Thermally Stimulated Depolarisation Currents in Urea and Thiourea

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Thermally Stimulated Depolarisation Currents in Urea and Thiourea

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Thermally stimulated depolarisation currents (TSDC) are observed in Urea and Thiourea. Urea gives a single TSDC peak at 278 K, while for Thiourea there is a prominent peak at 290°K and the spectrum below 290°K is little complicated. The prominent peaks are interpreted in terms of molecular relaxations. For Urea, space charge polarisation peak above RT was also observed.

INTRODUCTION

Urea, $(NH_2)_2 CO$ and Thiourea $(NH_2)_2 CS$ are molecular crystals that have simple crystal structures. The crystal structure of urea is tetragonal with two molecules per unit cell[1-5] whereas thiourea has an orthorhombic structure with four molecules per unit cell.[6-8] In urea, packing is determined by $N—H \cdots O$ hydrogen bonds and the molecule is coplanar. It was shown by neutron diffraction experiments[8] that the same is true for thiourea also, though the hydrogen bonding is not as strong as in urea.

Thiourea was discovered to be ferroelectric by Solomon in 1956[9] and the dielectric properties were subsequently investigated by Goldsmith and White.[7] The solid exists in five distinct phases: Solid I below 169°K (ferroelectric), Solid II from 169°K to 170.5°K (antiferroelectric), Solid III from 170.5°K to 175°K (ferroelectric), Solid IV from 177°K to 202°K (antiferroelectric) Solid V above 202°K (paraelectric). Dielectric loss measurements of thiourea[10] showed a broad dipolar resonance absorption corresponding to a potential barrier of 0.11 eV in the region 169–171°K and a discontinuity in the loss curve around 177°K. Later experiments by Mckenzie *et al.*[11] established additional distinct ferroelectric regions within phase II. The results of more recent studies by Czapla *et al.*[12] suggest that the relaxation in phase V is very similar to that of phase IV near the transition temperature.

Thus these peculiar features of thiourea necessarily distinguish it from the other ferroelectrics. It has to be noted that ice is the only ferroelectric crystal in which thermally stimulated currents are reported.[13]

With a view that the thermally stimulated depolarisation currents from urea and thiourea may throw some light on the molecular relaxation behaviour the present investigations are taken up on these simple but yet complicated systems. It has to be noted that except for the studies on TL in these materials[14,15] no results on any of the thermally stimulated processes are reported till now.

EXPERIMENTAL

Micro crystallite powder of Analar grade of urea pressed in the form of a pellet with area varying from 0.25 cm^2 to 1 cm^2 and thickness 0.5–2 mm was used. The electrodes were formed by evaporative coating of silver on both sides of the pellet. Single crystals grown in aqueous or ethanol medium were too small for the study. Hence the investigations pertain only to pellets of urea.

Powder of thiourea made as pellet with evaporated silver electrodes, as in the above case, were made use of. Single crystals of thiourea were also grown in aqueous medium. The evaporation rate is adjusted so that crystals are formed over a period of several weeks. The crystals form as six sided orthorhombic prisms. They exhibit distinct cleavage in the plane perpendicular to ⟨010⟩ which is ferroelectric direction. Specimens for the measurement were prepared by cleaving suitable samples and applying silver paint. Considerable care has to be taken to avoid overheating of the pellet while evaporative coating and the electroded samples must be protected from prolonged exposure to atmospheric humidity. Thiourea is decomposed even by moderate heating and in the presence of moisture reacts with silver to form the sulfide. Experiments were done on the pellet as well as on the crystal with the electric field both in ⟨010⟩ and ⟨001⟩.

The low temperature measurements were made by mounting the samples in a suitable cryostat. Current recordings were done using 610 C Keithley electrometer and a "Servogor" recorder. Temperature of the samples was monitered by copper-constantan thermocouple. Because of the reactivity of thiourea it was never taken above RT.

RESULTS

Pellets of urea when polarised at 260°K with a field 2 kv/cm and cooled to 90°K yield a single TSDC peak at 278°K on subsequent warming at 6°K/min. The peak position was independent of the thickness of the specimen used as
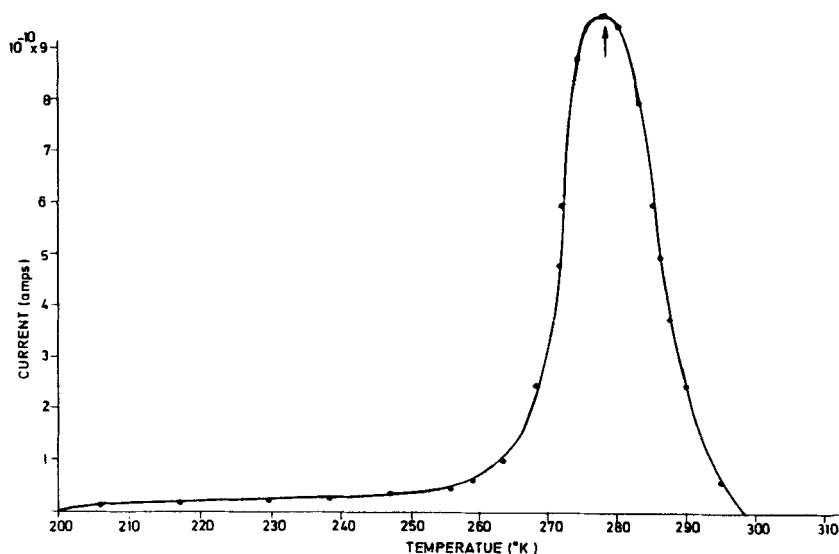
Fig. 1 T.S.O.C. IN UREA PELLET
Vp = 200 V, Tp = 260°K, tp = 20 mts.

well as of the polarisation temperatures. A typical spectrum is shown in Figure 1.

The thermoelectret behaviour of urea in the high temperature region (300°K–395°K) is explained in Figure 2. Polarisation was done at different temperatures above RT. The sample was then cooled to RT and then heated up at the rate of 4°K/min. In all the cases represented the total polarising time was one hour. TSDC peaks very near to the melting point were obtained as shown. As the polarisation temperature was increased from 325°K to 345°K the peak position shifted from 387.5°K to 391°K. However further increase in T_p resulted in the decrease of the maximum to 385.5°K. This is rather a surprising behaviour. When the heating rate was lowered to 1°K/min the peak position did not shift; instead the entire peak is broadened out centering around 390°K. The inset in Figure 2, shows the variation of the maximum intensity with the field. It can be seen that saturation is reached at low field levels of the order 2.0 kv/cm.

Crystals of thiourea, of various thicknesses ranging from 0.5–2 mm were used. The electric field was applied along $\langle 001 \rangle$ at 275°K and the crystal cooled to 90°K. On warming in short circuit conditions TSDC spectrum as the one shown in Figure 3. was obtained, Two peaks, one at 290°K and another at 265°K, could be seen. However, when the polarisation and the measurement were done along $\langle 010 \rangle$, the ferroelectric direction, a TSDC thermogram with
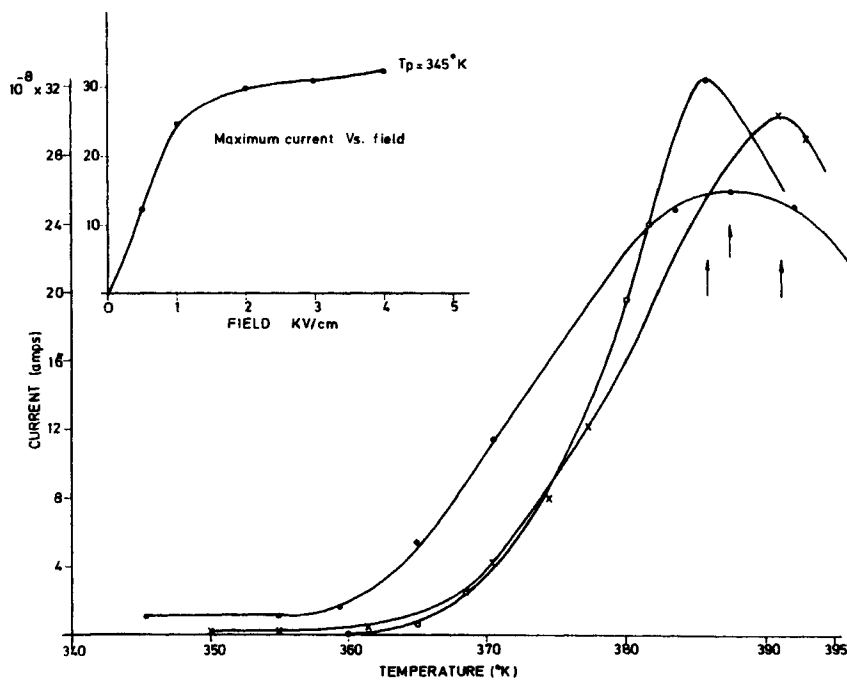
Fig. 2   T.S.D.C. IN UREA PELLET.
Tp = 325°K for (1) , 345°K for(2) and 365°K for (3)
Vp = 300V, tp = 1 hr.
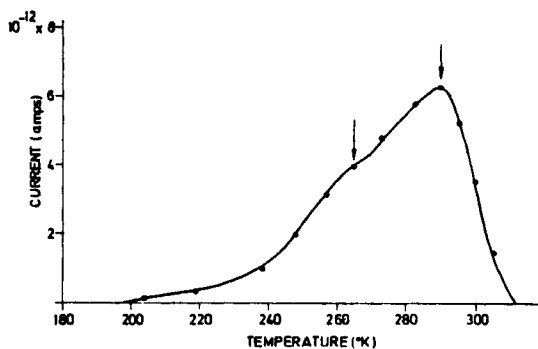
Fig. 3   T.S.D.C. IN THIOUREA : $\vec{E}$ along (001) ;
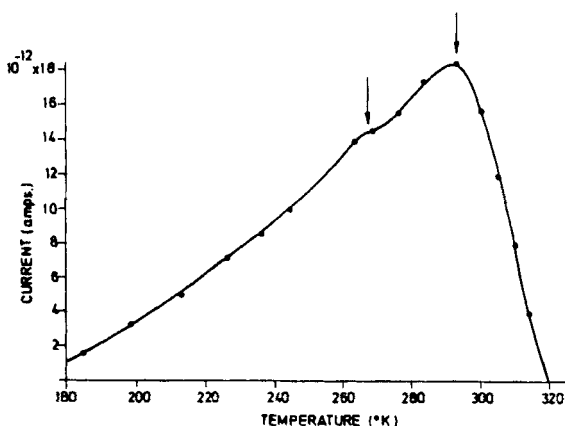Vp = 50V,   Tp = 275°K , tp = 15mts.

Fig. 4   T.S.D.C. IN THIOUREA : $\overrightarrow{E}$ along (010) :
Vp = 100V, Tp = 275°K, tp = 15 mts.

intensity one order more than the previous one was obtained. A typical
spectrum is given in Figure 4. The behaviour of the peak at 265°K region in
both the cases was peculiar. It did not either grow with the field or shift with
a change in polarisation temperature. Whereas the peak at 290°K increased
in intensity with the increasing field strength. Also when the polarisation
temperature was lowered to 180°K the intensity of the peak increased by
almost two orders of magnitude. However, apart from the peak at 265°K
there was yet another at 246°K as can be seen from the inset of Figure 5. The
single peak at 290°K is the one obtained after peak cleaning.

TSDC behaviour in thiourea pellet is extremely simple as the one for urea.
A typical thermogram with a peak at 293°K is given in Figure 6. The results
for urea and thiourea are summarised in Table I. The form factors δ/ω where
$\delta = T_2 - T_m$ (T_2 the upper half width temperature, T_m the peak position) and
$\omega = T_2 - T_1$ (T_1 the lower half width temperature) for the TSDC peaks of
urea and thiourea are listed in Table II. The isolated peaks of urea and

TABLE I

T.S.D.C. data for urea and thiourea

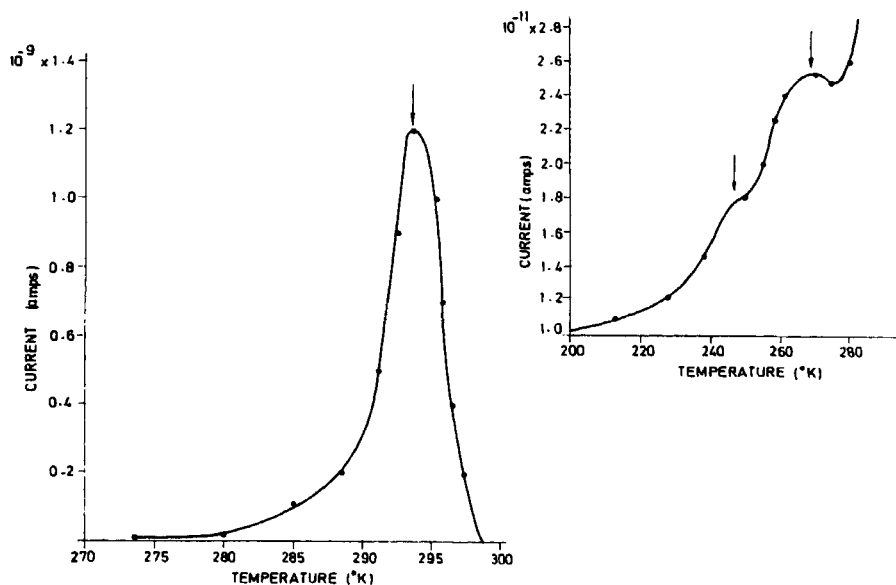| Sample	Field direction	T_p (K)	T_m (K)
Urea pellet	—	260	278
Thiourea pellet	—	260	293
Thiourea crystal	001	275	290, 265
	010	275	290.5, 267
	010	180	293.5, 269
			246

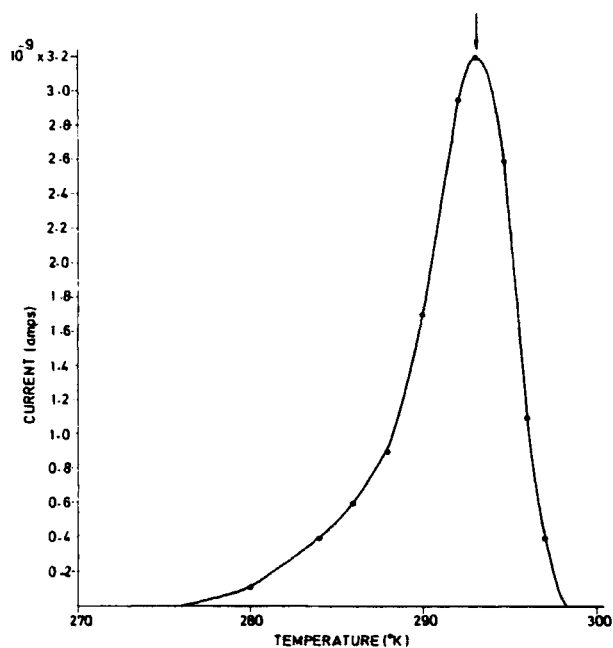Fig. 5   T.S.D.C. IN THIOUREA : $\vec{E}$ along (010), Vp = 120 V, Tp = 180°K, tp = 5 mts.

Fig. 6   T.S.D.C. IN THIOUREA PELLET
Vp = 50V, Tp = 260°K, tp = 15 mts.

thiourea yield an activation energy of 0.7 eV respectively by initial rise method. No rigorous analysis could be undertaken due to the poor knowledge of the questions for the effects observed.

DISCUSSION

The dielectric measurements of urea and thiourea[16,17] suggest that both urea and thiourea exhibit Zwitter ion characters. Molecules are said to exist in Zwitter ion forms when positive and negative charges exist in different parts of the molecule. The Zwitter ion structure for urea is given as:
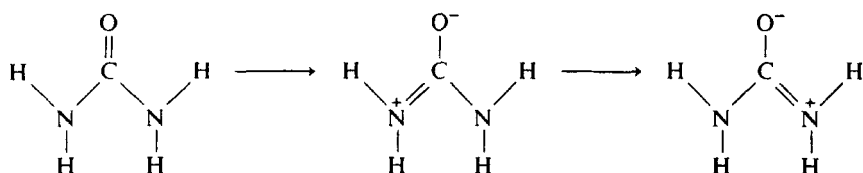
Thiourea also exhibits similar structure. The term "Zwitter ion" was carried over to this structure although it is a resonance hybrid and not a typical Zwitter ion. Hence in all the discussions about urea and thiourea, the term Zwitter ion means a molecule with a complete separation of charge regardless of how it comes about.

There is spectroscopic evidence for such resonance structure[18] from the fact that C—N bonds exhibit double bond character. For the ionic form a net negative charge is centered around oxygen atom and the positive charge is distributed over the two nitrogen atoms. The resultant asymmetric molecule is an effective dipole in a gross definition, with very high dipole moment. The process of denaturation of protein by urea was explained successfully using the Zwitter ion character of urea.[19] The ionic form of thiourea was also made use of in the calculation of spontaneous polarization by Calve[20] and Futema.[21] Studies on Raman Spectrum of thiourea crystals support the predominant ionic form.[22]

Considering the TSDC peaks as those due to the relaxation of Zwitter ion dipoles the polarisation P_o attained by the systems can be calculated from the expression

$$P_o = \frac{N\mu^2}{3KT_p} E_p \tag{1}$$

where N is the concentration of dipoles μ its dipole moment, E_p the polarising field, T_p the polarisation temperature and K is the Boltzmann constant.

TABLE II

Form-factors for the TSDC peaks in urea and thiourea

Sample	δ $(T_2 - T_m)$ K	ω $(T_2 - T_1)$ K	δ/ω
Urea pellet	8.0	14.5	0.55
Thiourea pellet	2.4	5.6	0.42
Thiourea crystal	2.5	4.25	0.51

The dipole moment of the ionic structure is found to be 12 Debye.[21] In the case of urea the percentage of Zwitter ions is 60 percent whereas it is 75 percent in thiourea. The values of P_o for urea and thiourea thus calculated are compared with the area under the curve in Table III. It has to be noted that such comparisons have been made in the results pertaining to ionic crystals,[23,24] ice crystal[25] and naphthalene.[26]

The agreement between the two values in the present case suggests the possibility of the relaxation of ionic dipoles being responsible for the process observed. However, apart from this ionic contribution there will always be a molecular contribution. For urea pellet the result is simple whereas for thiourea the results are little complex. Thiourea, unlike urea, exhibits five different phases and hence the complexity in the TSDC spectrum is under-standable. The broad bands on the low temperature side of the prominent peak obtained in the single crystal may tentatively be attributed to the phase changes. Nevertheless the absence of such bands in the studies on pellet is rather surprising.

It is interesting to note that ice is the only ferroelectric crystal in which TSDC results are reported. Even in that case the spectrum was observed to exhibit a complex nature.[25] The disagreement between the values of polarisation obtained from the expression $N\mu^2 E_p/3KT_p$ and from TSDC peak was attributed either to the existence of ferroelectric domains oriented in opposition to the field or to a non uniform field distribution throughout the sample.

The application of an external field has two consequences on the ferro-electric domains: (i) the polarisation within each domain changes, at low

TABLE III

Polarisation for urea and thiourea

Sample	$N\mu^2 E_p/3KT_p$ (As)	Area under the curve (As)
Urea pellet	1.8×10^{-7}	1.4×10^{-7}
Thiourea pellet	1.08×10^{-7}	1.8×10^{-7}
Crystal (010)	4.5×10^{-8}	5.1×10^{-8}

field strengths this change is linearly related to the applied field and at not so low fields the polarisation of a domain tends to vary non-linearly with field; (ii) the configuration of domains changes if the applied field exceeds the coercive field for some domains and domains switch gradually or discontinuously into the direction, of the field. The present results are for low polarising field strengths and hence do not correspond to a single domain crystal and there is always a possibility of the existence of ferroelectric domains oriented antiparallel to the field. Though no information about the domain-wall motion could be obtained from the present investigations, yet the results are promising and suggestive of the use of the thermocurrent technique for ferroelectric crystals.

Another feature of the spectra obtained for urea and thiourea that has to be commented on, is the shape of the curve, which is normally determined by the value of the form factor δ/ω. It can be noted from Table II that the half width (ω) of the peak for thiourea is unusually small, which physically means the polarisation built up decays faster within a small temperature region. A small variation in (ω) can be seen for single crystal and pellet. However the effective form factor corresponds to a value of 0.42 for pellet and 0.51 for single crystal. For urea it is 0.55. Attempts to fit the experimental curve to the general TSDC equation were not successful. A similar behaviour of the thermocurrent peaks was observed in ice crystal also.[25] However no such complication was exhibited by naphthalene[26] which is another molecular crystal widely studied by this technique.

The high temperature peak obtained for urea is attributed to the space charge polarisation. The variation of maximum intensity with the field as shown in Figure 2 suggests this assignment. In the case of thiourea the experiments were not done in that temperature region owing to the fact that thiourea is decomposed and the sulphide of the silver electrode is formed.

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