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Electrical properties and phase transitions in ethylenediammonium dinitrate

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dc and ac electrical conductivities, dielectric constant and dielectric loss factor in single crystals of ethylenediammonium dinitrate (EDN) have been measured axiswise as a function of temperature. All the above properties exhibit anomalous variations at 404 K thereby confirming the occurrence of a phase transition in EDN at this temperature. Electrical conductivity parameters have been evaluated and possible conduction mechanisms are discussed. The role of protons in electrical transport phenomena is established by chemical analysis.

1. INTRODUCTION

Electrical properties and phase transitions in crystals containing ammonium ions have been extensively studied with special reference to the protonic conduction in them [1-6]. However, only very rarely substituted ammonium compounds have been investigated in any detail. Takahashi et al [7] have studied the ionic conductivity in triethylenediammonium sulphate and established protonic conductivity in them. Ethylenediammonium dinitrate $(H_3NCH_2CH_2NH_3)(NO_3)_2$ is a structurally interesting compound, belonging to the category of organic solid ion conductors. The crystal structure of this compound has been elucidated by Mylrajan and Srinivasan [8]. At room temperature, the crystal belongs to the triclinic space group $P\bar{1}$ with $Z = 1$ with one molecule per unit cell having dimensions $a = 5.068(2)$, $b = 5.514(3)$, $c = 7.173(3)$ Å $\alpha = 104.93(3)$, $\beta = 90.16(4)$ and $\gamma = 93.65(4)$ at 300 K. They have also identified high temperature phase transitions in this material by infrared and Raman spectroscopy and DSC. In this paper we present a detailed investigation of the temperature dependent variations of dc and ac electrical conductivity, dielectric constant and dielectric loss in single crystals of ethylenediammonium dinitrate (abbreviated as EDN) along c-axis and perpendicular to it (c*-axis). We have confirmed and accurately identified the high temperature phase transition and evaluated the activation parameters for the electrical conduction in different temperature ranges.

2. EXPERIMENTAL

EDN was prepared by mixing solutions of distilled ethylenediammine (Glaxo Laboratories) and nitric acid (BDH Analar) in 1:2 mole ratio. The solution was evaporated on a waterbath and the microcrystals were collected by filtration. Large transparent single crystals were grown by slow evaporation of the saturated solution of the material in double distilled water at ambient temperature. Stoichiometry of the final product was confirmed by chemical analysis.

Crystals of EDN are not hygroscopic. Samples of typical dimensions 5mmx5mmx1mm were cut parallel to and perpendicular to the cleavage plane, which is the (001) plane just as in the case of ethylenediammonium chloride [9]. The two broad faces of the samples were vacuum deposited with silver to render good electrical contact. The sample holder and the chamber used for the measurement of electrical properties were similar to those described by Syamaprasad and Vallabhan [10]. The samples were annealed at 100°C in vacuum for 30 minutes before making the measurements. All the measurements were made in a dynamic vacuum of 10^{-3} Torr in the temperature range 100 to 420 K.

In the measurement of dc conductivity, a steady dc bias of 10–100 V was applied across the specimen and the current was measured using Keithley electrometer model 617. The ac conductance G, capacitance C and dielectric loss $\tan\delta$ were measured as a function of frequency as well as temperature using Hewlett

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Packard LF Impedance Analyzer model 4192A. Knowing the dimensions of the sample, the specific conductance was calculated. Dielectric constant was derived from the measured values of capacitance after eliminating the lead and fringe capacitance using standard methods [11]. DSC traces were recorded using Perkin Elmer DSC-7 instrument with single crystals as well as with finely powdered samples. The temperature corresponding to the onset of thermal anomaly is reported as the transition temperature in the present work.

3. RESULTS

3.1 dc Electrical Conductivity

Fig.1 shows the $\log\sigma$ vs. $10^3/T$ plots within the temperature range range 300 to 410 K for EDN along c and c*-axes, where σ is the dc conductivity. Each plot consists of two straight line segments below 400 K. The segments fit into the equation $\sigma = \sigma_0 \exp(-E/kT)$ where σ_0 is a constant, k is the Boltzmann's constant and E is the activation energy. In the first heating cycle which was terminated at 408 K three straight line regions separated by knees at 328 K and 378 K and an abrupt change at 404 K were observed. The measurements do not show any anomalous variation in the temperature region below 328 K, ruling out the possibility of any phase transition in this region. In the second run the conductivity at room temperature was found to be increased by one order of magnitude and the knee at 328 K suppressed. In the ensuing runs the plots were reproducible. Measurements were repeated using a number of samples.

The sudden jump in the conductivity resulting in a Λ-type anomaly at 404 K indicates a phase transition. The activation energy E and "infinite temperature intercept" $\log\sigma_0$ obtained by analysing different segments of the Arrhenius plots are presented in Table 1.

Table 1
Activation energy E and intercept $\log\sigma_0$ for dc conductivity of EDN single crystal along c and c*-axes.

Axis	Temperature range (K)	Activation energy (eV)	$\log\sigma_0$
c	300 to 378	1.22	7.9
	378 to 400	2.12	15.8
c*	300 to 378	1.11	5.2
	378 to 400	2.17	16.6

3.2 ac Conductivity

Fig.2 is a typical plot of $\log\sigma_{ac}$ against $10^3/T$ for EDN over the temperature range 320 to 410 K at 30 kHz, the data covering several heating and cooling runs. The abrupt change in σ_{ac} at 404 K indicates again the phase transition occurring in the crystal at that temperature in conformity with dc measurements.

Fig.3 presents the Arrhenius plots

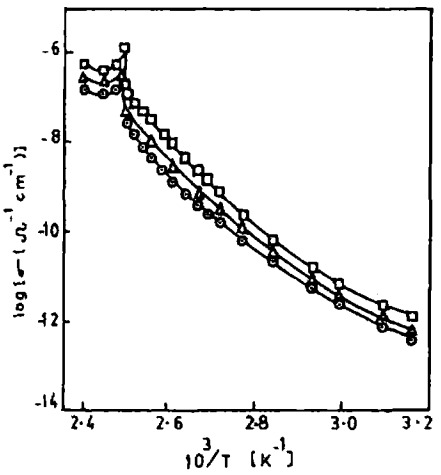

Fig.1. dc conductivity versus temperature plots for EDN. ○ -along c-axis in the heating run, Δ - cooling run, □ - along c*-axis in the heating run.

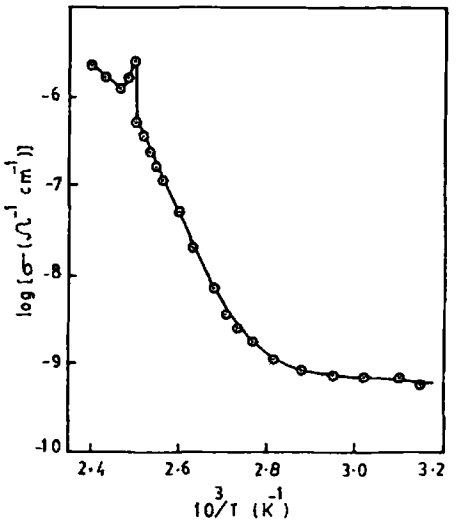

Fig.2. Variation of ac conductivity with temperature along c-axis at 30 kHz.

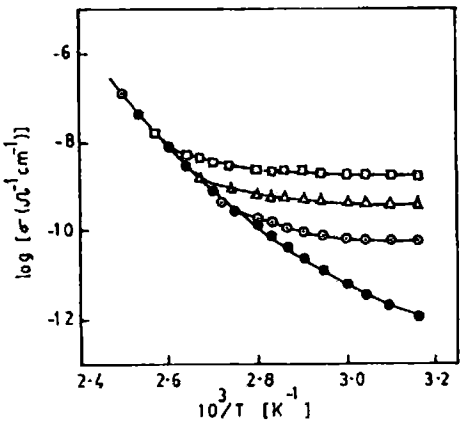

Fig.3. ac and dc conductivities of EDN as a function of temperature. ● - σ_{dc}, ⊙ - σ_{ac} at 1 kHz, △ - σ_{ac} at 30 kHz, □ - σ_{ac} at 100 kHz. (along c*-axis).

($\log \sigma$ vs. $10^3/T$) for the ac and dc conductivity data obtained using pure EDN single crystals along c*-axis. It is observed that σ_{ac} approaches σ_{dc} at higher temperatures but deviates from σ_{ac} at low temperatures, the deviation being larger for higher frequencies. In the temperature range from ambient upto 378 K the plots are frequency dependent. The temperature dependence of σ_{ac} is not very significant below this temperature. The ac conductivity curves merge together themselves and also with the dc conductivity curve above 378 K, showing that the same conduction mechanism is operative in this high temperature region.

3.3 Dielectric Constant

Fig.4 displays the temperature dependence of dielectric constant along c and c*-axis at different frequencies. The variations of dielectric loss along c*-axis is represented in Fig.5. The dielectric constant and dielectric loss vary slowly upto 378 K. Above this temperature the variations are rapid and an abrupt change occurs at 404 K, confirming the phase transition at this temperature.

The results of the measurements of dielectric constant on single crystals of EDN in the temperature range 375 K to 410 K are shown in Fig.6. Dielectric constant shows an abrupt increase at 404 K. In the cooling run it shows a hysterisis of 3 K. Similar results were obtained by measurements in the c*-axis also.

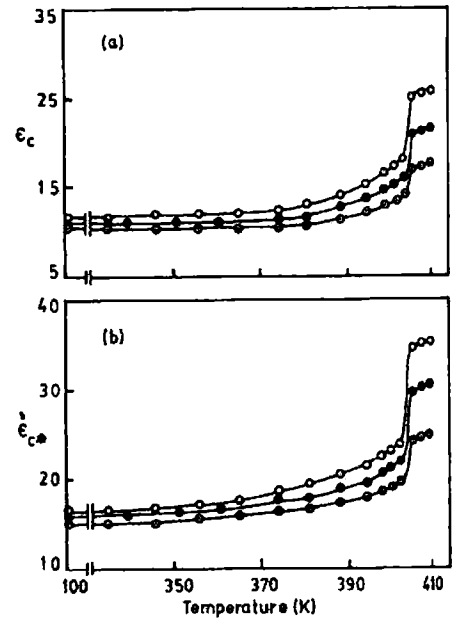

Fig.4. Dielectric constant of EDN as a function of temperature at different frequencies along c-axis (a) and c*-axis (b) ⊙ - 100 kHz, ● - 30 kHz, ○ - 1 kHz.

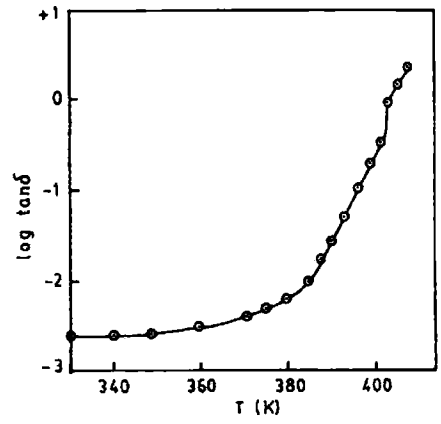

Fig.5. Variation of tan δ with temperature along c*-axis.

4. DISCUSSION

The electrical conduction in ammonium containing crystals has been discussed by different workers. While explaining the mechanism of conduction in ammonium chloride, Herrington and Stavely [12] have postulated that there is significant amount of

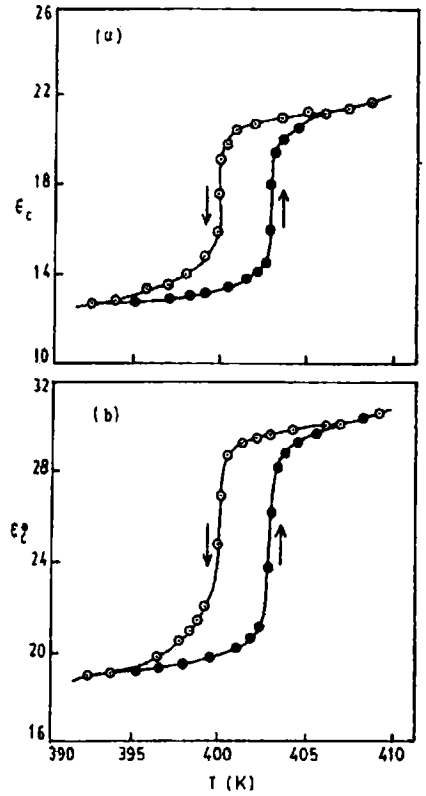

Fig.6. Dielectric constant versus temperature plots for EDN along c-axis (a) and c*-axis (b) in the heating and cooling runs.

dissociation in these crystals to form molecular species which may be represented by $NH_4^+ + Cl^- \longrightarrow NH_3 + HCl$. They proposed a three stage proton switch mechanism in which (i) the proton leaves the NH_4^+ ion and joins the Cl^- ion forming NH_3 and HCl molecules (ii) a vacancy and the appropriate molecule exchange positions and (iii) the proton jumps back to NH_3 forming NH_4^+ and Cl^- ions again. Thus a net displacement of charge can be accomplished by an applied electric field. The possibility of a proton switch mechanism in ammonium salts has further been supported by the work of Fuller and Pattern [13] and Taylor and Lasker [2]. The concepts put forward by Herrington and Stavely seem to be applicable to explain the mechanism of conduction in EDN also where the cations and anions are connected by hydrogen bonds. Here the initial step in the transport process can be the breaking of a hydrogen bond and the transfer of the proton directly to the neighbouring nitrate ion. Thermal disorder giving rise to fluctuations of the electrostatic field will also be in favour of such a proton transfer. Subsequently the neutral HNO_3 molecule may migrate to an adjacent vacancy and in the final step a reversal of the proton switch may occur. It may be noted that the activation energy for conduction in EDN below 378 K (Table 1) compares very well with the activation energies for proton conduction in NH_4Cl and NH_4Br [2,14,15].

A sharp demarcation into 3 straight line regions for the conductivity plot for c-axis is not clearly discernible in comparison with that for c*-axis (Fig.1). This could probably be due to the existence of a continuously variable barrier [16] along this direction. Also the higher value of σ_{dc} along c*-axis (Fig.1) could be due to the higher mobility of carriers along this axis, which is parallel to the cleavage plane. The change in the slope of σ_{dc} vs. $10^3/T$ plot near 378 K indicates a change in the dominant conduction mechanism. It is also seen that the log σ_{ac} vs. $10^3/T$ plots merge together and become identical with the corresponding dc conductivity plot at about 378 K. Around this temperature it is expected that the rotational reorientation of the NH_3 groups of EDN is initiated as indicated by the infrared studies [8] which show a gradual shift in the NH_3^- rocking frequencies.

The magnitudes of ac and dc conductivities of EDN single crystals show a significant difference in the low temperature region (Fig.3). Similar behaviour was observed by Barteit et al [17] in NH_4Br. The difference can be attributed to loosely bound protons which are able to jump with the field. Thus in an ac field the hopping probability becomes proportional to the frequency of the field and the ac conductivity shows an increase with increase in frequency.

The dielectric constant of EDN single crystals at 300 K along c*-axis (16) is found to be greater than that along c-axis (11). Ionic crystals with non-cubic structure usually exhibit such anisotropy in dielectric properties. The abrupt changes in dc and ac conductivity, dielectric constant and dielectric loss at 404 K are certainly due to the structural phase transition occurring at this temperature as revealed by earlier studies [8]. The thermal hysteresis observed in the dielectric measurement at this temperature is indicative of a first order transition. The sharp rise in conductivity can be due to the large-scale availability of the mobile carriers released during the rearrangement of the lattice as a whole. The higher value of dielectric constant observed at the transition point arises evidently from the contribution to

the orientational polarizability from the freely rotating NH_3 groups. The mechanism involved in this transition is analogous to those observed in many other crystals containing ammonium groups [6,7,14,18].

From the DSC and IR and Raman Spectral studies, Mylrajan and Srinivasan [8] have reported the existence of three phases in EDN below its melting point at 463 K, viz., Phase III $\xrightarrow{404\ K}$ Phase II $\xrightarrow{412\ K}$ Phase I. Their DSC thermograms indicated two peaks at 404 K and 412 K in the forward run, whereas only one broad peak was observed at 392 K in the reverse direction. They attributed the broad peak at 392 K to the merging of closely occurring phase transitions. The phase transition at 404 K is associated with a distinct change in frequency for all the modes. Splitting of the NH_3 assymmetric stretching bands was observed at 3193 and 3228 cm^{-1} in the Raman Spectrum at 90 K, while a single broad band at 3210 cm^{-1} was seen at 420 K. The band at 58 cm^{-1} at 300 K moved to low frequencies as the temperature was increased. At 420 K it shifted to 40 cm^{-1} and appeared as a shoulder of the Rayleigh wing, indicating tendency for mode softening. The infrared-active C-N stretch and NH_3 rocking modes appeared to be the most sensitive to the phase transitions, and especially NH_3 rocking mode at 1088 cm^{-1} showed a large shift with increasing temperature. This was observed with increased half bandwidth at 1070 cm^{-1} at 410 K and at 1068 cm^{-1} at 420 K. These changes clearly indicate rearrangement of the skeleton. Appreciable NH_3 reorientation is evident from the broad and weak nature of NH_3 stretching rocking and bending modes in the spectrum of the high temperature phase of this material. This is in good agreement with the results of our dielectric measurements which indicate the existence of fairly freely rotating polar groups in the high temperature phase. However, it is to be noted that (C-N) stretching frequency showed only slight changes near 412 K. X-ray and/or neutron diffraction studies will be needed to get a clear picture regarding the crystal structure in the high temperature phase.

In the present investigation it is found that the samples of EDN single crystals remained transparent after the phase transition at 404 K. The reproducibility of the results was good in all runs terminated at 408 K. Our results suggest that if the sample is heated to a temperature too close to the reported second transition temperature of 412 K, the pattern is not well reproducible. If this temperature is exceeded, the sample turns opalescent and the

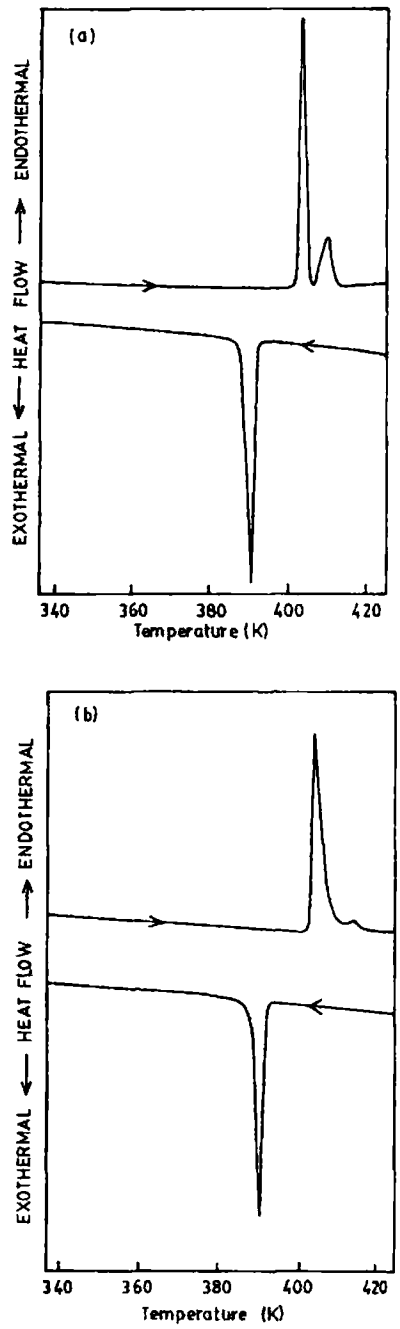

Fig.7. DSC traces for EDN (a) single crystal (b) powder.

electrical measurements yield erratic results. To alleviate the vagueness regarding the nature of the reported phase transition at 412 K, we have approached the problem from two different

angles: (i) what is the influence of the physical form of the sample (ie., powder or single crystal) on the phase transitions and (ii) does the sample undergo any transformation with loss of material in volatile form?

To ascertain the nature of the physical form of the material near this transition, DSC thermograms were recorded with single crystals as well as with finely powdered samples of nearly the same weight. The results are shown in Fig.7. The peak at 412 K is of pronounced intensity in single crystals while it is hardly measurable with finely powdered samples.

To check the formation of any volatile component at the transition temperature, the following methodology was used. Samples of EDN were heated to a temperature above 412 K in a tube fitted to a capillary scrubber wetted with distilled water. The vapour was flushed out in a slow stream of dry nitrogen and trapped in the scrubber. The scrubber liquid was tested with diphenylamine in sulphuric acid [19]. The results indicated the evolution of nitric acid. In a separate experiment EDN sample was heated to 416 ± 1 K. The evolved vapours were swept in a stream of nitrogen for 30 minutes and absorbed in a trail of bulbs containing triply distilled water. The amount of nitric acid collected was determined by spectrophotometry [20]. The experiment was repeated and the sample gave out an average of 0.15 mg of HNO_3 per gram of EDN.

5. CONCLUSIONS

Axiswise measurements of dc and ac conductivity, dielectric constant and dielectric loss factor in EDN have been carried out within the temperature range 100 to 410 K using single crystals. The occurrence of a phase transition in this material is confirmed and the transition temperature has been accurately fixed at 404 K. The hysteresis shown in the dielectric behaviour indicates that the transition is of first order. The irreversible peak at 412 K in the DSC trace has been established as due to the formation of HNO_3. Protons have been found to play a vital role in the conduction mechanism.

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