



Evaluation Of Dielectric Relaxation Parameters From Ionic Thermocurrent Measurements

□ **DR. Praveen Kumar Singh**

Introduction:

A method is suggested for the evaluations of dielectric relaxation parameters including order of kinetics from the Ionic thermocurrent measurements. These parameters in a number of cases have been evaluated following the suggested method of analysis. The correctness of the evaluated parameters has been checked through the known value of evaluated parameters calculated by Bucci, Fieschi and Guidi method.

Introduction:

Dielectric relaxation parameter of impurity-vacancy (IV) dipoles are evaluated after analyzing the ionic thermocurrent (ITC) spectrum following either the method suggested by Carlick and Gibson or by Bucci, Fieschi and Guidi. The earlier method is the convenient and quick method for the evaluation of dielectric relaxation parameters. Since this method utilizes that portion of the ITC spectrum where uncertainties are more due to background current. Thus, the background current plays a significant role in deciding the accuracy of the evaluated parameters. The other method for the evaluation of dielectric relaxation parameters is Bucci, Fieschi and Guidi (BFG) method, which incorporates the graphical integration of the whole ITC spectrum. For simple non interacting dipoles having single relaxation mechanisms, one gets a simple ITC peak. For system involving multiple relaxation processes, the recorded ITC spectrum is complicated Peak corresponding to different relaxation processes can be scanned in such cases following peak cleaning technique. In BFG method the evaluation of the area enclosed in ITC spectrum associated with each individual peak involve a fair degree of uncertainty in the peak cleaning technique, which leads to increase the value of dielectric relaxation parameters. Obviously BFG method is not that effective in the case where multiple relaxation times are involved. In the present paper, an improvement method has been suggested. Improve method of analysis has been applied to a numbers of cases for the evaluation of dielectric relaxation parameters. The accuracy of the evaluated parameters has been checked through the BFG method.

Proposed Method of Analysis:

In ionic crystal dielectric properties will be either due to the orientation of IV dipoles or due to the drift of the defects in the presence of an electric field or due to both. To record an ITC spectrum, the system consisting of frozen-in IV dipoles is heated at a constant linear heating rate and the resultant depolarization current is measured as a function of temperature. At the low temperature the relaxation time is practically infinite which decrease exponentially with the increase in the temperature. While heating the sample a stage comes when IV dipoles just become able to reorient in the lattice with the simultaneous appearance of the depolarization current. With further increase in the temperature, one records the ITC Spectrum. The shape of the ITC spectrum gives information about the type of kinetic involved and also about the extent of distribution in the relaxation time.

Assistant Professor, Physics, S.G.N. Govt. P.G. College M. Bad Gohana Mau (U.P.), India

After the application of the electric field, the polarization P(t) increases exponentially with t controlled through the relaxation time t depends on the temperature through the relation..

$$\tau = \tau_0 \exp [E_a/kT] \tag{1}$$

where τ_0 is the relaxation time at infinite temperature and is now as pre-exponential factor or fundamental relaxation time and E_a is the activation energy for orientation /disorientation of IV dipoles.

The decay of polarization i.e. depolarization will be controlled by

$$d \{P(t)\}/dt = - (l / (2l - 1)) [P(t)/ \tau] \tag{2}$$

where l is the order of kinetics involved in the system. Eqn. (2) after integration gives

$$P(t) = P_0 \exp[- (l / (2l - 1)) (t/ \tau)] \tag{3}$$

where P_0 is the equilibrium or steady state polarization, which depends on polarizing electric field E_p and polarization temperature T_p as

$$P_0 = [\alpha N_d \mu^2 E_p / kT_p] \tag{4}$$

where N_d is the number of IV dipoles per unit volume each with dipole movement μ , k is the Boltzmann constant and α is a geometrical parameter which for freely rotating dipoles has a value (1/3).

The depolarization current density J(t) is expressed as

$$J(t) = - (1 / l) [d P(t) / dt] \tag{5}$$

Eqn.(5) can be written as

$$J(t) = (P_0 / (2l - 1) \tau) \exp[-(l / (2l - 1)) b \tau_0] \int_{T_0}^T \exp (-E_a / kT') dT' \tag{6}$$

With the help of Eqns.(1) and (6), one can write down the expression for the depolarization current i(T) as

$$i(T) = (Q / (2l - 1) \tau_0) \exp[(-E_a / kT) - (l / (2l - 1)) b \tau_0] \int \exp (-E_a / kT') dT' \tag{7}$$

where Q is the total charge released in the ITC measurement and is related to P_0 through

$$Q = P_0 A = [\alpha N_d \mu^2 E_p A / kT_p] \tag{8}$$

where A is the effective area of the specimen.

Condition for the Peak of the ITC spectrum:

Maximum depolarization current (i_M) appear at a temperature T_M according to

$$T_M^2 = [((2\tau_M - 1) / \tau_M) b E_p \tau_M / k] \tag{9}$$

Where τ_M is the corresponding relaxation time at T_M .

Evaluation of dielectric Relaxation Parameters:

From Eqn.(5) one gets

$$i(t) = (-1/\tau) dQ/dt \tag{10}$$

If the system is heated following a constant linear heating rate b, as par Eqn.

$$T = T_0 + b t \tag{11}$$

Eqn.(10) after integration can be rearranged as

$$Q_T = (\tau / b) \int_T^\infty i(T') dT' = \tau A_T \tag{12}$$

where Q_T is the number of remaining charge carrier par unit volume at the temperature T corresponding to time t and A_T represent the area of the ITC spectrum enclosed within the temperature range T to ∞ such that

$$A_T = (\tau / b) \int_T^\infty i(T') dT' \tag{13}$$

Further Eqn.(10) can also be represents as

$$Q = (\tau / b) \int_T^\infty i(T') dT' = \tau A_0 \tag{14}$$

where A_0 represent the total area enclosed within the ITC spectrum such that

where A_0 represent the total area enclosed within the ITC spectrum such that

$$A_0 = (l / b) \int_T^{\infty} i(T') dT' \quad (15)$$

Rearrangement of Eqns.(5) and (12) gives

$$X_T = [(2l - 1) \tau_0 / l] \exp(E_a / kT) \quad (16)$$

where $X_T = (A_T / i(T)) \quad (17)$

Eqn.(16) can further be written as

$$\ln(X_T) = \ln[(2l - 1) \tau_0 / l] + (E_a / kT) \quad (18)$$

For a given ITC curve l , τ_0 and E_a are constant, so the plot of $\ln(X_T)$ vs $(1/T)$ will be a straight line with the slope (E_a/k) and intercept equal to $\ln[(2l - 1) \tau_0 / l]$. Thus the activation energy can be evaluated from the slope of the straight line plot. The intercept gives the value of either l or τ_0 provided the other is known. In order to evaluate the order of kinetics we have calculated the value of form factor $\gamma = [T_M / (T_2 - T_M)]$. The calculated value of form factor for different sets of E_a , τ_0 and l are presented in Table(1). From this table it is clear that the average value of form factor for first order kinetics is 30.37 and for second order kinetics it is 29.61 and for third order kinetics it is found to be 28.63. A graph plotted between the average value of the form factor vs order of kinetics is shown in Fig.(1). From this curve, for a known value of form factor corresponding to an ITC spectrum of a system, the order of kinetics involved can be ascertained. Once the order of kinetics is known, the relaxation time can be evaluated from the intercept of the straight line plot drawn in accordance with Eqn.(18). Thus the dielectric relaxation parameters l , τ_0 and E_a can be evaluated.

Proposed method of analysis and evaluation has been applied in a number of causes of ITC spectra. Experimental data of ITC spectrum have been utilized to evaluate the dielectric relaxation parameter following proposed method of analysis. Evaluated dielectric relaxation parameters are presented in Table (2). It is obvious from the table that there is the good agreement in between the reported and evaluated values of dielectric relaxation parameters. It is worth mentioning that reported value corresponds to a monomolecular kinetics. Table (2) includes of monovalent, divalent and trivalent doped alkali halide crystals where data have been recorded following ITC technique. Corresponding references in different investigated systems have also been including in the table. It is obvious that a agreement exists in between the reported values evaluated following BFG method (assuming monomolecular kinetics) and those evaluated following the proposed method of analysis. For the systems presented in Table (2), values of l have been evaluated with the help of Fig. (1), after knowing the value of form factor from their respective ITC curves. The value of l has been determined with an accuracy of 10%. In most of the system presented in Table (2) the value of l have been found to be 1 suggested that

monomolecular kinetics is involved in these systems leading 100% recombination. However, in some of the system presented in Table 2, τ has been found to be greater than unity leading to simultaneous presence of recombination and retrapping. Consequently, the evaluated value of τ_0 does not agree well with the reported value as expected. However, E_a remain unaffected by the value of τ as it is evaluated from the slope of the straight line curve. Hence, reported and evaluated values of E_a are found to be in good agreement even in the cases when $\tau > 1$. The data presented in Table (2) thus justify the validity of the proposed method of analysis.

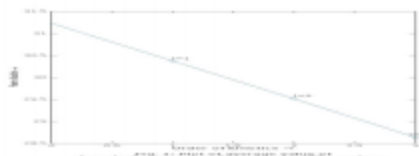
The accuracy of evaluated parameters depends on the extents to which the area of the ITC spectrum and the depolarization current are evaluated accurately. It should be mentioned, however, that the exact evaluation of area and current is restricted due to uncertainties in the background current. However, a slight error in the background current will not create a significant change in the magnitudes of τ , τ_0 and E_a .

Table - 1
Form Factor for ITC Spectra for Different Set of τ , E_a And τ_0

E_a (e.V.)	τ_0 (s)	Form Factor $\gamma = [T_M / (T_2 - T_M)]$		
		$l = 1$	$l = 2$	$l = 3$
0.60	1.0×10^{-12}	30.42	29.58	28.45
0.60	2.0×10^{-12}	30.28	29.49	28.72
0.60	3.0×10^{-12}	30.31	29.41	28.60
0.60	4.0×10^{-12}	30.35	29.58	28.70
0.65	1.0×10^{-12}	30.45	29.46	28.78
0.65	2.0×10^{-12}	30.60	29.59	28.70
0.65	3.0×10^{-12}	30.42	29.44	28.65
0.65	4.0×10^{-12}	30.27	29.67	28.70
0.70	1.0×10^{-12}	30.25	29.28	28.65
0.70	2.0×10^{-12}	30.20	29.58	28.25
0.70	3.0×10^{-12}	30.51	29.51	28.65
0.70	4.0×10^{-12}	30.36	29.73	28.75
Average Value		30.37	29.51	28.63

Table -2
Reported and Evaluated Values of Dielectric Relaxation Parameters

System	Reported			Evaluated			
	b (K ⁻¹)	E _a (e.V.)	τ ₀ (s)	Form Factor	l	E _a (e.V.)	τ ₀ (s)
N ₂ Cl : Mn ²⁺	0.1	0.670	9.1 × 10 ⁻¹⁶	30.33	1.0	0.668	8.8 × 10 ⁻¹⁶
: Cu ²⁺	0.1	0.695	8.3 × 10 ⁻¹⁶	30.40	1.0	0.700	8.9 × 10 ⁻¹⁶
: Co ²⁺	0.1	0.670	2.8 × 10 ⁻¹⁴	30.38	1.0	0.674	3.4 × 10 ⁻¹⁴
: Mg ²⁺	0.1	0.630	2.9 × 10 ⁻¹⁶	30.32	1.0	0.627	2.5 × 10 ⁻¹⁶
: NCO ⁻	0.012	0.192	2.0 × 10 ⁻¹³	30.24	1.0	0.184	1.8 × 10 ⁻¹³
: NO ₂ ⁻	0.022	0.040	7.0 × 10 ⁻¹⁰	30.18	1.0	0.039	6.7 × 10 ⁻¹⁰
KCl : Ba ²⁺	0.05	0.24	1.00 × 10 ⁻⁸	30.29	1.0	0.230	0.90 × 10 ⁻⁸
: Ni ²⁺	0.10	0.46	1.16 × 10 ⁻¹¹	30.19	1.0	0.455	1.10 × 10 ⁻¹¹
: Ca ²⁺	0.10	0.61	3.03 × 10 ⁻¹³	30.24	1.0	0.604	2.98 × 10 ⁻¹³
: Br ²⁺	0.10	0.71	3.23 × 10 ⁻¹⁴	30.34	1.0	0.708	3.20 × 10 ⁻¹⁴
: Mg ²⁺	0.10	0.49	3.85 × 10 ⁻¹⁰	30.22	1.0	0.495	4.01 × 10 ⁻¹⁰
: Y ²⁺	0.10	0.67	1.10 × 10 ⁻¹⁴	30.34	1.0	0.672	1.14 × 10 ⁻¹⁴
: Sr ²⁺	0.10	0.63	3.70 × 10 ⁻¹³	30.43	1.0	0.629	3.64 × 10 ⁻¹³



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