Comparative study of mechanisms and analysis techniques involved in Thermally Stimulated Depolarization and Thermoluminescence Processes

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Abstract

In the present work a comparative study have been done between two thermally stimulated processes, namely Thermally Stimulated Depolarization (TSD) and Thermoluminescence(TL). The depolarization current density or ionic thermocurrent density J depends on the rate of depolarization of IV dipoles and the occurrence TL glow curves are goverened by Adirovitch set of equations. The thermally stimulated spectrums of both the processes are of same nature. In this paper the similarities and counter quantities in both the processes have been discussed. It has also been found that the analysis technique, for determination of dielectric relaxation parameters, decay parameters and order of kinetics, are also similar for both processes.

Key words: Thermally stimulated depolarization, Thermoluminescence, Dielectric relaxation parameters, TL decay parameters, Order of kinetics.

1. Introduction

The physical phenomenon in which a certain property of the material under study is measured as a function of temperature is known as thermally stimulated process (TSP). The property of the material under consideration is initially perturbed from a stable configuration,

and is thermally stimulated back to equilibrium by raising temperature. The property under consideration is measured during heating of the sample. The resulting thermal curve, measured property as a function of temperature is Thermally Stimulated Spectrum. Among the wide variety of thermally stimulated processes, we discuss here only "Thermally Stimulated Depolarisation (TSD)" process also known as "Ionic Thermocurrent (ITC)" and "Thermoluminescence (T L)" process. These are based on the measurement of depolarization of polarized dipoles in terms of Thermally Stimulated Depolarization Current (TSDC) or ionic thermocurrent (ITC) and emission of photons or release of electrons from trap centre during thermal stimulation respectively.

2.1 Mechanism Involved in Thermally Stimulated Depolarization Process:

When an impurity ion substituted in alkali halide matrix, compensation is usually accomplished by the incorporation of lattice vacancies, interstitial host ions, another species of impurity ion in interstitial or substitutional sites or a combination thereof. If the compensating ion is in the local environment of the impurity ion, then a impurity-vacancy (IV) dipole is formed which may be able to reorient by a thermally activated jump of the one of ions involved in the halide matrix. Jump of this type is characterized by temperature dependent relaxation time at temperature T is given by Arrhenius relation (1889).

$$\tau(T) = \tau_o \exp\left(\frac{E_a}{kT}\right) \qquad (1)$$

where τ_o is the fundamental relaxation time or the reciprocal frequency factor and E_a is the activation energy for orientation and k is the Boltzmann's constant. In the presence of an electric field, IV dipole tries to align along the electric field direction. 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, a stage comes 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. In the resulting asymmetric cuvre, ionic thermocurrent I as a function of temperature is given by [1]

$$I = \left(\frac{Q_o}{\tau_o}\right) \exp\left[\left(-\frac{E_a}{kT}\right) - \left(\frac{1}{b\tau_o}\right)\int_{T_o}^{T} \exp\left(-\frac{E_a}{kT'}\right)dT'\right] \quad (2)$$

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

$$Q_o = \frac{1}{b}\int_{T_o}^{\infty} I(T')dT' \qquad (3)$$

b is the constant linear heating rate as per equation

$$T = T_o + b\,t \qquad (4)$$

In eq. (4), T represents the absolute temperature corresponding to time t and T_o is the temperature wherefrom ITC curve starts to appear. 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. (2). The peak of the ITC spectrum appears at T_m such that

$$T_m^2 = \{\frac{bE_a\tau_m}{k}\} \tag{5}$$

where τ_m is the relaxation time at T_m. Eq.(1) for the ionicthermocurrent is true only for monomolecular kinetics. The parameter kinetics depends on experimental conditions of the process. 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. It has been also observed that order of kinetics involved in the ITC spectrum does not represent any specific feature of the system under investigation. 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

$$J = -\frac{dP}{dt} \tag{6}$$

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 by Prakash[2] that it also depends on the order of kinetics ℓ involved. According to him the rate of depolarization is proposed to be expressed by

$$-\frac{dP}{dt} = \left(\frac{1}{\ell}\right)\left(\frac{P}{\tau}\right) \tag{7}$$

It is obvious that for $\ell = 1$, eq. (7) changes to conventional equation reported in the literature[3].

Following the idea of Prakash[2] equation of ionicthermocurrent (ITC) for general order kinetics is given by

$$I = Q_o \left(\frac{1}{\ell\tau_o}\right) exp\left[-\left(\frac{E_a}{kT}\right) - \left(\frac{1}{b\ell\tau_o}\right)\int_{T_o}^{T} \exp\left(-\frac{E_a}{kT'}\right)dT'\right] \tag{8}$$

Eq. (8) represents the general equation for ITC spectrum involving ℓ^{th} order of kinetics. It is obvious that for $\ell = 1$, eq. (8) changes to eq.(2) 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. (8) after substituting the corresponding values of ℓ into it.

Condition for peak temperature in ITC spectrum of general order kinetics is given by

$$T_m^2 = \left(\frac{\ell\, b\, E_a\, \tau_m}{k}\right) \tag{9}$$

It can be seen that eq. (9) changes to eq. (5) for $\ell = 1$ corresponding to monomolecular kinetics. Eq. (9) happens to be a general equation wherefrom equations corresponding to different order of kinetics can be obtained after substituting the values of ℓ.

2.2 Analysis technique of TSD spectrum or ITC spectrum:

Here we discuss how the dielectric relaxation parameters, activation energy E_a

and relaxation time τ_o, and order of kinetics ℓ can be evaluated from given ITC spectrum.

Eq. (6) with the help of eq. (4) can be arranged to give

$$P_o = \frac{1}{b} \int_{T_o}^{\infty} J(T')dT' \qquad (10)$$

which gives the value of Q_o through

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

The same expression has been mentioned already as eq. (3) and represents the total charge released during ITC run and equals to the area enclosed in the ITC spectrum.

Eq. (6) can also be rearranged to give

$$P = \frac{1}{b} \int_{T}^{\infty} J(T')dT' \qquad (11)$$

where P is the polarization remaining at the temperature T. Corresponding value of Q(= P A, where A is the cross-sectional area of the crystal specimen) at T is given by

$$Q = \frac{1}{b} \int_{T}^{\infty} I(T')dT' \qquad (12)$$

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. (3) and (12), respectively.

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

$$P_o = \frac{N p^2 E}{3 k T_p} \qquad (13)$$

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_o is proportional to N provided E and T_p are kept constant. Obviously, P_o will be more if N is more leading to faster decay of polarization which results into higher magnitude of J. Hence, dielectric relaxation parameters E_a and τ_o can be obtained from eq. (8) after substituting $\ell = 1$ in it. In such a case eq. (8) with few simplifications for $\ell = 1$ can be written as

$$I = \frac{Q}{\tau_o} \exp\left(-\frac{E_a}{k T}\right) \qquad (14)$$

Which can be rearranged as

$$ln\left(\frac{Q}{I}\right) = ln(\tau_o) + \left(\frac{E_a}{k}\right)\frac{1}{T} \qquad (15)$$

It is obvious that ln [Q / I] when plotted against (1 / T) will give a straight line in accordance with eq. (15). The slope and intercept of the straight line give the values of E_a and τ_o, respectively. This is effectively BFG method of analysis[4] written in a changed form. Knowing the values of E_a and τ_o, order of kinetics can be obtained from eq. (9). The value of N can also be estimated using eq. (13). Due to uncertainty in the value of T_P[5,6], eq. (13) gives the approximate value of N. Thus, the values of E_a, τ_o, ℓ and N can be obtained with the help of the above discussed methodology conveniently and easily.

2.3 Mechanism Involved in Thermoluminescence Process:

Among the different techniques of

thermally stimulated processes for investigation of trap levels in insulating solids, thermoluminescence (TL) is an important and convenient method.

Thermoluminescence is a potentially powerful tool for the understanding of the mechanism of light emission during thermal stimulation.

Whenever an insulator or a semiconductor is irradiated, electrons are excited from the valence band to the conduction band. Most of the excited electrons return to the valence band after a very short time ($\sim 10^{-8}$s) emitting a photon. If the excited electron instead of returning back to the valence band goes to some metastable state or is trapped in some trap level present in the forbidden gap, the electron can stay there for a longer time. Once the electron is trapped, it needs energy to be raised to the conduction band and then can return to the valence band. As soon as it gets the required amount of energy it shows a delayed luminescence. If the required energy is supplied thermally, the phenomenon is called thermoluminescence (TL). The plot of TL intensity as a function of temperature is known as TL glow curve or thermoluminescence spectrum. Thermoluminescence process is governed by Adirovitch (1956) which controls the traffic of electrons from trap centre to recombination centre via conduction band. These equations are

$$I = -\frac{dm}{dt} = m\, n_c\, A_m \ , \qquad (16)$$

$$-\frac{dn}{dt} = n\, s \exp\left(-\frac{E_a}{k\,T}\right) - n_c(N-n)A_n \quad (17)$$

and

$$m = n + n_c \qquad (18)$$

where I is the intensity of TL glow curve, m and n densities of holes and electrons in the respective recombination and trap centres, n_c the density of electrons in the conduction band, A_m the transition probability from conduction band to recombination centre, A_n the transition probability from conduction band to trap centre, E_a the activation energy or trap depth, s the preexponential or escape frequency factor, k the Boltzmann's constant, T the absolute temperature, t the time corresponding to T and N the density of total trap centre. In eq. (17), second term on the right hand side represents the retrapping of electrons in the trap centre from the conduction band whereas first term represents the excitation of electrons from the trap centre to the conduction band. Eqs. (16) to (18) are considered to be the basic equations which have been used by various workers to explain the occurrence of TL glow curve.

The TL intensity of first order kinetics or monomolecular kinetics are supposed to be recombination dominant with negligible or zero retrapping is given by [7]

$$I = n_o s \exp\left[-\frac{E_a}{kT} - \frac{s}{b}\int_{T_o}^{T} \exp\left(-\frac{E_a}{kT'}\right)dT'\right] (19)$$

Where n_o is the initial concentration of trapped electrons per unit volume at T_o corresponding to t = 0, T_o the initial temperature wherefrom TL glow curve starts to appear, s the frequency factor or pre-exponential factor, E_a the activation energy, k the Boltzmann's constant, b the linear heating rate and T' an arbitrary temperature in the range T_0 to T.

Peak TL intensity for first order glow curve appears at T_m and is given by

$$\frac{b\,E_a}{k\,T_m^2} = s\,\exp\left(-\frac{E_a}{k\,T}\right) \qquad (20)$$

In order to derive a general equation for TL intensity and TL peak, which can express equations for any order of kinetics, Prakash[8] proposed modified form of Adirovitch set of equations as follows:

In a sample, m and n are equal leading to the fact that sample as a whole is neutral. So, charge neutrality condition requires

$$m = n \qquad (21)$$

After excitation from trap centre one gets n_c in conduction band. During this process n decreases by the same amount. Thus, charge neutrality equation can be represented as

$$m = (n - n_c) + n_c$$

where $(n-n_c)$ represents the electrons remaining in the trap centre after excitation. Above relation obviously leads to eq. (21) representing the charge neutrality condition. And hence, should not come in picture in charge neutrality equation as proposed by Adirovitch in eq. (18).

When the specimen is heated, trapped electrons are excited to the conduction band where they may stay for $\approx 10^{-8}$ s. Thus, for the process of excitation one may write down

$$-\frac{dn}{dt} = n\,s\,\exp\left(-\frac{E_a}{k\,T}\right) = \frac{n}{\tau} \qquad (22)$$

where τ is the relaxation time at T which is represented with the help of Arrhenius relation eq. (1). Fundamental relaxation time τ_o and

escape frequency factor s are related to each other through the relation

$$\tau_o = \frac{1}{s} \qquad (23)$$

Out of excited electrons in conduction band, obtained through eq. (22), some are retrapped and balance get recombined. And hence, effective rate of decrease of n or effective rate of excitation with time as a result of excitation and retrapping is expressed as

$$-\frac{dn}{dt} = n\,s\,exp\left(-\frac{E_a}{k\,T}\right) - x\,n\,s\,exp\left(-\frac{E_a}{k\,T}\right) \quad (24)$$

where first term on the right hand side represents the electrons in conduction band obtained after excitation and second term represents part of it which is retrapped. x represents the fraction or part of excited electrons which are retrapped such that $0 \le x \le 1$. Obviously, retrapping depends on x. For $x = 0$, retrapping is zero corresponding to first order kinetics and for $x = 0.5$, retrapping is 50% corresponding to second order kinetics and so on. Eq. (24) is further expressed as

$$-\frac{dn}{dt} = (1 - x)n\,s\,\exp\left(-\frac{E_a}{k\,T}\right) \qquad (25)$$

Remaining electrons in the conduction band represented by right hand side of eq. (25) recombine with oppositely charge centres present at the recombination centre .Thus the rate of recombination and hence the intensity of TL glow curve will be represented as

$$I = -\frac{dm}{dt} = \left(1 - x\right)n\,s\,\exp\left(-\frac{E_a}{k\,T}\right) \qquad (26)$$

As a result of recombination, m

decreases and hence a negative sign in eq. (26). It is obvious that for $x = 0$, it is 100% recombination whereas for $x = 0.5$ the recombination probability is 50% and so on. With the help of eqs. (24) and (26), it can be shown just for the sake of justification that excited electrons become equal to the sum of retrapped and recombined electrons as expected. Thus, once the extent of retrapping is determined, the extent of simultaneous recombination shall automatically be decided.

Eq. (21) suggests $m = n$ and hence

$$\frac{dm}{dt} = \frac{dn}{dt} \tag{27}$$

Eqs. (21),(25) and (26) represent the modified Adirovitch set of equations. Eq.(25) can be solved to give

$$n = n_o \exp\left[-\{s\,t\,(1-x)\}\exp\left(-\frac{E_a}{k\,T}\right)\right] \tag{28}$$

Non-isothermal form of eq. (28) is expressed as

$$n = n_o \exp\left[-\{s\,(1-x)\}\int_o^t \exp\left(-\frac{E_a}{k\,T}\right) dt\right] \tag{29}$$

This value of n when substituted in eq. (26) results into

$$I = (1-x)n_o\,s\,\exp\left[-\left(\frac{E_a}{k\,T}\right) - \{s\,(1-x)\}\int_o^t \exp\left(-\frac{E_a}{k\,T}\right) dt\right] \tag{30}$$

If the system is heated following a constant linear heating rate b given vide eq.(4), eq. (21) results into

$$I = (1-x)n_o\,s\,\exp\left[-\left(\frac{E_a}{k\,T}\right) - \frac{s(1-x)}{b}\int_{T_o}^T \exp\left(-\frac{E_a}{kT'}\right) dT'\right] \tag{31}$$

This is the expression for the intensity of TL glow curve involving retrapping to the extent of x.

Eq. (26) with the help of eqs. (1) and (23) can be rearranged as

$$I = \frac{(1-x)n}{\tau} \tag{32}$$

Differentiation of eq. (32) with time, using eqs. (26) and (27) and after few simplifications with condition of maxima one gets

$$T_m^2 = \frac{bE_a\tau_m}{(1-x)k} \tag{33}$$

where τ_m is the relaxation time at T_m. Eq. (33) gives the location of TL peak in systems involving retrapping to the extent of x. It is obvious that T_m is independent of n_o as expected. Expression for T_m corresponding to different values of x can be obtained from eq. (33). For monomolecular or first order kinetics eq. (33) with $x = 0$ results into eq.(20).

2.4 Analysis technique of TL glow or Thermoluminescence spectrum:

Here we discuss how the TL decay parameters, activation energy E_a and escape frequnncy factor s, and extent of retrapping can be evaluated from given TL glow curve.

Eq. (26) with the help of eq. (27) gives

$$\int_{n_o}^o dn = -\int_o^\infty I\,dt \tag{34}$$

which gives,

$$n_o = \frac{1}{b}\int_{T_o}^\infty I(T')dT' = A_o \tag{35}$$

where A_o is the total area enclosed by the TL glow curve.

Also, eq. (34) in the limits t to ∞ can be represented as

$$\int_n^o dn = -\int_t^\infty I dt \qquad (36)$$

which gives,

$$n = \frac{1}{b}\int_T^\infty I(T') dT' = A_T \qquad (37)$$

where A_T is the area of the TL glow curve in the temperature range T to ∞.

From the experimental findings of Bucci, Fieschi and Guidi[4], it is clear that TL decay parameters *i.e.*, E_a and *s*, do not depend on concentration n_o or extent of retrapping x. The evaluated values of E_a and s may correspond to a case of zero retrapping in the system. Thus, the values of E_a and *s* can be obtained after substituting $x = 0$ in the relevant equations. In such condition eq. (26) for $x = 0$ becomes

$$I = n s \exp\left(-\frac{E_a}{k T}\right)$$

which can be rearranged as

$$\ln\left(\frac{n}{I}\right) = \ln\left(\frac{1}{s}\right) + \frac{E_a}{k T} \qquad (38)$$

It is obvious that one gets a straight line when *ln (n/I)* is plotted against *(1 / T)* in accordance with eq. (38). The slope of the line gives the value of E_a and from the intercept one gets the value of *s*. Thus, TL decay parameters E_a

and s are evaluated. Consequently, the value of x has been evaluated using eq. (33).

3. Conclusion of comparison between TSD and TL processes:

Bucci, Fieschi and Guidi[4] have mentioned that the variation of current in the ITC spectrum is very much similar to the intensity of a TL glow curve involving monomolecular or first order kinetics. To establish this similarity for higher order kinetics, it will be fruitful to compare the mechanisms inherent in these processes. After comparing general equations of ionic thermocurrent (8) and thermoluminescence intensity (31), one finds a relationship between x and ℓ as

$$\ell = \frac{1}{1-x} \qquad (39)$$

Thus, retrapping to the extent of x in TL mechanism is equivalent to involvement of ℓth order of kinetics in the dipolor reorientation process. The same relation is also obtained between ℓ and x when one compares eqs. (9) and (33) for T_m of both these processes. For this relationship in ℓ and x represented through eq.(39), expressions for I and T_m for ITC and TL processes become identical . This obviously establishes a similarity between TL and ITC processes involving any extent of retrapping or any order of kinetics. Further, method of evaluation of dielectric relaxation parameters with the help of eq.(15) is identical to the evaluation procedure of TL decay parameters through eq. (38). Moreover, expressions for Q [eq.(12)] and Q_o [eq.(3)] of ITC process are also similar to those of n [eq.(37)] and n_o

[eq.(35)] of TL process.

Eq. (31) with the help of eq. (39) can be rearranged in terms of ℓ as

$$I = \frac{1}{\ell} n_o \, s \exp\left[-\frac{E_a}{kT} - \frac{s}{\ell b}\int_{T_o}^{T} exp\left(-\frac{E_a}{kT'}\right)dT'\right]$$

(40)

This expression represents a TL glow curve which involves ℓ^{th} order of kinetics. Exactly the same expression has been developed by Prakash *et al.*[9] where number of assumptions have been taken into consideration. Also, parameters A_m and A_n have been used by Prakash *et al.* in expressing the modified Adirovitch set of equations. It has already been mentioned that A_m and A_n do play part in the recombination and retrapping processes, but it is the extents of recombination and simultaneous retrapping which decide the order of kinetics involved. It is because of this reason that A_m and A_n do not come in picture directly while developing either eq. (31) or eqn. (40). It is worth mentioning that ITC spectrum[4] is very much similar to a TL glow curve involving monomolecular or first order kinetics. And hence, eq. (40) is equally valid to represent the mechanisms inherent in an ITC spectrum involving ℓ^{th} order of kinetics as also obvious from eq. (8). Q_o of eq. (40) corresponds to n_o.

In both the processes dipole relaxation parameters or TL decay parameters, as the case may be, are characteristic features of the specimen and do not depend on the experimental conditions like, initial concentration of dipoles N, experimental conditions of polarization, rate of rapid cooling and heating rate in case of ionic thermocurrent and irradiation dose or initial concentration of trapped electron or concentration of trapped electrons n_c , extent of retrapping or recombination and heating rate in case of thermoluminescence. Experimental data recorded in KCl:Sr^{2+} single crystals[4] following initial rise method supports this statement. Whereas the parameter order of kinetics for both the processes depends on the experimental condition of specimen under investigation. Dependence of order of kinetics ℓ on experimental conditions is supported by experimental work done on AgCl:Ni^{2+} [10] and KBr:AsO_2^- [11] crystals.

Suggested model by Prakash has been found to be simpler and free from any assumption. The model can be applied to analyse ITC and TL data equally effectively. It has been established that ITC spectrum is very much similar to TL glow curve involving any extent of retrapping or any order of kinetics.

Acknowledgements

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