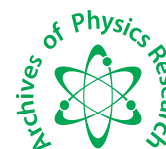




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The determination of the dielectric relaxation parameters and order of kinetics of TSD spectrum by using Prakash method

Devendra Prasad

Department of Physics (Basic Science), U P Textile Technology Institute, 11/208, Souterganj Kanpur, (U P), India

ABSTRACT

In this paper we analyze the suitability and feasibility of the method proposed by Prakash for the determination of the dielectric relaxation parameters, namely activation energy and fundamental relaxation time, and order of kinetics, of a thermally stimulated depolarization (TSD) spectrum, also known as ionic thermocurrent (ITC) spectrum, by applying it both to numerically generated TSD spectrum of hypothetical system and experimentally reported TSD spectrums of AgCl:Pb^{2+} and KI:S^{2-} . It is found that the method is simpler, convenient and can be used for the analysis of TSD spectrum or ITC spectrum involving any order of kinetics.

Keywords: Dielectric relaxation parameters, Order of kinetics, Thermally stimulated depolarization, Ionic thermocurrent.

INTRODUCTION

The specimen of alkali halide matrix having impurity vacancy (IV) dipoles gets polarized in the presence of an electric field. With the electric field still on, if the specimen 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 specimen 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 thermally stimulated depolarization current as a function of temperature is known as TSD spectrum or ITC spectrum. TSDC or ITC technique is employed to determine the characteristic dielectric relaxation parameters, namely activation energy (E_a) and fundamental relaxation time (τ_0) of specimen. There are several methods for this, as reported in literature suggested by different workers engaged in the same work, and the technique has been employed successfully. Most of the already existed methods focus on evaluation of dielectric relaxation parameters, only few methods are focused on order of kinetics parameter also [1,2]. In all the discussed methods, there are some anomalies, like few of them are not concerned with order of kinetics, few of them are suitable only for monomolecular or first order kinetics, few of them have suggested different methods for different order of kinetics and most of them are not interested whether the evaluated values of dielectric relaxation parameters (E_a and τ_0) satisfies equation of peak temperature. Starting from the basic idea that ITC curve corresponding to monomolecular kinetics is very much similar to a thermoluminescence (TL) glow curve involving monomolecular kinetics [3], and TL glow curves involving second and higher order kinetics [4-8] have already been reported in the literature. It was hence thought proper by Prakash [9] to assess the involvement of second and higher order kinetics in ITC spectra. ITC technique has emerged as an effective and very useful tool [3] for studying the reorientational behavior of dipoles because of its sensitivity, accuracy and convenience.

2. Prakash method of analysis

Following Prakash [9] the expression for ionic thermocurrent (I) involving general order kinetics is given by

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

where Q_o is the total charge released during ITC run, ℓ is order of kinetics involved, k the Boltzmann's constant, T the absolute temperature, b is linear heating rate, T_o is the temperature wherefrom ITC spectrum starts to appear and T' any temperature between T_o and T . Equations for ITC spectra involving first, second or higher order can be obtained from above equation after substituting the corresponding value of ℓ into it.

Total released charged during ITC run is given by

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

and charge released in ITC run in between temperature range T to ∞ is given by

$$Q = \frac{1}{b} \int_T^{\infty} I(T') dT' \quad (3)$$

Q_o and Q can be obtained from ITC spectrum using eqs.(2) and (3) respectively.

Equations for remaining polarization P and current density J at temperature T in specimen is given by [9]

$$P = P_o \exp\left[-\frac{1}{b \ell \tau_o} \int_{T_o}^T \exp\left(-\frac{E_a}{kT'}\right) dT'\right] \quad (4)$$

and

$$J = \frac{P_o}{\ell \tau_o} \exp\left[-\frac{E_a}{kT} - \frac{1}{b \ell \tau_o} \int_{T_o}^T \exp\left(-\frac{E_a}{kT'}\right) dT'\right] \quad (5)$$

where P_o is the maximum polarization or initial polarization.

In order to establish a method for the analysis of TSD or ITC spectrum with a view to determine dielectric relaxation parameters and order of kinetics, Prakash has considered the mechanisms responsible for the TSD or ITC processes. It has been established that the dielectric relaxation parameters, activation energy E_a and fundamental relaxation time τ_o , are characteristic features of the specimen and does not depend anyway on experimental conditions of polarization and rate of rapid cooling. However, the experimental conditions of polarization and rate of rapid cooling are the prime parameters which decide the involvement of different order of kinetics in TSD or ITC spectrum. The analysis of TSD or ITC spectrums of same specimen under different experimental conditions of polarization and rate of rapid cooling results in same value of E_a and τ_o . Thus the evaluated values of E_a and τ_o correspond to an TSD or ITC spectrum of first order kinetics and remain unaffected with either number of IV dipoles per unit volume or order of kinetics ℓ . The order of kinetics ℓ does not represent the characteristic feature of the system under consideration. The experimentally reported data for single crystal [3] KCl:Sr²⁺ support this statement.

Thus, E_a and τ_o , are the characteristic dielectric relaxation parameters of the system and are found to be independent of the order of kinetics and experimental conditions. Hence, these parameters can be obtained from eq.(1) after substituting $\ell = 1$ in it. In such a case eq.(1) with the help of eqs.(4) and (5) for $\ell = 1$ can be written as

$$I = \frac{Q}{\tau_o} \exp\left(-\frac{E_a}{kT}\right) \quad (6)$$

which can be rearranged as

$$\ln\left(\frac{Q}{I}\right) = \ln(\tau_o) + \frac{E_a}{kT} \quad (7)$$

From eq.(7) it is obvious that when $\ln\left(\frac{Q}{I}\right)$ plotted against $\left(\frac{1}{T}\right)$ will give a straight line. The slope and intercept of the straight line give the values of E_a and τ_o , respectively. Knowing the values of E_a and τ_o , order of kinetics ℓ can be obtained from equation of peak temperature T_m , given by

$$T_m^2 = \frac{\ell b E_a \tau_m}{k} \tag{8}$$

where τ_m is relaxation time at peak temperature and given by Arrhenius relation [10] as

$$\tau_m = \tau_o \exp\left(\frac{E_a}{k T_m}\right) \tag{9}$$

3. Analysis of TSD spectrum

In above discussion it is clear that, in order to determine dielectric relaxation parameters by Prakash method, one has to evaluate $\left(\frac{Q}{I}\right)$ which is given by the area of a TSD spectrum from the temperature under consideration until the end point and corresponding current.

3.1. Analysis of experimentally reported TSD spectrums

Following the method suggested by Prakash, experimentally observed TSD spectrums, already reported in literature, of specimens AgCl:Pb²⁺ [11] and KI:S²⁻ [12] are analyzed and the results are given below:

Data collected from already reported TSD spectrum of specimen AgCl:Pb²⁺ [11] are given in Table.1. As per the eq.(7) plot of $\ln[Q/I]$ vs $1/T$ is shown in Fig.1. From experimentally reported spectrum, $T_m = 112.3K$, $I_m = 1.796E-13A$, $b=(1/30)K/s$, $Q_0 = 4.872E-09 C$. Boltzman’s constant $k = 8.617E-5 eV/K$. From Fig.1 slope = 4348.2 and intercept = -29.9. Using eqs.(7), (8) and (9) calculated values of different parameters are as given below

- (i) Activation Energy $E_a = 0.3746885 eV$,
- (ii) Fundamental Relaxation Time $\tau_o = 1.06851E-13 s$ and
- (iii) Order of Kinetics $\ell = 0.01244336$.

Data collected from already reported TSD spectrum of specimen KI:S²⁻ [12] are given in Table.2. As per the eq.(7) plot of $\ln[Q/I]$ vs $1/T$ of Specimen KI:S²⁻ is shown in Fig.2

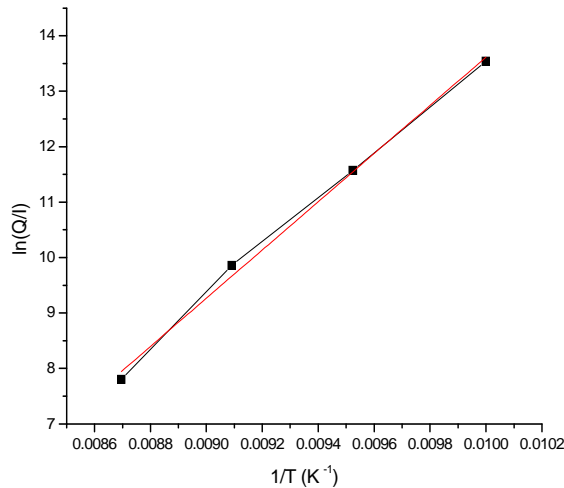


Fig.1: Plot of $\ln [Q/I]$ versus $[1 / T]$ for experimentally reported TSD curve of specimen AgCl:Pb²⁺ [11]

TABLE 1 DATA FROM EXPERIMENTALLY REPORTED CURVE [11]

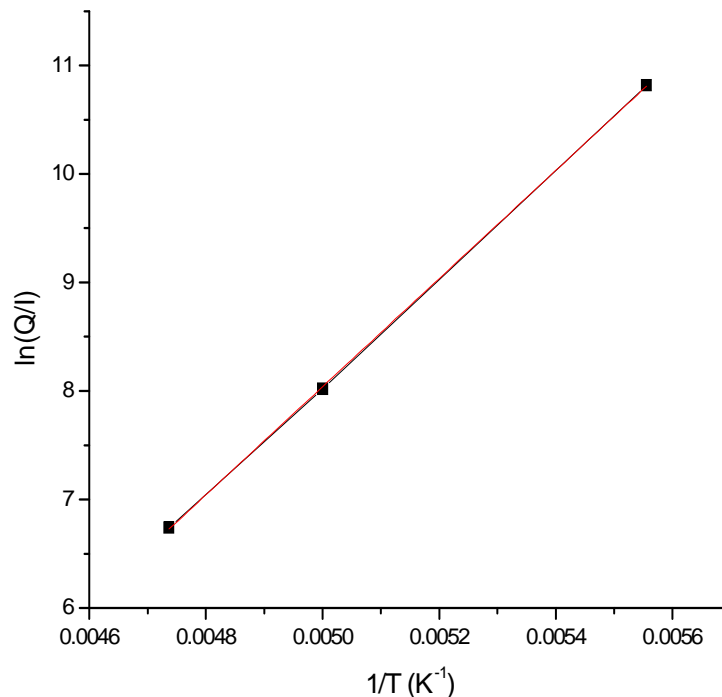
Specimen- AgCl:Pb ²⁺					
T (K)	1/T (K ⁻¹)	Q (C)	I (A)	Q/I (CA ⁻¹)	ln[Q/I]
100	0.01	4.818E-09	6.34E-15	759936.9	13.54099069
105	0.00952381	4.467E-09	4.225E-14	105727.8	11.56862325
110	0.009090909	2.862E-09	1.5E-13	19080	9.856395945
115	0.008695652	4.38E-10	1.7958E-13	2439.024	7.799353398

TABLE 2 DATA FROM EXPERIMENTALLY REPORTED CURVE [12]

Specimen- KI:S ²					
T (K)	1/T (K ⁻¹)	Q (C)	I (A)	Q/I (CA ⁻¹)	ln[Q/I]
180	0.005555556	1.812E-09	3.63636E-14	49830	10.81637249
200	0.005	1.078E-09	3.54545E-13	3040.513	8.019781471
211	0.004736842	1.46E-10	1.72727E-13	845.2632	6.739648008

From experimentally reported spectrum, $T_m = 204\text{K}$, $I_m = 3.6\text{E-}13\text{A}$, $b=0.05\text{K/s}$, $Q_0 = 1.922\text{E-}09\text{ C}$. Boltzman's constant $k = 8.617\text{E-}5\text{ eV/K}$. From Fig.2 slope = 4987.864 and intercept = -16.9002. Using eqs.(7), (8) and (9) calculated values of different parameters are as given below

- (i) Activation Energy $E_a = 0.429804243\text{ eV}$,
- (ii) Fundamental Relaxation Time $\tau_o = 4.57442\text{E-}08\text{ s}$ and
- (iii) Order of Kinetics $\ell = 0.087781491$.

Fig.2: Plot of $\ln [Q/I]$ versus $[1 / T]$ for experimentally reported TSD curve of specimen - KI:S² [12]

3.2. Analysis of hypothetically generated TSD spectrum

Here we consider a hypothetical system with $E_a = 0.60\text{ eV}$, $\tau_o = 5.0 \times 10^{-13}\text{ s}$, $Q_o = 3.0 \times 10^{-11}\text{ C}$ and $b = 0.05\text{ Ks}^{-1}$ and plot current versus temperature curve for different values of order of kinetics ℓ in accordance with eq.(1). The resulting TSD spectrum is shown in Fig.3. According to equation (7) a single straight line is obtained, as shown in Fig.4, for all the curves of Fig.3 particularly because of the fact that dielectric relaxation parameters and Q_o are same for them and slope and intercept evaluated using eq. (7) do not depend on Q_o . It is due to this reason that a single straight line results in Fig 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 using eqs. (8) and (9). The values are same as assumed for hypothetical system.

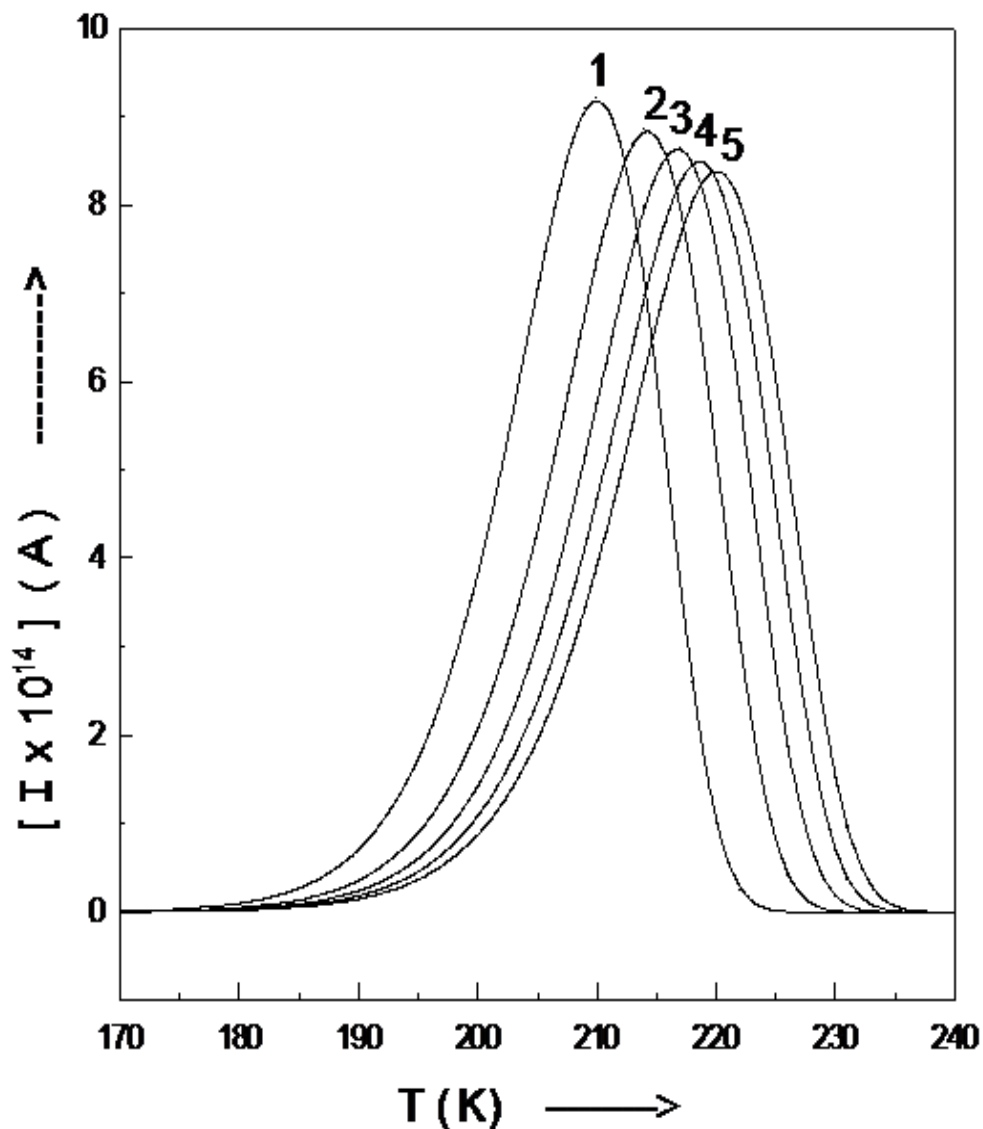


Fig.3: TSD spectra involving different order of kinetics for a hypothetical system with $E_a = 0.60$ eV, $\tau_0 = 5.0 \times 10^{-13}$ s, $Q_0 = 3.0 \times 10^{11}$ C and $b = 0.05$ ks⁻¹. the number on the curves represents the involved order of kinetics

CONCLUSION

In the present paper we have analyze experimentally reported TSD spectrums of different specimen and numerically generated TSD spectrum of hypothetical system, and evaluate all the three parameters E_a , s and ℓ , following the Prakash method. This method for the evaluation of dielectric relaxation parameters E_a and τ_0 is in fact BFG method [3] represented through eqs. (7). Consequently, the accuracies associated with the evaluation of E_a and τ_0 shall be the same as that obtained in BFG method. It is obvious that the Prakash method is simpler and convenient for the evaluation of dielectric relaxation parameters. No simplifying assumptions have been incorporated by Prakash in developing eq. (1). Activation energy and relaxation time are characteristic features of the specimen and unaffected by the experimental conditions. 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 TSD runs recorded on the same specimen give different values of order of kinetics. Futher, the dependence of peak temperature T_m on Q_0 is also excluded in the suggested model.

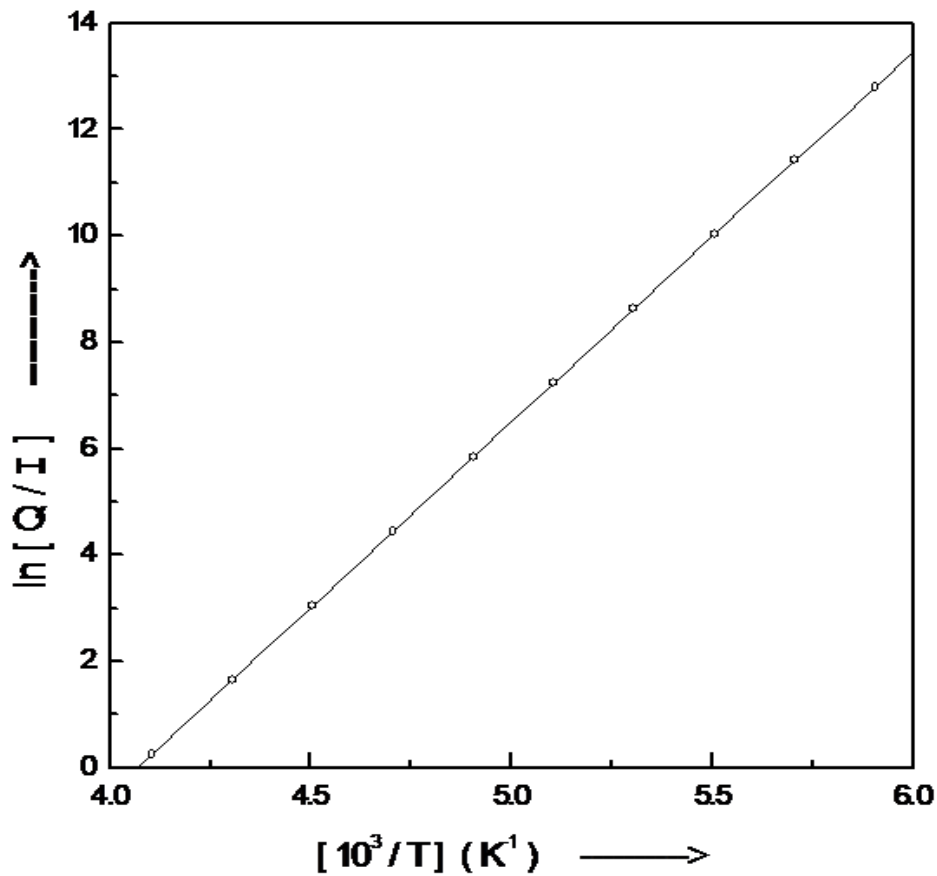


Fig.4: Plot of $\ln [Q/T]$ versus $[1/T]$ for TSD curve of Fig. 3

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REFERENCES

- [1] R Chen and Y Kirsch, 'Analysis of Thermally Stimulated Processes' Pergamon Press, New York, **1981**.
- [2] R Chen and S W S Mckeever, 'Theory of Thermoluminescence and Related Phenomena', World Scientific, **1997**.
- [3] C Bucci, R Fieschi and G Guidi, *Phys Rev*, **1966**, 148, 816.
- [4] R Chen and S A A Winer, *J Appl Phys (USA)*, **1970**, 41, 5227.
- [5] R Chen, D J Huntley, G W Berger, *Phys Stat Soli a (Germany)*, **1983**, 79, 251.
- [6] J Prakash and D Prasad, *Phys Stat Soli a*, **1994**, 142, 281.
- [7] J Prakash, *Solid State Commun*, **1993**, 85, 647.
- [8] J Prakash, P K Singh and D K Dwivedi, *Indian J. Pure Appl. Phys.*, **2006**, 44, 532.
- [9] J Prakash, *Pramana J of Phys*, **2013**, 80, 2.
- [10] S Z Arrhenius, *Phys Chem*, **1889**, 226.
- [11] I. Kunze & P. Müller, *Phys Status Solidi (Germany)*, **1969**, 33, 91.
- [12] J. Prakash and F. Fischer *Phys. Stat. Solidi*, a, **1977**, 39, 499.