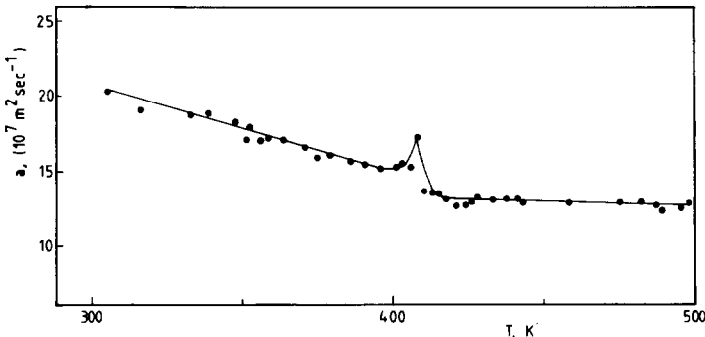


Fig. 4. The variation of thermal diffusivity of KNO_3 with temperature.

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