

A model for the occurrence and analysis of ionic thermocurrent spectrum involving different orders of kinetics

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Abstract. Ionic thermocurrent (ITC) spectrum is much similar to a thermoluminescence (TL) glow curve involving monomolecular kinetics. It has already been reported that different orders of kinetics are involved in TL processes, which depend specifically on the extent of recombination and simultaneous retrapping. It is found that the involvement of different orders of kinetics in ITC spectrum depends on the experimental conditions of polarization and rate of rapid cooling. Consequently, order of kinetics involved in the ITC spectrum does not represent any specific feature of the system under investigation. An equation is developed which explains the occurrence of ITC spectrum involving any order of kinetics. Dielectric relaxation parameters, order of kinetics and approximate number of dipoles per unit volume are evaluated conveniently and easily following the proposed model.

Keywords. Ionic thermocurrent; order of kinetics; thermally stimulated processes; thermoluminescence.

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1. Introduction

A divalent impurity ion when substituted in an alkali halide matrix results in the subsequent creation of a vacancy for the sake of charge compensation. Because of the Coulombic force of attraction, the vacancy is generally created in the neighbourhood of the impurity ion at the next nearest location. In such a situation, an impurity-vacancy (IV) dipole is formed with dipole moment $\sqrt{2}ea$, where e is the electronic charge and a is the interatomic separation. The created vacancy has an equal probability of being located

at one of the 12 equivalent sites around the impurity ion along (1 1 0) direction. In the presence of an electric field, IV dipole tries to align along the electric field direction. In such an attempt, vacancy makes ω_1 jump around the impurity ion [1,2]. Thus, the system having IV dipoles gets polarized in the presence of an electric field. With the electric field still on, if the system is rapidly cooled down to a fairly low temperature, where the relaxation time is very large or practically infinite, IV dipoles are frozen-in in the crystalline lattice and remain polarized even after switching off the electric field. If the system is heated at a constant linear heating rate, there is a stage when frozen-in polarized dipoles start depolarizing. Consequently, thermally stimulated depolarization current (TSDC) or ionic thermocurrent (ITC) starts appearing. The plot of ionic thermocurrent as a function of temperature is known as ITC spectrum. It is an asymmetric curve and is much similar to a thermoluminescence (TL) glow curve involving monomolecular or first-order kinetics [3]. Ionic thermocurrent I as a function of temperature is expressed in ref. [4].

$$I = (Q_o/\tau_o) \exp \left[(-E_a/kT) - \{1/(b\tau_o)\} \int_{T_o}^T \exp(-E_a/kT')dT' \right], \quad (1)$$

where Q_o is the total charge released during ITC run and is given by

$$Q_o = (1/b) \int_{T_o}^{\infty} I(T')dT'. \quad (2)$$

b is the constant linear heating rate according to the equation

$$T = T_o + bt. \quad (3)$$

In eq. (3), T represents the absolute temperature corresponding to time t and T_o is the temperature wherefrom ITC curve starts to appear. In eq. (1), τ_o is the fundamental relaxation time or the relaxation time at infinite temperature given by Arrhenius relation [5] as

$$\tau = \tau_o \exp(E_a/kT), \quad (4)$$

where τ is the relaxation time at T , k the Boltzmann's constant and E_a the activation energy for the orientation of IV dipole. ITC technique has emerged as an effective and very useful tool [3] for studying the reorientational behaviour of dipoles because of its sensitivity, accuracy and convenience.

In ITC spectrum, the current initially increases slowly in accordance with $\exp(-E_a/kT)$ and falls off rapidly at high temperature as per the second exponential of eq. (1). The peak of the ITC spectrum appears at T_m such that

$$T_m^2 = \{(bE_a\tau_m)/k\}, \quad (5)$$

where τ_m is the relaxation time at T_m . It has been mentioned that eq. (1) corresponds to a TL glow curve involving monomolecular kinetics, and hence TL glow curves involving bimolecular or higher-order kinetics may also lead to give corresponding equations for ITC spectra. TL glow curves involving second- and higher-order kinetics [6–9] have already been reported in the literature. It was hence thought proper to assess the involvement of second- and higher-order kinetics in ITC spectra also. With this aim in view, the present work has been initiated and carried out. An attempt has been made to probe into the involvement of different orders of kinetics in ITC measurements. It has been observed

that experimental conditions of polarization and rate of rapid cooling for getting frozen-in polarized dipoles do initiate the involvement of monomolecular or higher-order kinetics in the ITC spectrum. The dielectric relaxation parameters E_a and τ_o are, however, found to be independent of polarization temperature, rate of rapid cooling, order of kinetics and polarizing electric field. E_a and τ_o are found to depend specifically on the system under investigation and not on the experimental conditions. It has been observed that order of kinetics involved in the ITC spectrum does not represent any specific feature of the system under investigation.

2. Proposed model

In TL studies, order of kinetics higher than the first has been reported in [6–9] and also in the references cited therein. A model for the occurrence of TL glow curve involving different orders of kinetics has been developed by Prakash [10]. Orders of kinetics involved in TL processes are found to depend on the extent of recombination and simultaneous retrapping. In ITC measurements, dielectric relaxation parameters E_a and τ_o are usually evaluated following Bucci, Fieschi and Guidi (BFG) method [3]. Such evaluated values of E_a and τ_o are expected to satisfy eq. (5). However, it has been observed that evaluated values of E_a and τ_o do not satisfy eq. (5) in general. Such conclusion has been arrived at by Prakash and Nishad [11], while developing characteristic relaxation time for a lattice:dopant system. The same was unfortunately ignored and could not be then reported by the authors because of lack of vision, insight and proper explanation. Some representative data in support are presented in table 1. It is obvious from the table that T_m^2 is different from $[(bE_a\tau_m)/k]$, which must have been equal as per eq. (5). Similar situation is observed in many other cases also. This clearly indicates and suggests the presence of a multiplying factor on the right-hand side of eq. (5) such that the two sides of the equation become equal. It is anticipated that the multiplying factor may include order of kinetics which when taken into account may lead to a situation where eq. (5) is satisfied. With this point in view and considering the outcome of the model suggested by Prakash [10] for the occurrence of TL glow curve involving different orders of kinetics, a model has been developed for the occurrence of ITC spectrum.

2.1 ITC spectrum

It has already been mentioned that depolarization current starts appearing when frozen-in polarized dipoles depolarize or disorient. The depolarization current density or ionic thermocurrent density J depends on the rate of depolarization of IV dipoles and is expressed as

$$J = -dP/dt. \quad (6)$$

The rate of depolarization, however, depends on the characteristic features of the system. As reported in the literature, it depends on the remaining polarization P present at that time and on the relaxation time τ at the corresponding temperature T . It has been proposed here that it also depends on the order of kinetics ℓ involved. Thus, the rate of depolarization is proposed to be expressed by

$$-dP/dt = (1/\ell)(P/\tau). \quad (7)$$

Table 1. Representative dielectric relaxation data of some doped alkali halide systems supposedly involving first-order kinetics.

System	b (K s ⁻¹)	T_m (K)	E_a (eV)	τ_o (s)	T_m^2 (K ²)	$\{(bE_a\tau_m)/k\}$ (K ²)	Reference
NaCl:Mn ²⁺	0.1	214.3	0.67	9.1×10^{-15}	45925	40989	[19]
NaCl:Mg ²⁺	0.067	206	0.49	8.8×10^{-11}	42436	32962	[20]
NaCl:NCO ⁻	0.012	65	0.192	2.0×10^{-13}	4225	4176	[21]
NaCl:NO ₂ ⁻	0.022	18.9	0.04	7.0×10^{-10}	357	335	[22]
KCl:Mg ²⁺	0.1	189	0.49	3.85×10^{-12}	35721	25799	[23]
KCl:Mn ²⁺	0.1	192	0.49	6.2×10^{-12}	36864	25959	[23]
KCl:Yb ²⁺	0.1	215	0.67	1.1×10^{-14}	46225	44025	[23]
KCl:AsO ₂ ⁻	0.1	58.3	0.161	1.6×10^{-13}	3399	2505	[17]
KBr:AsO ₂ ⁻	0.01	60	0.169	2.4×10^{-13}	3600	748	[17]
KBr:Sr ²⁺	0.05	215	0.66	4.0×10^{-14}	46225	45952	[24]
KBr:Se ²⁻	0.05	230	0.72	2.0×10^{-14}	52900	50691	[25]
KBr:NCO ⁻	0.014	41	0.119	2.0×10^{-13}	1681	1663	[21]
KBr:Cu ⁺	0.184	70.2	0.196	1.0×10^{-13}	4928	4995	[26]
KI:Pb ²⁺	0.059	201.2	0.61	4.5×10^{-14}	40481	36287	[20]
KI:Se ²⁻	0.046	215	0.64	1.3×10^{-13}	46225	45249	[27]
KI:AsO ₂ ⁻	0.016	60.5	0.172	3.5×10^{-13}	3660	2410	[17]
KI:Te ²⁻	0.066	217	0.62	4.0×10^{-14}	47089	4828	[28]

It is obvious that for $\ell = 1$, eq. (7) changes to conventional equation reported in [12]. Equations (6) and (7) result in

$$J = (1/\ell)(P/\tau). \tag{8}$$

Now, eq. (7) can be solved to give

$$P = P_o \exp[-(1/\ell)(t/\tau)], \tag{9}$$

where P_o is the maximum polarization or initial polarization at $t = 0$, i.e. the polarization at the start of the experiment. Isothermal decay of polarization for a hypothetical system for different orders of kinetics evaluated using eq. (9) is shown in figure 1. It is obvious from the figure that the decay is fastest for first-order kinetics. The decay becomes slower and slower with increasing order of kinetics. Thus, eq. (8) represents the mechanisms inherent in the ITC processes.

With the help of eq. (4), one can write down eq. (9) as

$$P = P_o \exp[-(1/\ell)(t/\tau_o) \exp(-E_a/kT)]. \tag{10}$$

The parameter $(\ell\tau_o)$ can be named as the effective fundamental relaxation time. With increasing order of kinetics, $(\ell\tau_o)$ will increase leading to increased value of effective relaxation time $(\ell\tau)$, which will consequently lead to decrease in the rate of depolarization in accordance with eq. (7). This statement is also supported by figure 1. It would be justified to mention that the Arrhenius eq. (4) will remain unchanged because the relaxation

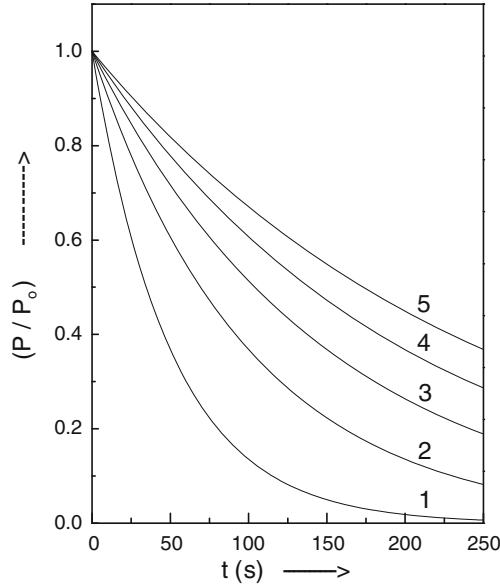


Figure 1. Isothermal decay of polarization for a hypothetical system with $\tau = 50$ s. Number on the curves represents the order of kinetics.

time τ changes to $(\ell\tau)$ due to effective fundamental relaxation time $(\ell\tau_0)$. Thus, the fundamental relaxation time of the system is τ_0 , but the effective fundamental relaxation time of the system is $(\ell\tau_0)$. In situations when $\ell = 1$, fundamental relaxation time becomes equal to effective fundamental relaxation time. It is this effective fundamental relaxation time, which when taken into consideration, may probably lead to satisfy eq. (5). It is due to experimental conditions prevailing during polarization and rate of rapid cooling that the fundamental relaxation time τ_0 of the system under investigation appears as $(\ell\tau_0)$. It is a well-established fact that characteristic dielectric relaxation parameters E_a and τ_0 are fixed for the system under investigation and are independent of the experimental conditions of polarization. Thus in ITC runs recorded on a specimen, ℓ is a representative of the experimental conditions of polarization and rapid cooling rate leaving E_a and τ_0 unaffected.

Non-isothermal form of eq. (10) can be written as

$$P = P_0 \exp \left[- \{1/(\ell\tau_0)\} \int_0^t \exp(-E_a/kT) dt \right]. \quad (11)$$

When the system is heated following a constant linear heating rate b in accordance with eq. (3), one gets from eq. (11)

$$P = P_0 \exp \left[- \{1/(b\ell\tau_0)\} \int_{T_0}^T \exp(-E_a/kT') dT' \right]. \quad (12)$$

Equations (4) and (12) when substituted in eq. (8) result in

$$J = P_o \{1/(\ell\tau_o)\} \exp\left[-(E_a/kT) - \{1/(b\ell\tau_o)\} \int_{T_o}^T \exp(-E_a/kT')dT'\right]. \quad (13)$$

Equation (13) in terms of current I can be written as

$$I = Q_o \{1/(\ell\tau_o)\} \exp\left[-(E_a/kT) - \{1/(b\ell\tau_o)\} \int_{T_o}^T \exp(-E_a/kT')dT'\right], \quad (14)$$

where Q_o is the total charge released during ITC run and equals to P_oA where A is the cross-sectional area of the crystal specimen.

Equation (14) represents the generalized equation for ITC spectrum involving ℓ th order of kinetics. It is obvious that for $\ell = 1$, eq. (14) changes to eq. (1) corresponding to an ITC spectrum involving monomolecular or first-order kinetics. Equations for ITC spectra involving second- and higher-order kinetics can be obtained from eq. (14) after substituting the corresponding values of ℓ into it. It would be justified to mention just for the sake of reference that an equation similar to eq. (14) for TL studies has been developed by Prakash *et al* [13], where number of simplifying assumptions has been taken into account. Equation (14) is, however, free from any assumption and is simpler and convenient in nature. It can be realized, however, from eq. (14) that for a fixed value of $(\ell\tau_o)$, same ITC spectrum is reproduced which poses a problem in deciding the order of kinetics involved and in evaluating the values of dielectric relaxation parameters. However, in actual systems $\ell\tau_o$ rarely happens to be the same particularly because of the fact that τ_o is different for different systems and ℓ depends on experimental conditions of polarization which ought to have been different in different ITC runs.

2.2 ITC peak

Equation (8) when differentiated with respect to time gives

$$\dot{J}\tau + J\dot{\tau} = (1/\ell)\dot{P}. \quad (15)$$

Now at the peak of the ITC spectrum, the value of \dot{J} is zero and hence one gets with the help of eq. (6)

$$J[\dot{\tau} + (1/\ell)] = 0. \quad (16)$$

Using the value of $\dot{\tau}$ from eq. (4), one can get

$$T_m^2 = \{(\ell b E_a \tau_m)/k\}. \quad (17)$$

It can be seen that eq. (17) changes to eq. (5) for $\ell = 1$ corresponding to monomolecular kinetics. Equation (17) happens to be a general equation, wherefrom equations corresponding to different orders of kinetics can be obtained after substituting the values of ℓ . It is obvious that the location of T_m is independent of the concentration of dipoles as expected and appears at the same location when b is kept fixed.

2.3 Analysis of ITC spectrum

Equation (6) with the help of eq. (3) can be arranged to give

$$P_o = (1/b) \int_{T_o}^{\infty} J(T')dT', \quad (18)$$

which gives the value of Q_o through

$$Q_o = (1/b) \int_{T_o}^{\infty} I(T')dT'.$$

The same expression has been mentioned already as eq. (2) and represents the total charge released during ITC run and equals to the area enclosed in the ITC spectrum. The role of Q_o is identical to n_o of TL measurements [4] representing the initial concentration of trapped electrons per unit volume and equals to the total area enclosed in the TL glow curve.

Equation (6) can also be rearranged to give

$$P = (1/b) \int_T^{\infty} J(T')dT', \quad (19)$$

where P is the polarization remaining at the temperature T . Corresponding value of $Q(=PA)$ at T is given by

$$Q = (1/b) \int_T^{\infty} I(T')dT', \quad (20)$$

where Q is the charge remaining at the temperature T and equals to the area of the ITC spectrum enclosed within the temperature range T to ∞ . Thus, Q_o and Q can be obtained from ITC spectrum using eqs (2) and (20), respectively. It would be justified to mention just for the sake of reference that similar equations for n and n_o have also been developed in TL studies [10]. In the quest for establishing a methodology to analyse ITC spectrum with a view to evaluate the values of dielectric relaxation parameters and order of kinetics, considerations of mechanisms inherent in the ITC processes may probably be helpful.

It is obvious from eq. (6) that the depolarization current density J depends on the rate of depolarization or decay of polarization. If decay of polarization is fast, the magnitude of J will obviously be large. Figure 1 suggests that decay of polarization becomes slower and slower with increasing order of kinetics leading to consequent decreased value of J . This conclusion finds a support through figure 2, where ITC curves of hypothetical systems involving different orders of kinetics evaluated using eq. (14) are shown. However, such a conclusion only provides a qualitative explanation. The decay of polarization as per eq. (7) depends on P , τ and ℓ . It is found that τ_o depends on the characteristic feature of the system and ℓ depends on the experimental conditions of polarization. Consequently, for a given ITC run of a system, τ_o and ℓ will behave as a constant quantity. Thus, isothermal decay of polarization for a system becomes proportional to P . More P means faster decay of polarization leading to large magnitude of J . Less value of P means slower decay of polarization leading to small magnitude of J . In a hypothetical system with same value of P but involving higher order of kinetics say $\ell = 2$, the effective remaining polarization P becomes half leading to smaller magnitude of J . Thus, involvement of higher order of

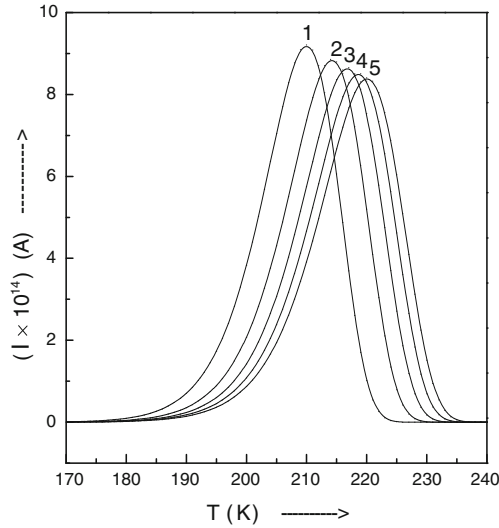


Figure 2. ITC spectra involving different orders of kinetics for a hypothetical system with $E_a = 0.60 \text{ eV}$, $\tau_0 = 5.0 \times 10^{-13} \text{ s}$, $Q_0 = 3.0 \times 10^{-11} \text{ C}$ and $b = 0.05 \text{ K s}^{-1}$. The number on the curves represents the involved order of kinetics.

kinetics means slower decay of polarization. Had first-order kinetics been involved, the decay of polarization would have been faster leading to higher magnitude of J . However, the characteristic features, i.e. dielectric relaxation parameters E_a and τ_0 of the system shall not change. Involvement of higher order of kinetics means slower decay of polarization, which will only decrease the magnitude of J , but the dielectric relaxation parameters E_a and τ_0 will remain unchanged. Thus, a system with lesser P_0 means a system having slower decay of polarization. Dipole–dipole interaction may be the reason for the involvement of higher order of kinetics. Fastest decay or exponential decay of polarization of figure 1 for first-order kinetics corresponds to Debye relaxation suitable for the cases having no dipolar interaction. In the presence of dipole–dipole interaction, the decay of polarization becomes non-exponential leading to slower and slower decay of polarization. Thus, it is obvious that the nature of decay of polarization decides the order of kinetics involved. The dielectric relaxation parameters E_a and τ_0 , however, remain unaffected. Mechanism responsible for non-exponential decay of polarization is discussed elsewhere [6,12,13].

In an alkali halide matrix having IV dipoles, P_0 at the polarization temperature T_p is given by

$$P_0 = \{(Np^2E)/(3kT_p)\}, \tag{21}$$

where N is the number of IV dipoles per unit volume each of dipole moment p and E is the polarizing electric field. In a given system, P_0 is proportional to N provided E and T_p are kept constant. Obviously, P_0 will be more if N is more leading to faster decay of polarization which results in higher magnitude of J . It has been observed experimentally that concentration of dipoles N does not change the values of dielectric relaxation parameters E_a and τ_0 , but the depolarization current density increases proportionally. Thus, involvement of higher order of kinetics means that a sample of the same system with lesser value

of N has been considered. It is hence obvious that experimental conditions of polarization and rate of rapid cooling are the prime parameters which decide the involvement of different orders of kinetics in ITC spectrum. However, the analysis of such an ITC spectrum will ultimately give the same values of E_a and τ_0 because the experiment is carried out on a sample of the same system. Had monomolecular kinetics been involved, J would have been more without affecting the values of E_a and τ_0 . Thus, the evaluated values of E_a and τ_0 correspond to an ITC spectrum involving monomolecular or first-order kinetics and remain unaffected with either N or ℓ . It is thus obvious that ℓ does not represent in any way the characteristic feature of the system under investigation. Experimental data recorded in $\text{KCl}:\text{Sr}^{2+}$ single crystals [3] presented in figure 3 following initial rise method support this statement. Parallel lines suggest that E_a is the same. The intercepts are different for different parallel lines because of changed value of N , which ultimately results in the same value of τ_0 . Thus, E_a and τ_0 are the characteristic dielectric relaxation parameters of the system and are found to be independent of the order of kinetics and experimental conditions. Hence, dielectric relaxation parameters E_a and τ_0 can be obtained from eq. (14) after substituting $\ell = 1$ in it. In such a case eq. (14) with the help of eqs (12) and (13) for $\ell = 1$ can be written as

$$I = (Q/\tau_0) \exp[-(E_a/kT)], \tag{22}$$

which can be rearranged as

$$\ln[Q/I] = \ln[\tau_0] + (E_a/kT). \tag{23}$$

It is obvious that $\ln[Q/I]$ when plotted against $(1/T)$ will give a straight line in accordance with eq. (23). The slope and intercept of the straight line give the values of E_a and τ_0 , respectively. This is effectively the BFG method of analysis [3] written in a changed form. For the ITC spectra of figure 2, a straight line is obtained when $\ln[Q/I]$ is plotted against $(1/T)$ as shown in figure 4. A single straight line is obtained for all the curves

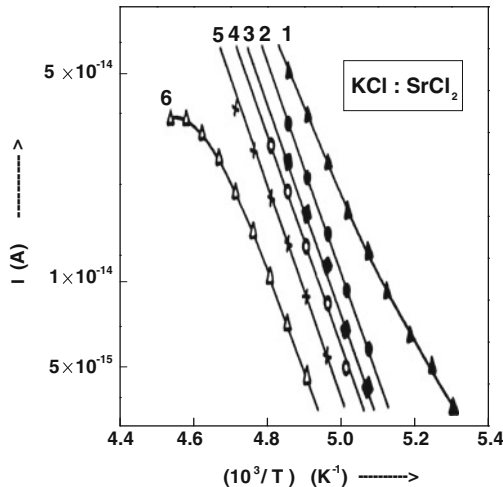


Figure 3. Plot of $\ln[I]$ vs. $[1/T]$ for six successive discharges recorded in $\text{KCl}:\text{Sr}^{2+}$ single crystals [3].

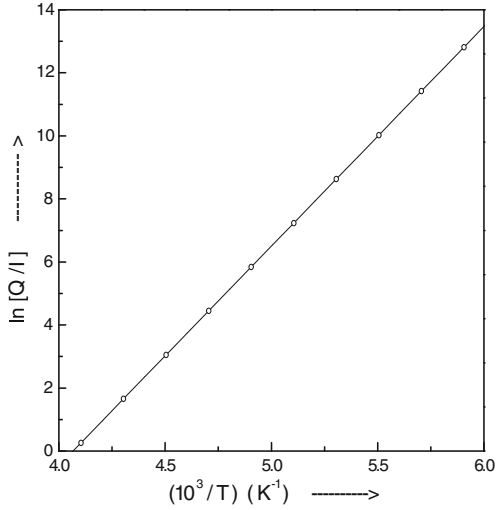


Figure 4. Plot of $\ln[Q/I]$ vs. $[1/T]$ for ITC spectra of figure 2.

of figure 2 particularly because of the fact that dielectric relaxation parameters and N are same for them. Further, it would be justified to mention here just for the sake of reference that slope and intercept evaluated using eq. (23) do not depend on N , contrary to that obtained in the initial rise method shown in figure 3. It is due to this reason that a single straight line results in figure 4. The slope and intercept of the straight line give the values of dielectric relaxation parameters E_a and τ_o , respectively. Knowing the values of E_a and τ_o , order of kinetics can be obtained from eq. (17). ℓ can also be obtained from eq. (14) through iteration after substituting the evaluated values of E_a and τ_o . The value of N can also be estimated using eq. (21). Due to uncertainty in the value of T_p [14,15], eq. (21) gives the approximate value of N . Thus, the values of E_a , τ_o , ℓ and N can be obtained conveniently and easily with the help of the suggested methodology.

3. Results and discussion

While analysing the ITC data presented in the literature, it has been observed that eq. (5) is not satisfied in general. Usually the values of dielectric relaxation parameters E_a and τ_o are evaluated following BFG method [3] and are reported as such without caring whether they satisfy eq. (5) or not. However, the evaluated values of E_a and τ_o must satisfy eq. (5). In such an attempt, it has been observed while analysing the reported data of ITC, that eq. (5) is not satisfied in general. This aspect has been overlooked by many workers engaged in ITC studies. Some representative cases are presented in table 1 just for the sake of reference. It is obvious from the table that T_m^2 is not found to be equal to $\{(bE_a\tau_m)/k\}$, which must have been equal as per eq. (5). Many more examples can be cited to justify the outcome of table 1. Similar situation has also been noticed by the author while developing characteristic relaxation time for a lattice:dopant system [11].

The same could not be then reported because of lack of vision, insight and proper explanation. This fact clearly indicates and suggests the presence of a multiplying factor on the right-hand side of eq. (5), which will possibly include the order of kinetics involved. With such a multiplying factor, eq. (5) will be satisfied with the evaluated dielectric relaxation parameters. Such a modified equation is developed and presented as eq. (17). Corresponding values of ℓ involved in the ITC spectra of the systems of table 1 are evaluated using eq. (17). Evaluated values of ℓ are presented in table 2. It would be justified to mention that the dielectric relaxation parameters E_a and τ_o represent the characteristic features of the system under investigation. Order of kinetics ℓ is found to be associated with the ITC spectrum and depends on the experimental conditions of polarization. During rapid cooling of the sample, polarization is obviously increasing with decreasing temperature unless the relaxation time becomes large enough or practically infinite [12]. The increase in polarization may be quite large depending on the cooling rate [14]. This also implies that the magnitude and area of the ITC spectrum will be a function of the cooling rate. This conclusion is supported through the experimental observations of Harasta [14] and Solunov *et al* [15]. It is on the basis of these findings that order of kinetics ℓ has been assumed to be a parameter which depends on the experimental conditions of polarization and on the rate of rapid cooling. Thus, ℓ does not depend on the system under investigation. This conclusion is supported and augmented through experimental observations [16, 17] recorded in AgCl:Ni²⁺ and KBr:AsO₂⁻ single crystals at different constant linear heating rates shown in figures 5 and 6, respectively. It is obvious that T_m^2 is invariably different from $\{(bE_a\tau_m)/k\}$ for both these systems as shown in table 3. Corresponding values of ℓ presented in table 3 are evaluated using eq. (17). It is obvious that ℓ is different for different heating rates for the same system and varies from 1.27 to 2.84 for AgCl:Ni²⁺ and from

Table 2. Order of kinetics involved in doped alkali halide systems of table 1.

System	T_m (K)	E_a (eV)	τ_o (s)	τ_m (s)	ℓ
NaCl:Mn ²⁺	214.3	0.67	9.1×10^{-15}	52.7	1.12
NaCl:Mg ²⁺	206	0.49	8.8×10^{-11}	86.5	1.29
NaCl:NCO ⁻	65	0.192	2.0×10^{-13}	156.1	1.01
NaCl:NO ₂ ⁻	18.9	0.04	7.0×10^{-10}	32.8	1.07
KCl:Mg ²⁺	189	0.49	3.85×10^{-12}	45.4	1.39
KCl:Mn ²⁺	192	0.49	6.2×10^{-12}	45.6	1.42
KCl:Yb ²⁺	215	0.67	1.1×10^{-14}	56.6	1.05
KCl:AsO ₂ ⁻	58.3	0.161	1.6×10^{-13}	13.4	1.36
KBr:AsO ₂ ⁻	60	0.169	2.4×10^{-13}	38.1	4.81
KBr:Sr ²⁺	215	0.66	4.0×10^{-14}	119.9	1.01
KBr:Se ²⁻	230	0.72	2.0×10^{-14}	121.3	1.04
KBr:NCO ⁻	41	0.119	2.0×10^{-13}	86.0	1.01
KBr:Cu ⁺	70.2	0.196	1.0×10^{-13}	11.9	0.99
KI:Pb ²⁺	201.2	0.61	4.5×10^{-14}	86.9	1.12
KI:Se ²⁻	215	0.64	13×10^{-14}	132.4	1.02
KI:AsO ₂ ⁻	60.5	0.172	3.5×10^{-13}	75.4	1.52
KI:Te ²⁻	217	0.62	4.0×10^{-14}	10.2	9.75

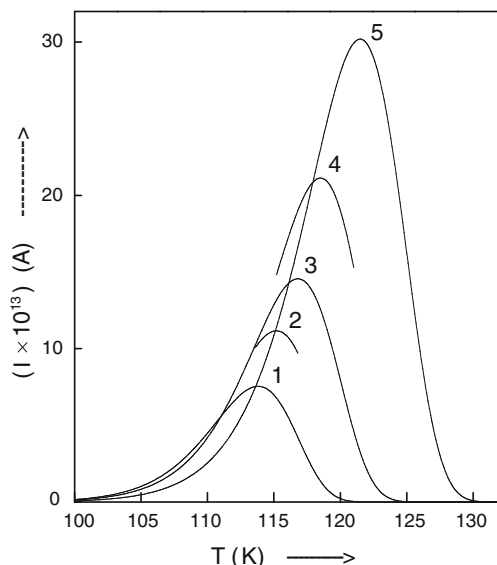


Figure 5. ITC spectra recorded in AgCl:Ni^{2+} system at different linear heating rates [16]. These curves are recorded following the constant linear heating rates of: (1) 0.033 K s^{-1} , (2) 0.05 K s^{-1} , (3) 0.067 K s^{-1} , (4) 0.01 K s^{-1} and (5) 0.15 K s^{-1} .

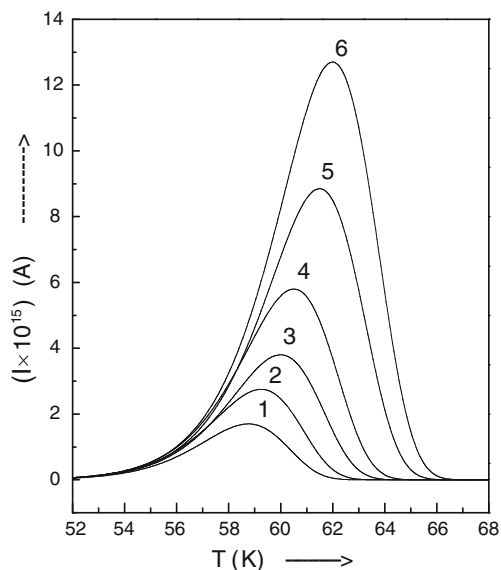


Figure 6. ITC spectra recorded in KBr:AsO_2^- system at different linear heating rates [17]. These curves are recorded following the constant linear heating rates of: (1) $8.33 \times 10^{-3} \text{ K s}^{-1}$, (2) $14.35 \times 10^{-3} \text{ K s}^{-1}$, (3) $19.17 \times 10^{-3} \text{ K s}^{-1}$, (4) $29.86 \times 10^{-3} \text{ K s}^{-1}$, (5) $50.00 \times 10^{-3} \text{ K s}^{-1}$ and (6) $69.20 \times 10^{-3} \text{ K s}^{-1}$.

Table 3. Data for AgCl:Ni²⁺ and KBr:AsO₂⁻ systems recorded at different constant linear heating rates.

b (K s ⁻¹)	T_m (K)	τ_m (s)	T_m^2 (K ²)	$\{(bE_a\tau_m)/k\}$ (K ²)	ℓ
(a) AgCl:Ni ²⁺ , $E_a = 0.339$ eV, $\tau_o = 7.54 \times 10^{-14}$ s					
0.033	113.8	78.75	12950	10227	1.27
0.05	115.2	51.73	13271	10178	1.30
0.067	116.8	32.39	13642	8542	1.60
0.10	118.5	19.98	14042	7862	1.79
0.15	121.5	8.80	14762	5194	2.84
(b) KBr:AsO ₂ ⁻ , $E_a = 172$ meV, $\tau_o = 2.8 \times 10^{-13}$ s					
8.33×10^{-3}	58.75	161.3	3452	2683	1.29
14.35×10^{-3}	59.25	121.1	3511	3470	1.01
19.17×10^{-3}	60.00	79.5	3600	3041	1.18
29.86×10^{-3}	60.50	60.3	3660	3598	1.02
50.00×10^{-3}	61.50	35.3	3782	3523	1.07
69.20×10^{-3}	62.00	27.2	3844	3752	1.02

1.01 to 1.29 for KBr:AsO₂⁻ systems. When experimental conditions of polarization happen to be fortuitously same in different runs of ITC, one gets same value of ℓ . Had ℓ been a characteristic feature of the system under investigation, it would have had the same value at different heating rates and in different polarization conditions. Thus, our conclusion is justified through these experimental observations that ℓ depends on the experimental conditions of polarization and does not represent the specific feature of the system under investigation. Same conclusion is also arrived at when data recorded in AsO₂⁻-doped KCl and KI [17] at different constant linear heating rates are considered. Thus, E_a and τ_o can be evaluated from eq. (23) and figure 4 following the methodology suggested in §2.3. It is found that evaluated values of E_a and τ_o come out to be the same as being the characteristic feature of the system under investigation. Knowing E_a and τ_o , one can evaluate the value of ℓ with the help of eq. (17). The proposed model is found to be convenient and simple for the analysis of ITC spectrum and gives the values of E_a , τ_o , ℓ and N easily.

It has been established in the preceding paragraph that ℓ depends on the experimental conditions of polarization and rate of rapid cooling. It will hence be advisable to have an idea about the dependence of ℓ on the shape of the ITC spectra. Figure 2 suggests that with increasing values of ℓ , peak position T_m shifts to higher temperature with a simultaneous decrease in the peak of the ITC spectrum I_m . It is obvious that change is more, when we go from $\ell = 1$ to $\ell = 2$, which goes on decreasing with increasing value of ℓ . The behaviour observed in figure 2 is found to be in accordance with eqs (14) and (17). Further, it is also obvious from eq. (17) that T_m is independent of N and appears at the same location if b is kept constant. Such a behaviour is shown in figure 7. T_m is found to depend on b such that T_m shifts to higher temperature with increasing b as shown in figures 5 and 6. Thus, T_m is found to depend on both b and ℓ as suggested by eq. (17) also. Linear heating rate b can be controlled and managed to be had at the required value but the parameter ℓ

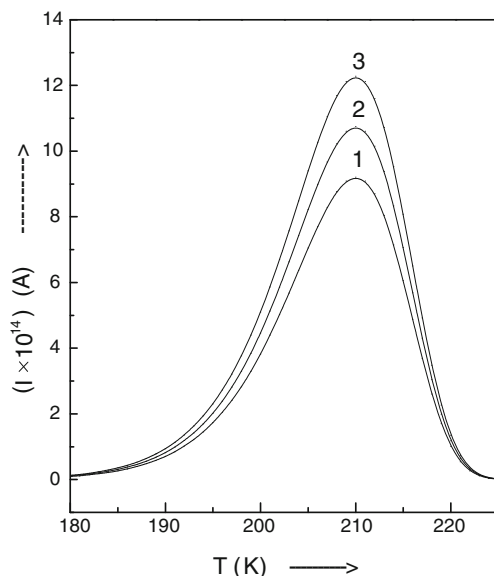


Figure 7. ITC spectra involving monomolecular kinetics for a hypothetical system with changing N or Q_0 having the parameters $E_a = 0.60$ eV, $\tau_0 = 5.0 \times 10^{-13}$ s and $b = 0.05$ K s $^{-1}$. Number on the curves represents the concentration or Q_0 such that curves 1, 2 and 3 correspond to $Q_0 = 3.0 \times 10^{-11}$ C, 3.5×10^{-11} C and 4.0×10^{-11} C, respectively.

is uncontrollable as it depends exclusively on the experimental conditions of polarization and rate of rapid cooling for getting frozen-in polarized dipoles. It is thus obvious that different runs of ITC recorded on the same specimen may not be reproducible even if b is kept constant as it depends exclusively on experimental conditions of polarization and rate of rapid cooling. However, the evaluated values of dielectric relaxation parameters E_a and τ_0 will be the same with different values of ℓ obtained from different runs of ITC spectra recorded on the same specimen. The value of ℓ for different runs of ITC may, however, be the same when experimental conditions of polarization and rate of rapid cooling for them are incidentally the same by chance. It is obvious from eq. (6) that depolarization current density depends on rate of depolarization. P_0 depends on the experimental conditions of polarization and rate of rapid cooling. Subsequently, depolarization current density becomes a function of the rate of depolarization and also of the experimental conditions of polarization. The effectiveness of the experimental conditions of polarization and rate of rapid cooling is expressed through the order of kinetics ℓ . In the light of these arguments, order of kinetics has, hence, been included in eq. (7). It is because of this reason that the rate of depolarization becomes slower for second-order kinetics and goes on decreasing with increasing order of kinetics as shown in figure 1. It is further obvious from eq. (14) that I_m is proportional to Q_0 , where Q_0 represents the total charge released during ITC run. Q_0 happens to be proportional to N through eq. (21). Consequently, I_m increases with increasing N as shown in figure 7. Further, the approximate value of N can also be evaluated with the help of eq. (21). Thus, in addition to dielectric relaxation parameters

E_a and τ_o , order of kinetics ℓ involved in the ITC spectrum and approximate number of dipoles per unit volume N can be evaluated conveniently and easily following the proposed model.

The relationship inbetween s_ℓ and s of TL studies [18] seems to be illogical and impracticable as they have the dimensions of $m^{3(\ell-1)}s^{-1}$ and s^{-1} , respectively. It would be justified to mention that s_ℓ and s must have the same dimension, i.e., s^{-1} as per the Arrhenius relation. In the proposed model no such relationship in s_ℓ and s exists. Thus, s_ℓ and s become independent of ℓ and deny the feasibility of any relationship between them. Further, various other anomalies [9] are also remedied in the proposed model.

Suggested methodology for the evaluation of dielectric relaxation parameters E_a and τ_o is in fact the BFG method [3] represented through eqs (20) and (23). Consequently, the accuracies associated with the evaluation of E_a and τ_o will be the same as that obtained in BFG method.

It is obvious that the proposed model is simpler and convenient for the evaluation of dielectric relaxation parameters. No simplifying assumptions have been incorporated in developing eq. (14). The experimental conditions of polarization for getting frozen-in polarized dipoles decide the order of kinetics involved. It is because of this reason that different ITC runs recorded on the same specimen give different values of order of kinetics as can be seen from table 3. Further, the dependence of T_m on N is also excluded in the suggested model.

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References

- [1] J Prakash, *Indian J. Pure Appl. Phys.* **28**, 365 (1990)
- [2] J Prakash, *Nat. Acad. Sci. Lett.* **28**, 35 (2005)
- [3] C Bucci, R Fieschi and G Guidi, *Phys. Rev.* **148**, 816 (1966)
- [4] R Chen and Y Kirsch, *Analysis of thermally stimulated processes* (Pergamon Press, New York, 1981)
S W S McKeever, *Thermoluminescence of solids* (Cambridge University Press, Cambridge, 1988)
- [5] S Z Arrhenius, *Phys. Chem.* **226** (1889)
- [6] R Chen, D J Huntley and G W Berger, *Phys. Status Solidi* **A79**, 251 (1983)
- [7] J Prakash and D Prasad, *Phys. Status Solidi* **A142**, 281 (1994)
- [8] J Prakash, *Solid State Commun.* **85**, 647 (1993)
- [9] J Prakash, P K Singh and D K Dwivedi, *Indian J. Pure Appl. Phys.* **44**, 532 (2006)
- [10] J Prakash, *J Lumin.* (Communicated)
- [11] J Prakash and A K Nishad, *Jap. J. Appl. Phys.* **27**, 2247 (1988)
- [12] J Vanderschuren and J Gasiot, *Topics in applied physics, thermally stimulated relaxation in solids* edited by P Bräunlich (Springer-Verlag, Berlin, 1979) Vol. 37, Chap. 4
Non-Debye relaxation in condensed matter edited by T V Ramkrishnan and M Ray Lakshmi (World Scientific, Singapore, 1987)

- [13] J Prakash, S K Rai, P K Singh and H O Gupta, *Indian J. Pure Appl. Phys.* **42**, 565 (2004)
V Correcher, Y Rodriguez-Lazcano, J Garcia-Guinea and E Crespo-Feo, *Braz. J. Phys.* **40**, 3 (2010)
- [14] V Harasta, *Fiz. Casop. (Czech.)* **19**, 232 (1969)
- [15] H Solunov, T Vassilev and P Hedvig, *Sci. Papers Phys.* **12**, 47 (1974)
- [16] I Kunze and P Müller, *Phys. Status Solidi* **33**, 91 (1969)
- [17] J Prakash, *Phys. Status Solidi* **B135**, 741 (1986)
- [18] R Chen and S A A Winer, *J. Appl. Phys.* **41**, 5227 (1970)
- [19] P Dansas, *J. Phys. Chem. Solids* **32**, 2699 (1971)
- [20] F Cusso and F Jaque, *J. Phys.* **C15**, 2875 (1982)
- [21] A Wilbrand, Diplomarbeit (Physikalisches Institut der Universität, Münster, FRG, 1979)
- [22] G Nierste, Diplomarbeit (Physikalisches Institut der Universität, Münster, FRG, 1981)
- [23] A Brun and P Dansas, *J. Phys.* **C7**, 2593 (1974)
- [24] R Muccillo and J Rolfe, *Phys. Stat. Solidi* **B61**, 579 (1974)
- [25] J Prakash, *J. Phys.* **C12**, L577 (1979)
- [26] M Siu Li, M de Souza and F Lüty, *Phys. Rev.* **B7**, 4677 (1973)
- [27] J Prakash, *Phys. Status Solidi* **B121**, 127 (1984)
- [28] Ch Kokott, Dissertation (Physikalisches Institut der Universität, Münster, FRG, 1975)
Ch Kokatt and F Fischer, *Phys. Status Solidi* **B106**, 141 (1981)