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Electrical and calorimetric properties of sodium hydrogen tartrate monohydrate

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Abstract

This report considers some electrical parameters (dielectric constant and resistivity) and some calorimetric properties (thermal heat capacity, thermal conductivity and thermal diffusivity) as well as the DTA thermogram in the temperature range $30 < T < 140\,^\circ C$ of sodium hydrogen tartrate monohydrate, $NaHC_4H_4O_6 \cdot H_2O$ (SHTMHD).

The accurate measurements of these parameters have revealed the presence of a structural phase transition at about 83 °C, in addition to the phase transformation that results from the loss of water (dehydration). The data are correlated to the restricted rotation of the tartrate ions as well as to the hydrogen bonding scheme.

INTRODUCTION

This work is a continuation of our investigation of the physical properties as related to the phase transitions in some tartrate salts. The hydrogen tartrates are of particular interest because of their important properties. For example ammonium hydrogen tartrate (AHT) and rubidium hydrogen tartrate (RHT) are ferroelectrics and are widely used in modulation and defocussing systems [1]. Single crystals of these two compounds are used extensively for controlling laser emission [1]. Their magnetic, electrical and calorimetric properties are now under investigation in our laboratory.

The hydrogen tartrates form a class of compounds of general molecular formula $MHC_4H_4O_6 \cdot XH_2O$, where M^+ is the univalent ion Na^+, K^+, Rb^+, ... and/or NH_4^+, and X is the number of water molecules ($X = 0, 1, 2, 3, \ldots$).

The crystal structures of some hydrogen tartrates of this series have been determined [2,3]. Usually, the structure is formed by layers of hydrogen-bonded tartaric anions separated by layers of M^+ cations. The tartrate ion consists of two planar halves each consisting of a carboxyl group, a tetrahedral carbon and a hydroxyl oxygen, Fig. 1.

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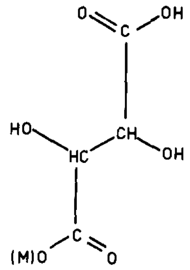

M = K, Na ..... and/or NH_4

Fig. 1. The structure of the hydrogen tartrate molecule.

Recently, we have investigated the electrical and magnetic properties of the sodium tartrate dihydrate, STD [4]. Our measurements indicated the existence of a structural phase change at 75 °C, in addition to the phase change that results from the loss of water molecules at about 130 °C. Also, the electrical and thermal studies of ammonium tartrate (AT) reveal the presence of two structural phase transitions at 62 and 92 °C [5].

In this paper, we report on the resistivity (ρ_{d_c}), dielectric constant (ϵ) and thermal properties (thermal heat capacity C_p thermal conductivity λ and thermal diffusivity σ), as well as the DTA thermogram as a function of temperature in the range $30 < T < 140\,^\circ C$ for sodium hydrogen tartrate monohydrate, $NaHC_4H_4O_6 \cdot H_2O$ (SHTMD). In studying the thermal properties of such materials, different mechanisms of heat transfer may exist according to whether thermal conduction is due to electrons or phonons. There may be one or more mechanisms which contribute to the total thermal conductivity. Because the electrical conductivity of these materials is very low, the electronic contribution to the total thermal conductivity can be neglected.

EXPERIMENTAL

The sodium hydrogen tartrate monohydrate was supplied by BDH. Fine needle-shaped crystals were obtained by slow evaporation of water from a solution of the salt in doubly redistilled water at room temperature.

For the measurement of the electrical properties, specimens were made by painting silver paste on two opposite faces of samples in the form of discs or pellets.

The dielectric constant was determined by an RLC bridge-type (Philips). The temperature was measured using a thermocouple with an accuracy of ±1 °C. The resistivity was measured by means of a digital electrometer (Keithley). In all the electrical measurements, three identical samples were used. The results were reproducible.

For the calorimetric measurements, the powder was pressed under a suitable pressure to form discs of diameter 15 mm and thickness 1–1.5 mm. The pulse method for measuring the thermal heat capacity and thermal diffusivity was used. The details of this method are given elsewhere [6].

The thermal diffusivity σ can be calculated by

$$\sigma = 0.139 \left(l^2/t_{0.5}\right)\mathrm{m^2 sec^{-1}}$$

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

The heat capacity C_p can be measured by the relation

$$C_p = q/MT_\mathrm{m}$$

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 with known heat capacity.

The thermal conductivity λ can be calculated from the relation

$$\lambda = \rho C_p \sigma$$

where ρ is the density of the sample.

The heat losses by radiation from the boundaries of the sample were taken into consideration. The ratio between the diameter of the sample and the thickness can be chosen. 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

In Fig. 2, the d.c. resistivity of the sample (Ω cm) is plotted as a function of temperature in the $40 < T < 140\,^\circ\mathrm{C}$ range. There is a rapid decrease in ρ_dc as the temperature increases to 70 °C, indicating that the material under investigation is a dielectric. This is also clear from the order of magnitude of ρ_dc and/or R. Similar behaviour has been found for STD [4].

In the range $75 < T < 90\,^\circ\mathrm{C}$, the variation of ρ_dc with temperature is slow, resulting in a broad minimum which is taken as evidence for a structural phase change at about 83 °C. This is followed by a rapid increase in ρ_dc as the temperature increases and then by a small shoulder at 130 °C as a result of loss of the water molecules. The latter has been checked by weighing the samples at different temperatures (60, 80, 100, 120, 125 and 130 °C). A loss of weight of about 10% between about 125 and 130 °C was observed.

The relationship between the dielectric constant ϵ and the temperature T (°C) is shown in Fig. 3. As can be seen from the curve, there is a gradual

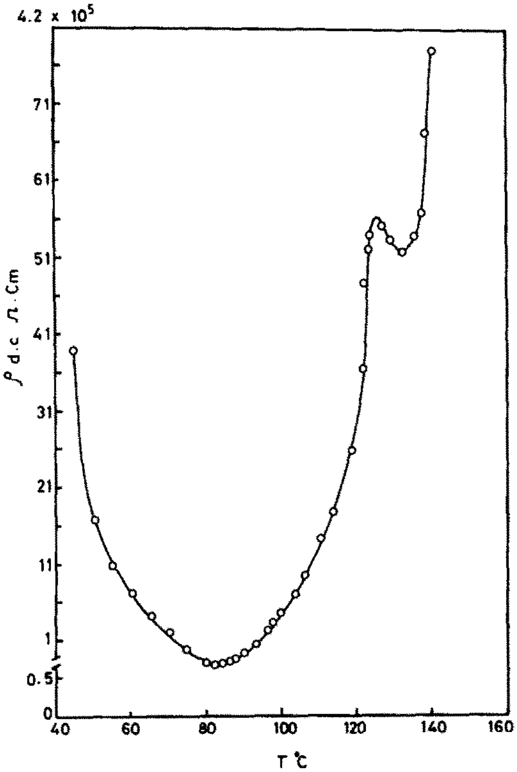

Fig. 2. The relation between resistivity ρ_{dc} (Ω cm) and temperature T (°C).

increase in ϵ as the temperature increases. The occurrence of a spike at about 83 °C is good evidence for the structural phase change. This spike is followed by a reduction in ϵ, and then with a small peak centred at about 130 °C, indicating the second phase transformation due to the loss of one molecule of water.

The calorimetric measurements were made in the range 30–140 °C, which exceeds the Debye temperature (θ_D) of the samples investigated. The variation in C_p of SHTMHD with temperature is shown in Fig. 4a. It can be seen that the curve consists of three parts. The first shows the behaviour of C_p below the structural phase transition at about 83 °C, in which C_p does not change with temperature. This behaviour obeys Debye's theory of the specific heat at high temperature (above θ_D). The second region lies in the temperature range $85 < T < 120$ °C. In this region, the Debye theory of the specific heat does not hold well because the lattice vibration is no longer harmonic. As the temperature approaches 120 °C, there is a decrease in C_p due to dehydration with the phase transition completed at 130 °C according to the equation

$$NaHC_4H_4O_6 \cdot H_2O \xrightarrow{130\,^\circ C} NaHC_4H_4O_6 + H_2O$$

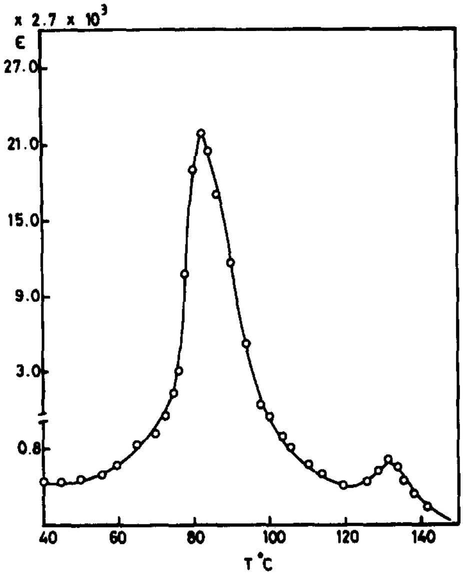

Fig. 3. The variation in the dielectric constant ϵ with temperature T (° C).

This is similar to the case of STD [4] discussed above and also to the case of $CaHPO_4 \cdot 2HO_2$ [7]

$$CaHPO_4 \cdot 2HO_2 \xrightarrow{300\,^\circ C} CaHPO_4 + 2H_2O$$

The loss of water was confirmed by weighing the sample at different temperatures, as above.

The variation of thermal conductivity λ with temperature T is given in Fig. 4b. The thermal conductivity of SHTMHD may be expressed in the form

$$\lambda_{\text{total}} = \lambda_{\text{ph}} + \lambda_{\text{e}}$$

where λ_{e} is the electronic part of thermal conductivity due to electron diffusion, which depends on the electrical conductivity of the material.

This sample is typically a dielectric, so the electronic contribution to the thermal conductivity is very small. Thus the main mechanism of heat transfer is due to phonons only

$$\lambda_{\text{total}} \approx \lambda_{\text{ph}}$$

The thermal diffusivity σ depends on the heat capacity C_p and the thermal conductivity λ through the relation

$$\sigma = \lambda / \rho C_p$$

where ρ is the density of the material.

Figure 4c shows the variation of σ with temperature in the range $30 < T < 140\,^\circ C$. From this relation, it is clear that in the temperature range

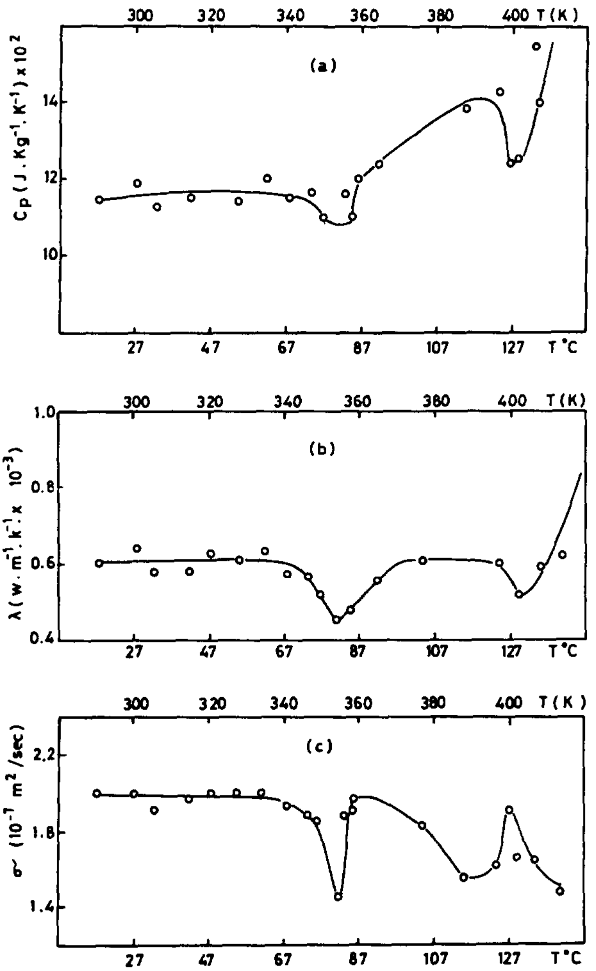

Fig. 4a, b, c. The relationship between the calorimetric parameters and temperature T (°C), respectively: a, C_b; b, λ; c, σ.

$30 < T < 60\,^\circ C$ the value of σ is practically temperature independent. This is followed by a gradual reduction in the values of σ resulting in a minimum value at 83 °C which corresponds to the structural phase change. This is followed by an increase in σ as the temperature increases up to 95 °C. The second phase transformation due to the dehydration is complete at about 130 °C.

The differential thermal analysis (DTA) of SHTMHD was performed in the temperature range $30 < T < 140\,^\circ C$ with a heating rate of $10\,^\circ C\ min^{-1}$ and with a sensitivity (ΔT) of about $10\ mV\ cm^{-1}$. The DTA thermogram is shown in Fig. 5. Two endothermic phase transformations are indicated.

The first endothermic phase transformation (structural) is complete at about 83 °C. The sudden change in ΔT suggests a first-order phase transition.

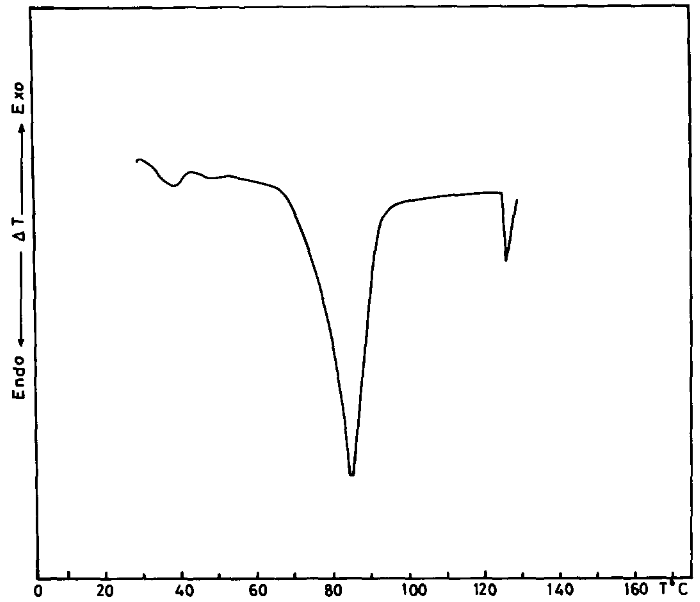

Fig. 5. DTA thermogram.

The endothermicity, the exothermicity and/or the rate of transition are measured by the height of the peak ΔT_{max}, where ΔT_{max} is the temperature at which the phase change is completed.

In conclusion, the phase transition observed in this salt at about 83 ° C may be attributed to the rotation of the tartrate ions by thermal energy. From the data for the crystal structure of some tartrates [2,3,8–10], this rotation is usually restricted and closely related to the hydrogen bonding system. Thus, one can say that in the present salt as the temperature approaches 83 ° C, the rotation of tartrate ions reaches the maximum allowed value as a result of the weakening of the hydrogen bonding system. This will affect the stability of the structure as a whole, resulting in the observed phase transition. This is also the case for STD [4] and AT [5].

The loss of the water molecules at about 130 ° C is the main reason for the second phase transformation.

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