

A method for the evaluation of the Dielectric Relaxation Parameters from ITC spectrum

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ABSTRACT

A convenient and simple method is suggested for the evaluation of the Dielectric Relaxation Parameters from the ionic thermo current spectrum. Total charge released during ITC measurement and the maximum depolarization current help in the evaluation of the dielectric relaxation parameters. This method is easier and accurate as compared to other methods

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INTRODUCTION:

To understand the mechanism of dipolar orientation due to non-interacting dipoles, number of experimental techniques has been used. Ionic thermo current measurement [1] is preferred over the others because it is convenient, sensitive and accurate. For system involving single relaxation time, one gets single peak in ITC measurements. Dielectric relaxation parameters from ITC spectrum are evaluated using Bucci, Fieschi and Guidi (BFG) method [1]. In the cases having several relaxation times, the recorded ITC spectrum is broadened and consists of no. of peaks. In such cases, different peaks can be scanned following the peak cleaning technique [1,2,3]. However, the evaluation of the area enclosed in the ITC spectrum associated with each individual peak involve a fair degree of uncertainty in peak-cleaning method, which leads to inaccurate values of dielectric relaxation parameters. It has been observed [4] that the peak and position of the maximum depolarization current change with the heating rate. In the case involving multiple relaxation times, dielectric relaxation parameters can be evaluated following the method proposed by Prakash et al. [5] which utilize the data of ITC runs at different heating rates. BFG method is basically a graphical integration method, where whole of the ITC spectrum is scanned. Presence of background current, which is unavoidable, limits the correct evaluation of the area enclosed in the ITC spectrum. In the present paper, an alternative but easier and convenient method is suggested to evaluate the dielectric relaxation parameters from the observed ITC spectrum.

EVALUATION OF RELAXATION PARAMETERS:

After the application of electric field, the system gets polarized due to the preferred orientation of IV dipoles. The polarization (P_0) depends on the polarization condition through relation

$$P_0 = \frac{\alpha N_d \mu^2 E_P}{k T_P^{eff}} P_0 \quad (1)$$

Where N_d is the number of IV dipoles per unit volume each with dipole moment μ , E_P is the polarizing electric field, T_P^{eff} the effective polarization temperature [6], k is the Boltzmann's constant and α is a geometrical parameter which for freely rotating dipoles has a value 1/3. In ITC measurement [1,7], the sample is polarized an electric field E_P at some suitable polarization temperature T_P . With the electric field still on, the sample is rapidly cooled down to a fairly low temperature where the electric field is switched off. At such a low temperature, the relaxation time is practically infinite and polarized dipoles are frozen-in in the crystalline Lattice. The frozen-in polarization is given by eqn. (1). The sample is then heated at a linear rate b and resulting depolarization current is recorded with the help of electrometer. The depolarization current (I) is expressed by [1]

$$I(T) = \frac{Q}{C_\tau} \exp\left[-\frac{1}{C_b \tau_0} \int_{T_f}^T \exp\left(-\frac{E_a}{kT'}\right) dT'\right] \quad (2)$$

Where T_f is the temperature wherefrom the depolarization current starts to appear [8], τ_0 is the pre exponential factor and E_a the activation energy for the orientation of IV dipoles. Q in eqn. (2) represents the total charge released in ITC measurement which is related to P_0 through equation

$$Q = P_0 A \quad (3)$$

Where A is effective area of the crystal. It is obvious from eqn. (2) that ITC spectrum will be an asymmetric band with its maximum depolarization current at T_M given by

$$T_M = \left[\frac{b E_a C_{\tau M}}{k}\right]^{1/2} \quad (4)$$

Where τ_M is relaxation time at T_M .

The temperature dependence of the relaxation time τ is expressed through Arrhenius relation

$$\tau C = C_{\tau 0} \exp\left[\frac{E_a}{kT}\right] \quad (5)$$

It is obvious from eqn. (5) that τ decreases exponentially with the increase in the temperature. While heating the sample a stage comes at T_f when IV dipoles become able to disorient with the simultaneous appearance of depolarization current.

To determine the value of E_a and τ_0 , we consider eqn. (2). The integral appearing in eqn. (2) cannot be solved without approximation. Since the depolarization starts to appear at T_F . One can safely replace T_F by 0 without incurring any error. Putting y at the place of (E_a/kT) , we can express the integral part of eqn. (2) as

$$\begin{aligned} \int_{T_f}^T \exp\left(-\frac{E_a}{kT'}\right) dT' &\simeq \int_0^T \exp\left(-\frac{E_a}{kT'}\right) dT' \\ &= \frac{E_a}{K} \left[\frac{\exp(-y)}{y^2} \left(1 - \frac{2!}{y} + \frac{3!}{y^2} + \frac{4!}{y^3} + \dots\right) \right] \end{aligned} \quad (6)$$

When y is large (which happens to be), we can drop [9] other terms except the first. Thus, eqn. (6) can be represented as

$$\int_{T_f}^T \exp\left(-\frac{E_a}{kT'}\right) dT' = \frac{kT^2}{E_a} \exp\left(-\frac{E_a}{kT}\right) \quad (7)$$

Hence eqn. (2) can be written as

$$I(T) = \frac{Q}{C_T} \cdot \exp\left[-\frac{kT^2}{bE_a C(T)}\right] \quad (8)$$

With the help of eqn. (8) and (4), maximum depolarization current I_M can be expressed as

$$I_M = \frac{Q}{C_M} \exp[-1] \quad (9)$$

For recording the depolarization current (I), the sample is heated at a linear rate b according to the scheme

$$T = T_F + bt \quad (10)$$

The total charge released in the ITC measurement (Q) equals the area of the whole ITC curve as

$$Q = \int_{t(T_f)}^{\infty} I(t) dt = \text{Area enclosed in ITC curve} \quad (11)$$

Eqn. (11) in conjugation with eqn. (10) can be expressed as

$$Q = \frac{1}{b} \int_{T_F}^{\infty} I(T) dT = \frac{\text{Area enclosed in ITC Spectrum}}{\text{corresponding linear heating rate}} \quad (12)$$

Table: 1 Values of the dielectric relaxation parameters in different systems.

System	Reported		Calculated		Reference
	E_a (eV)	τ_0 (s)	E_a (eV)	τ_0 (s)	
NaCl: Cd ²⁺	0.67	2.8 x 10 ⁻¹⁴	0.67	2.8 x 10 ⁻¹⁴	10
NaCl: Ca ²⁺	0.695	8.3 x 10 ⁻¹⁵	0.70	5.4 x 10 ⁻¹⁵	11
KCl: S ²⁻	0.77	1.3 x 10 ⁻¹⁴	0.76	1.6 x 10 ⁻¹⁴	12
KCl: Mg ²⁺	0.49	3.9 x 10 ⁻¹²	0.49	5.4 x 10 ⁻¹²	13
KBr: S ²⁻	0.70	5.4 x 10 ⁻¹⁴	0.68	1.6 x 10 ⁻¹³	14
KBr: Sr ²⁺	0.66	4.0 x 10 ⁻¹⁴	0.68	1.3 x 10 ⁻¹⁴	15
KI: S ²⁻	0.61	10 x 10 ⁻¹⁴	0.61	9.9 x 10 ⁻¹⁴	16
KI: Ca ²⁺	0.49	1.0 x 10 ⁻¹¹	0.49	7.1 x 10 ⁻¹²	17
AgCl: Mn ²⁺	0.31	6.2 x 10 ⁻¹³	0.32	3.5 x 10 ⁻¹³	18
AgCl: Pb ²⁺	0.33	10 x 10 ⁻¹⁴	0.34	5.6 x 10 ⁻¹⁴	18

A plot of **I** vs time (t) is named as ITC curve where in ITC spectrum **I** is plotted against temperature **T**. It is clear from eqn. (11) that the area enclosed in the ITC curve is independent of the heating rate **b**. Eqn. (12) shows that the area enclosed by the ITC is proportional to **b**.

RESULT AND DISCUSSION:

Knowing the value of the total area of the ITC spectrum, **Q** can be evaluated using equation [12] which in turn gives the value of τ_M following eqn. [9]. This value of τ_M helps in the evaluation of E_a using eqn. [4]. Once E_a is known, τ_0 can be evaluated with the help of the Arrhenius relation at T_M . Thus, the dielectric relaxation parameters from the ITC spectrum involving single relaxation mechanism can be evaluated whom **Q**, **b**, **I_M** and T_M are known. This method is to be verified using experimental data.

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