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Review Article

KINETICS OF THERMOGRAMS OF SEMICONDUCTING GLASSES

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ABSTRACT
In this paper we evaluate the order of kinetics involved in thermally stimulated relaxation processes of semiconductor glass ($40PbO\text{-}60Bi_2O_3$) in view of new model proposed for appearance of thermally stimulated depolarization curve. The involvement of different order of kinetics in Thermograms depends on the experimental conditions of polarization and rate of rapid cooling. From analysis of experimental data, already reported in literature, we study the effect of Polarizing field on order of kinetics.

Keywords: *Order of Kinetics, Thermally Stimulated Depolarization Processes, Thermogram*

INTRODUCTION
Thermally stimulated processes (TSPs) are the physical phenomena in which a certain property of the material under study is measured as a function of temperature. The resulting thermal curve, sometimes named as Thermally Stimulated Depolarization Curve (TSDC) or Thermally Stimulated spectrum or Thermogram or Glow Curve – where measured property of the specimen is presented as a function of temperature. This thermogram is typically, a curve consisting of one or more peaks. So many works has been reported in literature on thermally stimulated depolarization study of polymeric materials. This technique is a good and efficient tool for characterization of materials and quite helpful in selecting materials for different purposes in electrostatics. Sessler (1980) defined electrate as a dielectric material exhibiting a quasi-permanent electric charge. TSDC of polymer has become a widely used experimental technique for the investigation of various material parameters such as charge storage properties, determination of mean depth of internal charge, activation energies of traps and trap structure of material. The broad survey (Khare *et al.,* 1998; Srivastava *et al.,* 1981; Pissis *et al.,* 1994; Negau *et al.,* 1994; Swarkar *et al.,* 1997) of literature revealed that the thermally stimulated discharge current technique is extensively applied for the study of polymer thermorelectrerts. However, work on TSDC measurement is very scant in glass thermoelecterat. The basic principle of this technique is to study the charge decay by heating the electrets at a constant rate. This technique is proved as a basic tool for study of dipole reorientation process and trap and recombination levels in electerets.

Mechanism Involved and Analysis
Materials 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 material 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 The plot of ionic thermocurrent (ITC) as a function of temperature is known as ITC spectrum or also known as thermally stimulated depolarization current (TSDC) spectrum or a Thermogram. There are so many methods have been reported in literature for the analysis of TSDC thermogram. All these methods are based on different suggested mechanisms, as suggested by different workers engaged in the same work, for the appearance TSDC spectrum. Most of the previously discussed methods focus on evaluation of dielectric relaxation parameters, only few methods are focused on order of kinetics parameter also. 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_o) satisfies equation of peak temperature (Chen and Kirsch, 1988).

$$T_m^2 = \frac{b\,E_a\,\tau_m}{k} \quad (1)$$

where b is heating rate, Ea is activation energy, τm is relaxation time at peak temperature and k is Boltsman constant.

Burghate *et al.,* (2003) have studied thermally stimulated discharge current in semiconductor glass ($40PbO\text{-}60Bi_2O_3$). The results are presented in their paper in the form of thermograms which are curves between TSDC current and temperature of the sample at different polarizing fields. The experimental findings are summarized in Table 1. From reported data values of τ_m (with the help of Arrhenius relation), $\frac{bE_a\tau_m}{k}$ {R H S of eq.(1)} and T_m^2 {LHS of eq.(1)} are calculated and shown in columns 5,6 and 7 respectively.

Table 1: Relaxation parameters of glass sample polarized at fixed temperature by various polarizing fields

E_a (eV)	τ_0 (s)	b (^{0}K/s)	T_m (^{0}K)	τ_m (s)	$\frac{bE_a\tau_m}{k}$ ($^0K^2$)	T_m^2 ($^0K^2$)	E_p (kV/m)
0.456	4.60E-05	0.058333	333	366.7268	113205.66	110889	78
0.099	52.7	0.058333	333	1660.279	111269.69	110889	156
0.368	1.21E-03	0.058333	333	449.2472	111916.44	110889	234
0.108	29.6	0.058333	323	1433.785	104825.85	104329	312
0.144	6.19	0.058333	323	1092.984	106545.92	104329	390

According to eq.(1) values of T_m^2 and $\frac{bE_a\tau_m}{k}$ must be equal, but from columns 7 and 6 of Table.1 it is clear that they are not equal. In order to remove this anomaly, a new method of analysis has been proposed by Prasad *et al.,* (2012) to evaluate dielectric relaxation parameters and order of kinetics. The new method of analysis is simply BFG method in which concept of order of kinetics is incorporated. According to this method of analysis equation for peak temperature is now changed into

$$T_m^2 = \frac{\ell\,b\,E_a\,\tau_m}{k} \quad (2)$$

where ℓ is order of kinetics involved in TSDC spectrum. Following this method of analysis order of kinetics is calculated for different TSDC curves of thermograms of semiconductor glass and presented in Table 2.

Table 2: Order of kinetics with activation energy and relaxation time for different polarizing fields

E_p (kV/m)	T_m (^{0}K)	E_a (eV)	τ_0 (s)	ℓ
78	333	0.456	4.60E-05	0.979536
156	333	0.099	52.7	0.996579
234	333	0.368	1.21E-03	0.99082
312	323	0.108	29.6	0.99526
390	323	0.144	6.19	0.979193

Conclusion

Here we evaluate the order of kinetics involved in TSDC spectrums of semiconductor glass material following new method of analysis of TSDC thermogram. The nature of spectrum is clearly explained in terms of heterocurrent and homocurrent by Burghate *et al.,* (2003). The evaluation of order of kinetics is quite helpful in characterizing the electretes and in their selection for different purposes like electric charge storage.

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