Thermally stimulated discharge current (TSDC) and dielectric constant of semiconducting glasses

D K BURGHATE[†], V S DEOGAONKAR[†], S B SAWARKAR*, S P YAWALE[‡] and S V PAKADE[‡]

Department of Physics, Polytechnic Badnera, Amravati 444 701, India
[†]Department of Physics, Shri Shivaji Science College, Amravati 444 603, India
[‡]Department of Physics, Government Vidarbha Institute of Science and Humanities, Amravati 444 604, India

Abstract. In this paper the results of thermally stimulated discharge current (TSDC) and dielectric constant for 40PbO–60Bi$_2$O$_3$ glass thermoelectrets are presented. Measurements of TSDC and dielectric constant, ε', have been carried out in the temperature range 30–300°C. The thermoelectrets were prepared at different polarizing fields. The various observed peaks in the thermograms are discussed on the basis of space charge polarization. The trap energy is evaluated from the Garlick–Gibson plot of initial rise method. Similarly other parameters such as relaxation time, charge release etc are evaluated.

Keywords. Semiconducting glass; TSDC; trap energy; dielectric constant.

1. Introduction

A good amount of work has been reported on thermally stimulated discharge technique in polymeric materials during the past few years. Sessler (1980) gave a broad definition of the electret. He defined electret as a dielectric material exhibiting a quasi-permanent electric charge. Eguchi (1919) discovered the first electret, now known as thermoelectret. Khare *et al* (1998) measured the thermally stimulated discharge current (TSDC) and electrical conductivity in metal (1) and ethyl cellulose–metal (1)/(2) systems. 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 the internal charge, activation energies of traps and trap structure of the material. It is only in recent years that the possibility of technological application of electrification of polymer due to its contact with metal has been discovered (Srivastava *et al* 1981). The availability of new measuring techniques such as thermally stimulated discharge current (Turnhout 1975) has freshened interest in achieving a better understanding and application of the phenomena. Fridkin and Zheludev (1961), Gross (1964) and Latour (1972) extensively reviewed the methods of formation of thermoelectrets. Basically, three kinds of phenomena can occur in thermal charging, viz. (i) internal polarization with the sign of heterocharge due to dipole alignment or charge separation within the dielectric i.e. dielectric absorption,

(ii) homocharge deposition due to spark discharges in the air gaps and (iii) homocharge injection through contacting electrodes.

Pissis *et al* (1994) reported the electric and dielectric measurements of several conducting (polyethylene oxide) PEO-based electrolytes, by using thermally stimulated depolarization current (TSDC) and thermally stimulated polarization currents (TSPC). Negau and Negau (1994) obtained new results in thermally stimulated discharge current (TSDC) peak above room temperature.

Hong and Day (1979) applied the techniques of thermally stimulated polarization and depolarization current for studying alkaline ion motion in glasses of sodium silicate and lead silicate. The peaks observed are discussed on the basis of d.c. conductivity and short range Na$^+$ ion motion. The thermal detrapping of Na$^+$ ions from the Si–SiO$_2$ or SiO$_2$–Al electrode interface produces the thermally stimulated ionic current peaks from which the trap depths and Na$^+$ ions mobility can be calculated (Hickmott 1973, 1975). Most of the peaks which occurred in the thermograms of alkali silicate glasses are very much related to the structure and mobility of ions. The localized ion motion around the non-bridging oxygen ion and the limited conduction pathways are responsible for the TSDC peaks in high and low temperature regions (Agarwal and Day Delbert 1982). Sawarkar *et al* (1997) studied the depolarization currents in semiconducting 50PbO–50B$_2$O$_3$ glasses and evaluated the various parameters such as trap depth, trap density, activation energy etc. The results have been explained on the basis of space charge polarization and distribution of trap levels of charges inside the thermoelectret.

*Author for correspondence

Many workers (Pillai *et al* 1973; Pillai and Mollah 1980) have studied depolarization current in polymer thermo-electrets. Pasek and Magierski (1986) measured thermally stimulated discharge current in UV-irradiated borosilicate glasses containing alkali ions. Hong and Day (1979) and Doi (1983) used this technique of measurement of thermally stimulated current to investigate alkaline ion motion in glasses.

The detailed survey of literature revealed that the thermally stimulated discharge technique is extensively applied for the study of polymer thermoelectrets only. However, work on TSDC measurement is very scant in glass thermoelectret. Therefore, it has been decided to study the depolarization in lead–bismuth glass, using thermally stimulated discharge current (TSD) technique. The basic principle of this technique is to study the charge decay by heating the electret at a constant rate. This technique is a basic tool to identify and evaluate the dipole reorientation process, trapping and recombination levels in electrets.

2. Experimental

2.1 *Glass sample preparation*

The glass samples were prepared from AnalaR grade chemicals, PbO and Bi_2O_3. The component composition was 40 mol.% and 60 mol.%, respectively. Appropriate amounts in mol.% of PbO and Bi_2O_3 in powder form were weighed on K-Roy monopan balance having an accuracy of ± 0.00001 g. Repeated grinding of mixture was done to ensure homogenization. Homogeneous mixture was then transferred to fire clay crucibles which was then subjected to melting in an automatically controlled muffle furnace at temperatures ranging from 1000 to 1200 $\pm$ 10°C. The duration of melting was generally 4 h. The homogenized molten mass was cast in steel discs of 2·5 cm length and 0·7 cm thickness. The samples were quenched at 200°C to avoid cracking and shattering of glass.

After quenching, all samples were immediately transferred to an annealing furnace. Samples were annealed at 350°C for 2 h. The effect of annealing is to remove the air bubbles or cavities, if any, which may be formed by sudden quenching. All glasses after annealing were subjected to finishing processes such as cleaning and polishing. Sufficient number of glass samples were prepared from the same batch of composition.

For attaining exact parallel and plane surfaces of glasses, a fine lapping paper was used. A conducting silver paint was applied to either side of glass samples. All the samples were baked at 150°C for 2 h, for removal of mechanical stresses, if any, developed during polishing. Thickness of each sample was 0·380 cm. The X-ray diffractograms of all the samples were obtained for checking the amorphous nature of the sample. The absence of peak in the X-ray spectra, confirmed the amorphous nature of glass samples (figure 1).

2.2 *Electret preparation*

The glass sample $40PbO–60Bi_2O_3$ was mounted into the sample holder. The polarizing field, E_p, was maintained for 30 min between two opposite faces of glass at room temperature (30°C). Then the electric field across the sample was removed and the sample was short-circuited for 15 min to remove the stray charges by wrapping the sample in a conducting aluminum foil. The electrets were prepared at different polarizing fields: $E_p = 78$ kV/m, 156 kV/m, 234 kV/m, 312 kV/m and 390 kV/m, respectively at room temperature.

2.3 *Measurement of thermally stimulated discharge current*

After electret formation the sample holder assembly was placed in high temperature furnace. The sample was short circuited through a sensitive picoammeter (Model DPA III Scientific Equipment, Roorkee, having accuracy $\pm$ 1 pA) for the measurement of discharge current. Then the sample was heated at a uniform rate of 3·5°C/min from
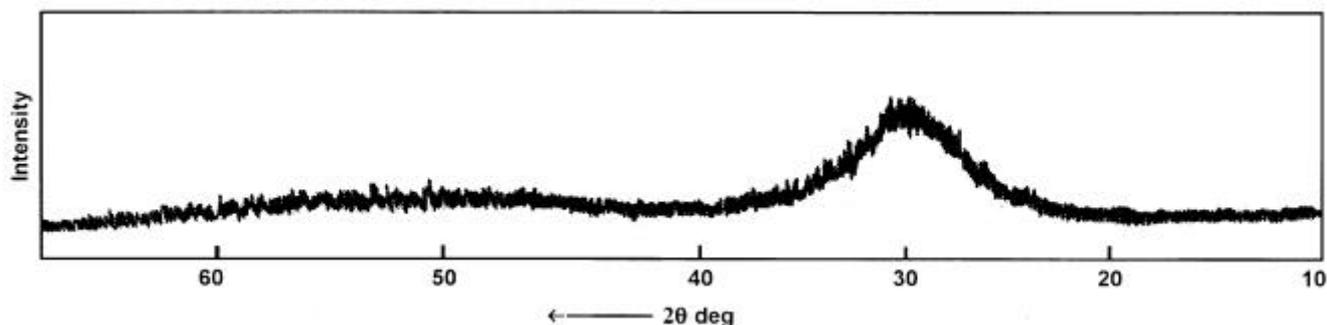

Figure 1. X-ray diffractogram of glass sample.

30 to 300°C. The short circuit current was also measured for unpolarized sample. The temperature was recorded by digital thermometer having an accuracy of ± 1°C.

The purpose of preparation of electrets was to observe the effect of polarizing field, E_p, on the properties of electrets.

3. Results

The results of the present study are reported in the thermograms which are curves between TSDC current and temperature of the sample at different polarizing fields (figure 2). The experimental findings are summarized as below.

(I) Each curve (excepting curve (a) for unpolarized sample) shows one a-peak at a temperature of about 50 to 60°C in the +ve current i.e. heterocharge region.

(II) (a) Each curve (excepting curve (a)) shows a reversal of polarity, which occurs gradually, (b) the unpolarized sample curve (a) shows –ve current only i.e. in the homocharge region and (c) the current in the homocharge region increases steeply beyond about 200°C in almost all curves.

(III) The curve (c) for sample polarized at 156 kV/m presents a second current peak, a_2, in the homocharge region

Figure 2. Thermally stimulated discharge current vs temperature plot of glass sample.

and a third current peak, a_3, which appreciably is larger than its a_1 peak.

(IV) The peak current, I_{max}, and hence the amount of stored charge first increases with polarizing field, attains a maximum value for curve (d) at field 234 kV/m and then decreases again (figure 2).

4. Discussion

The intensity of polarizing electric field, E_p, appreciably affects properties of the electret (Tareev 1979). When polarizing electric field, E_p, is small (approximately up to 1 mV/m), the obtained electret possesses charges opposite to the polarity of polarizing voltage, i.e. heterocharge. If the $E_p > 1$ mV/m, the electret receives charges of the same sign as the electrodes with which the surfaces of the electret were in contact during polarization i.e. homocharge.

The observed increase in I_{max} (and the total charge stored) with increase of polarizing field (up to 234 kV/m) may be due to the increased dipolar polarization. The dipoles get a better chance to orient themselves in the field direction, due to increased field. Considering only internal polarization, the two mechanisms, which are likely to be operative in the polarization process, are the relaxation of the polar group and space charge polarization. The disorientation of the dipoles merely requires local rotation and hence the current peak (a) appears at lower temperature (than the space charge polarization peak which may appear at higher temperature).

At higher temperature the self-motion of the space charges is accompanied by a second neutralization mechanism viz. recombination with thermally generated carriers. These carriers are generated uniformly in the entire specimen by dissociation of neutral entities. These charges become more mobile at higher temperature and constitute a homocurrent in the internal field of the electret. This current is opposite to the current due to dipolar disorientation. As the temperature is raised above heteropeak, the homocurrent starts increasing, as the number of thermally generated carriers increases. So a reversal is observed from heterocurrent to homocurrent. As temperature increases the current goes on increasing in the homoside for all curves except curve (c). Verma *et al* (1990) made similar observation on bakelite electrets.

In case of curve (c) [$E_p = 156$ kV/m], the increase of homocurrent is quite small, and yet it shows a homocurrent current peak, a_2. This is because of the dipoles of the closed dielectric domains, which are broken at this temperature and start contributing to the main displacement current, I_{het}, whose direction is opposite to the direction of I_{hom}. This results in the homo peak a_2 at about 250°C. The origin of the hetero-charge peak, a_1 (and homocharge peak, a_2) can be explained by two-charge theory of Gross (1944, 1949) as $I = I_{het} + I_{hom}$. The resultant
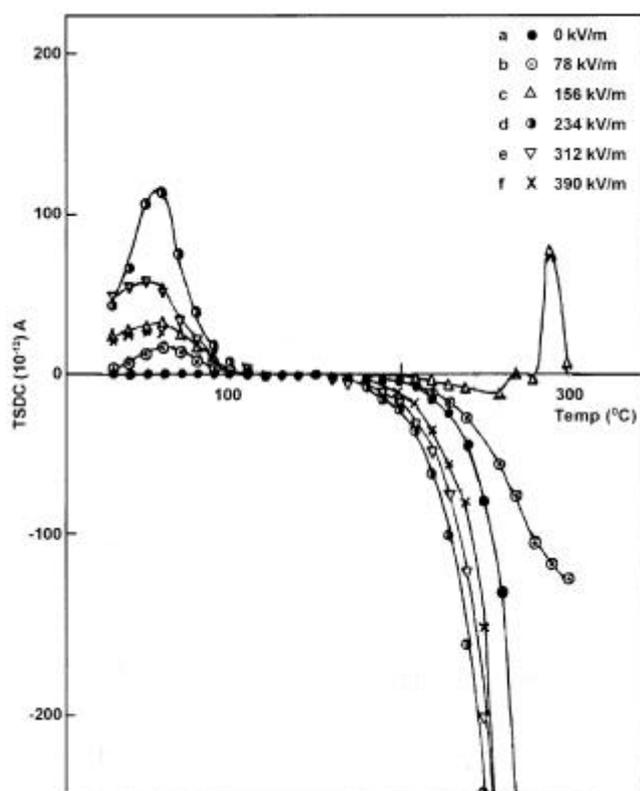
**Table 1.** TSDC parameters of glass samples polarized at fixed polarizing temperature and various polarizing fields.

Sr. no.	Polarizing field, E_p (kV/m)	Peak temperature, T_m (°C)	Trap energy, E (eV)	Characteristic relaxation time, t_0 (sec)	Attempt to escape frequency, n_0 (sec^{-1})	Capture cross section, s_D (m^2)	Charge released (Q 10^{-8} coulomb)
1	78	60	0·456	$4·60 \times 10^{-5}$	$4·06 \times 10^{4}$	$1·74 \times 10^{-25}$	3·60
2	156	60	0·099	$5·27 \times 10^{1}$	$7·24 \times 10^{-2}$	$3·10 \times 10^{-31}$	9·00
3	234	60	0·368	$1·21 \times 10^{-3}$	$1·13 \times 10^{3}$	$4·87 \times 10^{-27}$	24·00
4	312	50	0·108	$2·96 \times 10^{1}$	$1·97 \times 10^{-1}$	$9·00 \times 10^{-31}$	15·00
5	390	50	0·144	6·19	$5·59 \times 10^{-1}$	$2·55 \times 10^{-30}$	9·30
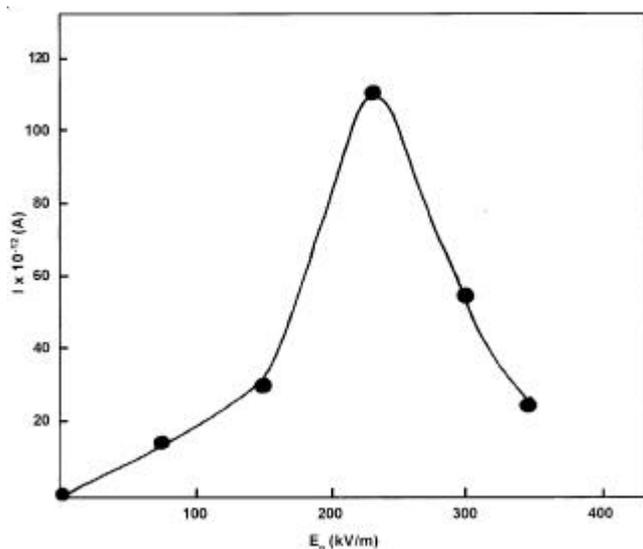
Figure 3. Variation of peak current with polarizing field.
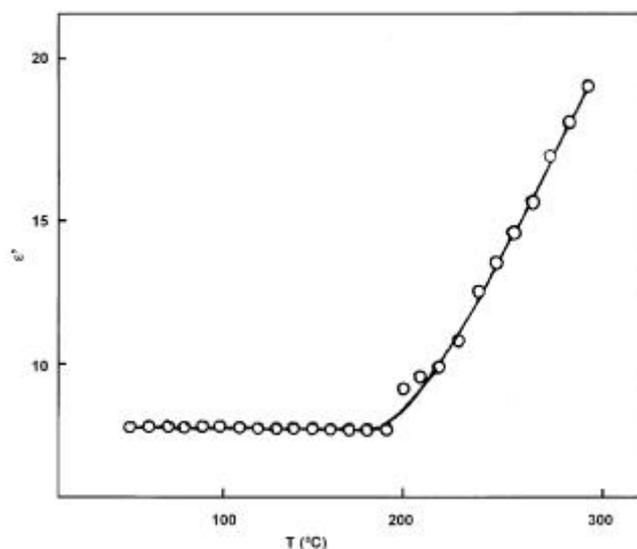
Figure 4. Variation of dielectric constant with temperature.

current generated is proportional to the net current, I_{het}–I_{hom}, since I_{het} and I_{hom} are assumed to have opposite sign. When the reorientation rate of dipoles is greater than the rate of neutralization by recombination with thermally generated carriers, we first find a heteropolar peak, a_1.

Figure 3 shows the variation of heterocurrent for peak (a) with the polarizing field. It can be observed that the peak current increases with polarizing field up to 234 kV/m, becomes maximum and then falls again with further increase in polarizing field. This may be explained as below.

The reorientation of the dipoles due to the polarizing field increases until it reaches a maximum value corresponding to the maximum number of available dipoles, and this shows heteropolar peak, a_1. Now even if the polarizing field is increased beyond this, there are no more dipoles to be reoriented and hence I_{het} does not increase. On the contrary the rate of neutralization by recombination at higher fields should have increased. Thus the peak current decreases beyond polarizing field, 234 kV/m. The values of TSDC parameters such as trap depth, characteristic relaxation time, attempt to escape frequency and capture cross section calculated by using

Garlick–Gibson (1948) method are reported in table 1. The relevant formulae for evaluation of these parameters are reported elsewhere (Sawarkar *et al* 1997). The charge released during the relaxation process calculated by measuring the area under TSDC peak (Simmons and Taylor 1972) is also reported in table 1. It is found that the charge released during relaxation process increases with increasing polarizing field up to 234 kV/m and then decreases with increasing field.

Figure 4 shows the variation of dielectric constant with temperature (30–300°C) at frequency 1 kHz. It is observed that the dielectric constant is independent of temperature up to 190°C and beyond 190°C it increases rapidly. This increase in dielectric constant is due to a change in electronic structure and partly due to thermal expansion. The dielectric constant, e', is found to be of the order of values of e' for glasses appearing in the literature (Van-Hipple 1954). The change in dielectric constant at high temperature is a characteristic of Debye-type relaxation process where symmetrical distribution of relaxation time takes place.

If we compare the graph of e' vs T (figure 4), with the graph of zero polarizing field (figure 2), a similarity in

nature is observed. The ε' of figure 4 and TSDC current of figure 2, remain almost constant up to about 200°C. Beyond this the ε' as well as TSDC current starts suddenly increasing. This is in fact what is expected. The increased ε' and hence increased capacity to store and release more charge (homo) with rising temperature is anticipated for the unpolarized sample. Two independent approaches viz. by dielectric and TSDC measurements, lead to the same basic behaviour of the sample, thereby corroborating the experimental findings.

We are attempting to see whether any relation can be observed in the behaviour of the polarized sample and its dielectric constant. Further work in this direction is in progress.

Acknowledgement

References

Agarwal A K and Day Delbert E 1982 *J. Am. Ceram. Soc.* **65** 111

Doi A 1983 *Jap. J. Appl. Phys.* **22** 228

Eguchi M 1919 *Proc. Phys. Math. Soc. Jpn* **1** 326

Fridkin V M and Zheludev I S 1961 *Photoelectrets and electrographic process* (NY: Consultants Bureau)

Garlick G F J and Gibson A F 1948 *Proc. Phys. Soc.* (*London*) **60** 574

Gross B 1944 *Rev. USA* **66** 26

Gross B 1949 *J. Chem. Phys. USA* **17** 866

Gross B 1964 *Charge storage in solid dielectrics* (Amsterdam: Elsevier)

Hickmott T W 1973 *Appl. Phys. Lett.* **22** 267

Hickmott T W 1975 *J. Appl. Phys.* **46** 2583

Hong C M and Day D E 1979 *J. Mater. Sci.* **14** 2493

Hong C M and Day D E 1981 *J. Am. Ceram. Soc.* **64** 61

Khare P K, Verma A and Paliwal S K 1998 *Bull. Mater. Sci.* **21** 207

Latour M 1972 *Appl. Phys.* (*Paris*) **7** 115

Negau E and Negau R 1994 *Proc. ISE* **8** 528

Pasek Ewa Rysiakiewiez and Magierski Wojciech 1986 *Opt. Appl.* **XVI** 273

Pillai P K C and Mollah M 1980 *J. Macromol. Sci. Phys.* **B17** 69

Pillai P K C, Jain K and Jain V K 1973 *Indian J. Pure Appl. Phys.* **11** 597

Pissis P, Laudat J, Thonas C, Apekis L and Kyritsis A 1994 *Proc. ISE* **8** 392

Sawarkar S B, Deogaonkar V S, Pakade S V and Yawale S P 1997 *Indian J. Pure Appl. Phys.* **35** 281

Sessler G M 1980 *Electrets* (Berlin: Springer-Verlag; New York: Heidelberg) pp 81–217

Simmons J G and Taylor G W 1972 *Phys. Rev.* **6** 4804

Srivastava S K, Ranade J D and Srivastava A P 1981 *Polymer* **22** 1645

Tareev B 1979 *Physics of dielectric materials* (Moscow: Mir publishers) p. 216

Turnhout J Van 1975 *Thermally stimulated discharge of polymer electret* (Amsterdam: Elsevier) p. 25

Verma J P, Thakur R S and Sinha S D 1990 *Indian J. Pure Appl. Phys.* **16** 281

Van-Hipple A R 1954 *Dielectric materials and applications* (London: Chapman and Hall) p. 309