

Specific heat capacity, thermal conductivity and thermal diffusivity of ammonium nitrate in the temperature interval 293 – 433 K

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Specific heat capacity (C_p), thermal conductivity (λ) and thermal diffusivity (a) of Ammonium Nitrate are measured in the temperature range 293 to 433K. Specific heat capacity shows three transition points at 358K, 398K and 404K. The mechanism of heat transfer is discussed and it was found that the main mechanism of heat transfer is due to phonons only.

Introduction:

Ammonium nitrate is a compound consisting of complex ions of two types: tetrahedral NH_4^+ cations and flat NO_3^- anions. These ions are coupled not only by electrostatic forces but also by hydrogen bonds in the crystal. Crystalline NH_4NO_3 has six stable modifications [1], which differ in structure in ion mobility, and in ion disorder in the lattice.

Phase I, II and III have disorder of ions of both types, whereas IV, V and VI differ in symmetry and in the orientational motions of the NH_4^+ ions. The room temperature phase IV is orthorhombic with a centric space group $P_{mnn}(D_{2h}^{13})$ and two molecules per unit cell [2,3]. At temperatures below 257K, the crystal transforms to another phase V. X-ray results [4] suggested that the crystal structure undergoes noncentric tetragonal in which the NO_3^- groups are involved in an approximately 90° reorientation about the C-axis and one-half of them flip over about axis perpendicular to the C-axis. The space group of phase V; is $P_{42}(C_4^3)$ with $Z = 8$. The NO_3^- groups occupy two non-equivalent sets of C_1 sites while the H_4 groups occupy four non-equivalent sets of C_2 sites. Both kinds of ions are aligned in columns along the C-axis which is a polar axis.

Measuring method:

The pulse method for measuring the thermal diffusivity (a) and specific heat capacity (C_p) was used [5]. The thermal diffusivity can be calculated by:

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

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 determined by the relation

$$C_p = q/MT_m$$

where q is the power dissipated through through the sample

M is the mass of the sample

T_m is the maximum temperature rise.

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

The thermal conductivity λ can be calculated from the relation

$$\lambda = d C_p a$$

where d is the density of the sample.

The heat losses by radiation from the boundaries of the sample were taken in considerations. The ratio between the diameter of the sample and the thickness can be chosen [5]. The experimental errors of these properties did not exceed 2% for heat capacity C_p , 3% for thermal diffusivity and 5% for thermal conductivity.

Results and Discussion:

1. Specific heat capacity

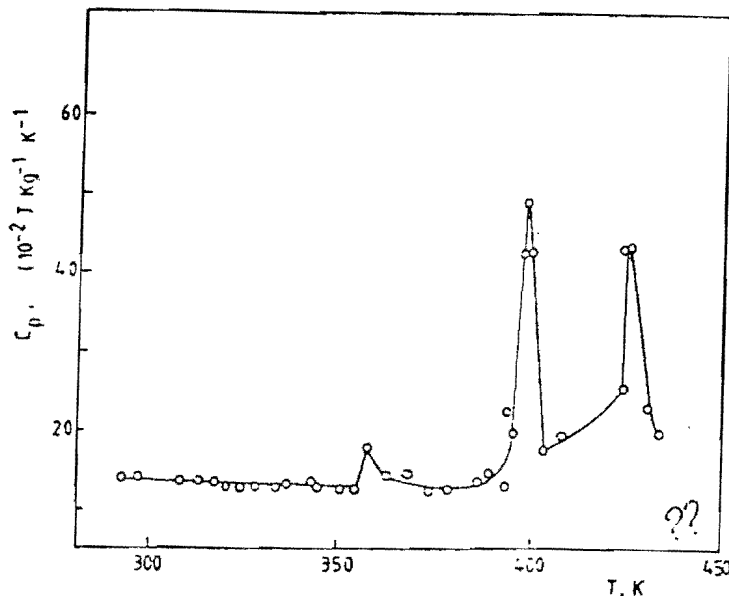


Fig.1. The variation of specific heat capacity with temperature for Ammonium Nitrate.

Fig.(1) shows the variation of specific heat capacity C_p with temperature in the temperature range 293 up to 433K. It was found that C_p does not change with temperature in the orthorhombic phase from 293 to 358K. The results obey Debye theory of specific heat. In the temperature 358 to 398K, the sample NH_4NO_3 change to tetragonal structure which has a unit cell dimensions $a = b = 5.74 \text{ \AA}$ and $c = 4.95 \text{ \AA}$ [6]. The variation of the specific heat capacity C_p with temperature in the internal region of the tetragonal phase due to the planer structure of NO_3 group causes a large anisotropy of the polarizability and there are two space groups of this phase

namely D_{2d}^3 or C_{4v}^2 . In the temperature region the NH_4^+ ions are in a nearly free rotational state in this phase [7-11]. In the temperature interval 398K up to 404K the specific heat also changes with temperature and the material changes to cubic structure. In this phase the nitrate group occupies the centre of the unit cell and the dimensions are $a = b = c = 4.4 \text{ \AA}$. Also the variation of the specific heat with temperature in this region refers to the nitrate group in this phase is fairly free to rotate, while the ammonium group are free to rotate. The temperature range of the two phases are summarized as follows:

Tetragonal 358 to 398 K

Cubic 398 to 404 K

After 405K, the material is melted and changed to liquid state.

2. Thermal conductivity λ :

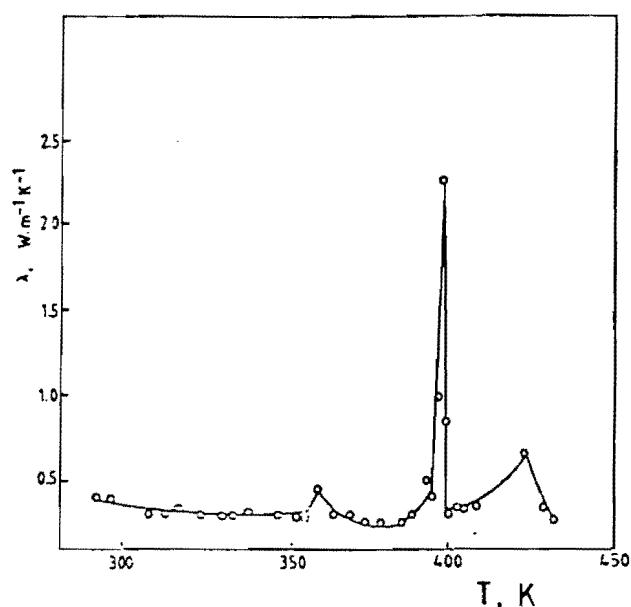


Fig.2. The variation of the thermal conductivity for NH_4NO_3 (Ammonium Nitrate) with temperature.

The thermal conductivity of ammonium nitrate is shown in Fig.(2). It was found that the thermal conductivity decreases as temperature increases. The points of phase transition also appeared at 385, 398 and 404K. The electronic part of thermal conductivity is negligible in the measured temperature range because of the insulating properties of this material. The decrease of thermal conductivity is related to the decrease of the mean free path of phonons with temperature according to the relation [12]

$$\lambda = \frac{1}{3} C_v V l$$

where C_v is the specific heat at constant volume

V is the velocity of sound

and l is the phonon mean free path

So we can conclude that the main mechanism of heat transfer of Ammonium Nitrate is due to phonons only.

3. Thermal diffusivity a :

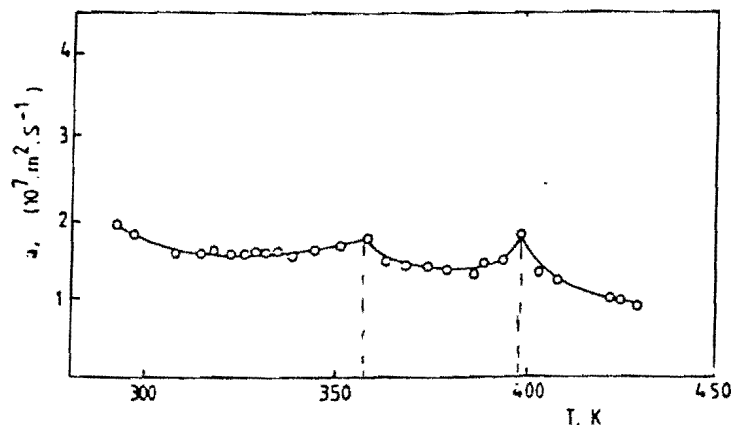


Fig.3. The variation of thermal diffusivity with temperature for Ammonium Nitrate.

The thermal diffusivity for ammonium nitrate is shown in Fig.(3). It was found that the thermal diffusivity decreases as temperature increases. This results indicate that the material is typical insulator. The thermal diffusivity related to the thermal conductivity and specific heat capacity by the relation

$$a = \lambda / d C_p$$

where d is the density of the investigated material.

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