Chapter 2

Review of Literature
2.1 Review of X-ray Diffraction Study and Infrared Study:

One of the most exiting areas in chemistry, chemical engineering and materials science is the preparation, characterisation and application of polymers. Polymers have become the most versatile commodity in today’s life style. Polymers belong to a relatively new branch of science. There has been tremendous development in polymers in past 70 years or so and as on today it is impossible to think of world without polymeric materials that we use in our day to day life. The use of synthetic polymers is increasing rapidly year by year and in many applications they are replacing conventional materials like metals, ceramics, wood, natural fibers such as cotton, wool etc. In fact, science of polymers has its roots in physics, chemistry, biology, engineering and technology and medicine and has grown to a full fledged discipline of science.

Polymers are not simple covalent crystals of conventional solid state physics (Seanor, 1982). They can exist as crystalline materials, as amorphous materials or as a mixture of crystalline and amorphous materials. Even highly crystalline polymers contain considerable amorphous materials. They are molecular materials, that is, each polymer chain is its own individual and interaction with other polymer chains is usually weak. Polymer chains can take up different conformations and can be oriented mechanically with in the individual polymer chains, the chemical units need not have a unique molecular weight but described in terms of weighted average and distribution about the mean.

Most properties of polymers are profoundly affected these differences. They are heat insulators and are usually soft and easily distorted. They are
electrically insulating and poor conductors of electric charge.

X-rays are usually produced by bombarding a metal target with a beam of high energy electrons. This is done inside a vacuum tube, the X-ray passing out through a beryllium or polyester film in the tube is a well defined beam. The choice of the target metal and the applied voltage determines the wavelength of X-rays produced. Experiments in which nearly monochromatic X-ray are used are of the greatest interest.

The diffracted X-ray may be detected by their action on photographic films or plates, or by means of a radiation counter and electronic equipment feeding data to a computer.

Each method has its advantages. Qualitative examination of the diffraction pattern and accurate measurement of angles and distances are best mode from photographic record, whereas for precise measurement of the intensity of the diffracted beam, the counting technique is preferred.

X-ray of a given wave length are diffracted only for specific orientation of the sample. If the sample is a single crystal, it must be placed in all possible orientations during the experiment, usually by rotating or oscillating the sample about one of the axes to achieve the desired orientation. Alternately, a sample made of a powder of very small crystals may be used. If the minute powdered particles are randomly oriented, all orientations will be included within the sample. The powder method is more convenient, but gives less information than the single crystal method, since the latter shows orientations about one crystal axis at a time to be investigated.
Identification of an unknown sample of plastic, rubber or a fibre may be required for a variety of reasons. Many of these polymers carry only their trade names and their detailed structure is not disclosed. In the field of industrial research, it may be necessary to analyse the polymer sample and identify it. Infrared spectroscopy is a powerful spectroscopic technique used for the identification and characterization of polymers.

Ramaswamy and Venkatachalapthy (1992) have reported the infrared spectra of sedimentary deposits from Neyveli lignite minecut-II in the region 4000-200 cm\(^{-1}\). The amounts of kaolinite present in the samples have been calculated from extinction coefficient (K) value at 3700 cm\(^{-1}\) band. The amount of iron substitution has been found from the Al / Al + Si ratio. Most of the samples have, kaolinite as the major clay mineral in well ordered form.

Samier et al (1994) studied the properties of polypyrrole powder, polypyrrole-polyvinyl alcohol composites and polythiophene-polystyrene composite chemically polymerised by using X-ray photoelectron spectroscopy (X-PS) and measurements of electrical conductivity. They reported that transport properties of these composites are characterised by the hopping between the bipolaramic clusters as the dominantly contributing mechanism.

da Cunha and Faria (1994) employed X-ray radiation induced conductivity in both ferro and paraelectric phases of P(VDF/TrFE) copolymers. They explained the results in terms of dispersive transport mechanism and used the Arkhipov model to fit the results.

Nogueira et al (1994) characterized the blends of PVDF and conducting
polymers using SEM and XRD techniques. They discussed the influence of conducting polymers on the characteristics of PVDF.

Yawale et al. (1995) have carried out structural investigation of some borate glasses. The amorphous nature of ZnO-Bi₂O₃-B₂O₃ glasses was confirmed from X-ray diffraction studies.

Goncalves et al. (1995) studied the flexible conducting and semicrystalline films of conducting blends of polyurethane (PU) and doped poly (o-methoxyaniline) (POMA) mixture with N-dimethyl formamide. They investigated the structure of homopolymers using X-ray diffraction and compared it with the blends by electron diffraction. They reported the amorphous nature of PU and the semicrystalline nature of POMA. They observed the crystalline regions in the blend even for PU: POMA 90:10 (by weight) composition.

The glass formation and structural properties of the unconventional lead cuprate glasses of composition X CuO-(100-X) PbO mol% are reported by Hazra and Ghosh (1995).

The infrared studies of lead-bismuth glasses was carried out by Burghate (1997). Spectral studies of all the glass samples show number of absorption peaks. The peaks are sharp, medium and broad. An attempt is made to explain the structure of lead-bismuth glasses with the help of IR-spectra.

Lukie et al. (2000) have reported the existence of the structural units in the bulk Cu-As-Se-I glasses using X-ray analysis.

The crystallization process of a ternary system Si₂O₅-CaO-MgO-Na₂O is analysed using X-RD and strength measurement by Alizaden and Marghussian (2000).
Venkatachalapathy et al (2001) carried out the FT-IR analysis of Neyveli lignite and flyash samples. They found that the extinction coefficient (K) values were calculated for the bands at 3450, 2900, 2835, 1695, 1600 cm\(^{-1}\) etc.

Microhardness and X-ray diffraction studies on polymer blends of polyethylmethacrylate (PEMA) and polyethyleneoxide (PEO) have been reported by Awasthi and Bajpai (2001). The increase in crystallinity of polymer blends with increasing content of PEO was observed by X-ray diffraction.

Sawarkar (2002) carried out X-RD studies of lead borate glasses. The amorphous behaviour of the prepared glass samples was checked by X-ray diffraction spectra. The possible crystallinity developed in the samples during quenching and annealing is observed from diffraction spectra.

Bhat and Deshmukh (2002) have carried out X-ray crystallographic studies of polymeric materials. In this paper, the results of X-RD of PET when subjected to thermal, chemical and plasma treatments have been presented. The results show that the percentage crystallinity can be varied from 17 to 50%.

Characterization of Zirconium dioxide thin films prepared by cwCO\(_2\) laser-assisted evaporation has been done by Choudhary et al (2003). The surface morphology of the films has been observed by scanning electron microscopy (SEM) and atomic force microscopy (AFM), and the structure has been studied by X-ray diffraction. The X-RD observation revealed that, the structure of the films, was tetragonal with lattice constant a = 0.507 nm and c = 0.572 nm, deposited at 250°C substrate temperature.
Saikia et al (2005) have carried out FTIR and impedance spectroscopy studies of PVC-PMMA-NH$_4$SCN-DBP based polymer blend electrolyte to see the formation of polymer-salt complex and to measure the ionic conductivity respectively.

Singh et al (2005) have reported, the preparation and characterization of polymer composites based on charge transfer complex of phenothiazine-iodine in polystyrene.

Vibrational spectral studies on 2,5 dichloroaniline have been carried by Rai et al (2006). All the bands have been assigned on the basis of normal coordinate analysis, which are in good agreement with the literature. The far IR region (20-600 cm$^{-1}$) has been investigated for the first time to pick up such fundamental frequencies, which have not been reported so far.

Dave et al (2006) have reported the growth and characterization of NbS$_x$Se$_{2x}$ single crystals. The stoichiometry of the crystals was confirmed on the basis of energy dispersive analysis by X-ray (EDAX).

Yadav et al (2006) studied the infrared (IR) absorption spectra of 5-chloro-2,3 dihydroxy pyridine in the region 400-4000 cm$^{-1}$. The bands observed in the IR spectra were discussed by assuming the compound under $C_3$ point group symmetry. The modes of vibration for the different fundamentals have been proposed. The thermodynamic functions have also been calculated by IR frequencies at different temperatures with the help of computer programming.
2.2 Review of Conduction Mechanism:

Polymer composites have steadily gained growing importance during the past decade. The electrical conduction in polymer film has much importance due to the discovery of the memory phenomenon (Kryezewski 1975) and has wide applications now-a-days in thin film devices (Mead 1961). Electrical properties constitute one of the most convenient and sensitive methods for studying the polymer structure (Kimura and Kajinara 1998). The interest in organic and polymeric semiconductors has arisen, particularly because of their electro photographic and solar cell applications. Many synthetic polymers (Kumar et al 1985) like polyacetylene, polypyrrole, poly-carbazol etc have been studied.

The studies on conductivity are aimed at understanding the origin of the charge carrying species, their number, and the way in which they move through the bulk of the material. Ultimately, these parameters are related to the chemical composition of the microstructure and the morphology of the particular material. Only when such relationships are known and understood will it be possible to predict electrical properties in a rational manner and to set out to synthesize well defined material with tailor made properties.

A current-voltage characteristic of PMMA was studied by Mazur (1985). He found that below the glass transition temperature $T_g$, the I-V characteristic was of subohmic shape ($j = gV^n$, where $n < 1$).

Electrical conduction in polypropylene was studied by Singh and Gupta (1985). They reported that the electrical conduction in this polymer material having various commercial applications. They studied the electrical conduction as
a function of applied electric field and thickness of sample. They observed that
the conduction was ohmic in low field (< 250 kV/m) and space charge limited in
intermediated field (250 kV/m-350 kV/m). They further reported that the
decrease in sample thickness enhances the range of ohmic and space charge
limited conduction and changed the mode of conduction from Poole-Frenkel
to Schottky in the high field region.

Electrical conduction in regenerated cellulose films have been investigated
by Bhat and Makwana (1987). They reported the conductivity for iodine doped as
well as aluminum sulphate treated cellophane films by studying the I-V
characteristic under vacuum for all the samples at different temperatures
varying from room temperature to 90°C. They observed that the iodine doped
films does not show much increase in the conductivity, but aluminum sulphate
treated films shows an increase in conductivity. The abrupt change in conduction
at 70°C does not appear in control cellophane film during its second cycle of
heating.

Electrical conduction in polyethylene terephthalate (PET) films were
reported by Karimi et al (1987). They investigated the electrical conductivity (σ)
of PET film as a function of thickness (125 to 250μm) and applied field (294 to
424 kV/m), at different temperatures, with M-P-M sandwich configuration.
The low values of activation energy (Ea < 1eV) were indicative of the
predominance of electronic conduction.

Chand et al (1988) studied the dc current characteristics of solution grown
polyvinylbutyral (PVB) films, as a function of voltage (30-1500V), temperature
(303-398K) and thickness (30-70μm) in two regions of conduction. The space charge limited currents were reported to govern the conduction process in high field region.

Paul and Radhakrishnan (1990) investigated the dc conduction in polypara-toluidine films in the thickness range of 500-3700ÅU prepared by glow discharge polymerization.

Singh and Singh (1990) reported electrical conduction in polyethylene alkathene WJG-11 (polymer used in cable industries) as a function of applied electric field and thickness of the sample at different temperatures by sandwiching the sample between copper electrodes. The conduction was observed to be ohmic in low fields (400 kV/m) and space charge limited in intermediate fields (400kV/m-1000kV/m).

Khare and Srivastava (1991) reported the electrical conduction of solution grown composite PMMA and malachite green doped films of thickness varying from 5 to 25μm in the field range of 2.5kV/cm to 20kV/cm and temperature range 363-383 K with three different electrodes Al, Cu and Ag. The Richardson-Schottky and space charge limited conduction were reported to be influential in the transport mechanism.

The electrical conductivity (σ) of montan wax (Romonta) sandwiched between copper electrodes as a function of temperature and thickness of sample at different applied voltages was investigated by Narayan and Singh (1991). The conduction through the sample was reported to be ohmic in low fields and space charge limited in intermediate fields. The decrease in sample thickness enhanced
the range of ohmic and space charge limited conduction. The conduction mechanism changes from Poole-Frenkel to Schottky.

The conductivity of iodine doped polystyrene, at various temperatures and doping concentration was reported by Chakraborty et al (1991). This was interpreted to be due to formation of CT complexes. The data obtained from the experiment supported the hopping mechanism.

Yawale and Pakade (1993) reported the dc conductivity and hopping mechanism in Bi$_2$O$_3$-B$_2$O$_3$ glasses.

Rangaswamy et al (1993) have measured the electrical dc conductivity of eight polyamides. They have reported a steep rise of conductivity with temperature and the predominance of electronic and ionic conductivity in low and high temperature regions respectively.

Khare et al (1993) reported the increase in conductivity due to the formation of CT complexes of malachite green doped ethyl cellulose films.

The I-V characteristics of malachite green doped cellulose acetate films were studied by Khare et al (1994). The electrical conductivity as a function of temperature, field, thickness and dopant concentration using conventional sandwich type cell was reported.

Electronic transport properties of conducting polymers and polymer blends were investigated by Kaiser et al (1995, 1997). They reported conductivity and thermopower data for polyaniline (PANI) blends with non-conducting polymers, making a comparison with polyacetylene and discussing general models for conduction. The blending of PANI with polyester (PET) reduced conductivity
while blending of PANI with PMMA and PVC increased conductivity. Especially at low temperature, this increase in conductivity is ascribed to the lessening of insulating barriers around PANI particles in these blends. The thermopower of the PANI/PET and PANI/PMMA blends were small and also increased with the increase of temperature.

Lal et al (1996) have reported that conducting polymers are novel materials for chemical and biosensors. The study showed that conducting polymers have tremendous potential in the area of sensors and, by extension to molecular electronics. One of the most attractive features of these devices has been reported to be the possibility of their effective fabrication by solution grown technique rather than the expensive ultra high vacuum methods.

The dc electrical conductivity of polystyrene thin films were studied by Sangawar and Adgaonkar (1996). They observed that the increase in electrical conductivity ($\sigma$) with pressure ($P$) upto a limit, which was followed by a drop upto 42 KPa.

Gawande et al (1996) studied the space charge limited conduction in amorphous semiconductor-polystyrene-semiconductor (SPS) sandwich material. Dc electrical conductivity was measured in the temperature range 303-373 K. They observed the Poole-Frenkel space charge limited conduction in SPS materials.

Mishra and Nath (1997) reported the electrical conduction mechanism in glycine. Results analyzed in terms of different mechanism suggest that Schottky-Richardson mechanism is primarily responsible for the observed dc conduction.

Electrical conduction mechanism in polycarbonate films in temperature
range (303-433K) with the applied field ranging from 4kV/cm to 22kV/cm was reported by Bahri and Seth (1997). The ohmic behaviour was observed for the films at low field at all temperature ranges. The Poole-Frenkel effect alone was reported to govern the conduction mechanism.

Belsare and Deogaonkar (1998) measured the electrical conductivity of iodine doped polyblend films of polystyrene (PS) and polymethylmethacrylate (PMMA) by studying the I-V characteristics at various temperatures in the range of 50-130°C. They observed that the electrical conductivity increases with the increase in the iodine percentage of doping and Poole-Frenkel mechanism govern the conduction process.

Zayed et al (2001) reported the transport properties of Sn Te x Se 1-x thin films. The structure and composition analysis of Sn Te x Se 1-x in powder and thin films form was investigated by X-ray diffraction and microprobe analysis technique respectively. It was found that the electrical conductivity σ increases, while the activation energy decreased with increasing composition.

Electrical properties of some chalco-germanide glassy alloys of the system Se 100-x In x have been studied by Abou and Hassen (2001). I-V characteristics of this system are discussed in terms of Poole-Frenkel and Schottky effect. According to Arrhenius equation of conductivity, the activation energy of conduction ΔW1 and ΔW2 for the two arms of conductivity have been found in the range from 0.18 to 1.2eV.

Optical and transport properties of CdTe x S 1-x alloyed thin films have been studied by Patil et al (2001). The estimated band gap decreased almost linearly with the composition x parameter. The room temperature electrical conductivity
was found to increase initially with the composition parameter, \(0 \leq x \leq 0.1\) decreases for a further increase in \(0.1 < x < 0.8\) and again increases for higher Te content in CdS.

Chowdhary and Bhuiyan (2002) have reported the dc-electrical conduction mechanism of heat treated, plasma-polymerized diphenyl (PPDP) thin films. It is seen that Poole-Frenkel mechanism is found to be operative in the heat treated PPDP films.

Memory switching current versus voltage (I-V) characteristics of Al-\(V_2O_5\)-Al sandwich devices for different \(V_2O_5\) film of thickness (40-350nm) and temperature (300-420K) were studied by Sarkar and Sarkar (2003). The values of activation energy were found to be in the ranges of 0.03-0.05 and 0.10-0.17eV for the temperature intervals 300-350K and 350-420K respectively.

The J-E characteristics and dc conductivity measurements have been carried out on the bulk amorphous \(Ge_{14}Se_{86-x}Ti_x\) samples as a function of composition and temperature by Ahmed et al (2003). Dc conductivity was found to increase with increasing free thallium and temperature.

Burghate et al (2004) studied the electrical conduction of succinic acid doped pellet in the temperature range of 313-353K. It is observed that Schottky-Richardson mechanism is primarily responsible for conduction.

Abd El-Kader et al (2004) prepared thin films of pure and Th (NO\(_3\))\(_4\) and Y(NO\(_3\))\(_3\) doped PVA with different concentrations. Electrical measurements were carried out to determine the thermal activation energy of the conduction process, drift mobility and charge carriers concentration.
Saraswat et al (2006) studied the I-V measurements of chalcongenide glass thin films of $\text{Se}_{85-x} \text{Te}_{15} \text{Sb}_x$. They reported that the conduction mechanism to be Poole-Frenkel type.

The conductivity of $\text{H}_2\text{SO}_4$ doped polyaniline samples were determined using four probe technique by Gaikwad et al (2006). The current voltage curve exhibits that polyaniline sample has an ohmic behaviour. It has been observed that at lower current as well as higher current, conductivity of the polyaniline sample is due to the electrons transferred to the conduction band.

2.3 Review of Thermally Stimulated Discharge Current:

Thermally stimulated discharge current 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 has been shown by thermally stimulated depolarization current technique that the characteristics of electrets are very sensitive to the structure of electret forming material. In this respect TSCD study of composite is likely to yield information about the extent of mixing between the components. Electrets prepared from the composite have better charge storage properties than the individual polymers and their study enables one to understand charge carrier mechanism, involved in the electret formation. This technique can be readily utilized to characterize doped polymeric films because thermally stimulated discharge current thermograms are sufficiently sensitive to additives. The study was carried out with view to
understand the electret forming characteristics, charge generation, transport and storage phenomena in the composites.

Srivastava et al (1980) studied electret properties of electrically charged silicon rubber. The electret properties like depth of penetration, initial trap density, mobility free lifetime product, dipolar concentration etc. have been obtained from thermally stimulated discharge current of thermoelectrically charged electrets of silicone rubber.

Lal and Prasad (1985) suggested a mechanism of charge decay of electrets. In this mechanism, the observed charge decay is apparent and is due to the screening (no cancellation) of the electret charge at the atomic or microscopic level by electric charges drawn from the ions in the atmosphere or by electrical loading.

α-relaxation in nylone with the help of TSD has been studied by Gill (1985). He suggested the onset of low frequency molecular motions in the polymer. It is concluded that the relaxation was due to large scale segmental motions at glass transition.

Careem and Jonscher (1986) have reported the measurements of thermally stimulated depolarization (TSD) current on stearic acid multilayers prepared by the Langmuir Blodgett technique and fitted with aluminum electrodes. The effect of UV irradiation has been reported. They found that the principal TSD current peak was due to the movement of hopping charges in the material.

Talwar et al (1987) have reported the electret effect in kidney stone. A linear plot of peak current Vs polarizing voltage confirmed the dipolar polarization
in this material. This dipolar polarization was attributed to the ionic nature of the main constituents viz calcium oxalate and calcium phosphate.

Thermally stimulated discharge currents in acrylic acid (AA) doped polystyrene have been studied by Baghel et al (1987). The observed peak positions, peak currents and activation energies were strongly affected by the concentration of AA and have been explained in terms of origination of localised states and formation of charge transfer complexes.

Verma and Sinha (1988) have studied thermally stimulated discharge current in Bakelite thermo-electrets. The characteristics features of TSDC curves were discussed on the basis of different theoretical models. It is concluded that at least two relaxation processes, namely space charge and dipolar relaxation seems to be operative in the case of Bakelite.

Khare and Srivastava (1991) studied the effect of sensitization on the thermally stimulated discharge current of polyvinyl acetate. They investigated the effect of sensitizer (Ferrocene and malachite green) concentration on TSDC spectra of PVA.

Khare and Srivastava (1992) have carried out thermally stimulated discharge current studies on ethyl cellulose and polyvinyl acetate blends as a function of the polarization temperature and polarizing field. Both polymers yield two peaks, in the temperature range of 50°C-60°C and 100°C-110°C, when studied separately, while their polymer blends A and B give only one peak in the temperature range 90°C-115°C. The effect of field of polarization and polarization temperatures on TSDC peaks indicates that the polarization in the blend may be due to the charge
carrier trapping in the deep traps, which leads to the induced dipole formation. The phenomenon of existence of various TSDC peaks has been analyzed and discussed.

Khare and Srivastava (1992) have measured short-circuit thermally stimulated discharge current (TSDC) on thermally polarized polyvinyl pyrrolidone (PVP) film as a function of temperature. The phenomena of the existence of these current maxima have been analysed and discussed in terms of dipole orientation phenomena and detrapping of charges injected from electrodes with subsequent space charge formation.

Khare et al (1992) have measured short-circuit thermally stimulated depolarization current in ethyl cellulose and composite films. The depolarization kinetic data of electrode variation in pure and composite film have been reported.

Singh et al (1992) have carried out surface charge and thermally stimulated current studies in polypropylene film electrets. A surface charge density and short circuit thermally stimulated current measurement was undertaken. The films have been negatively corona charged with various corona voltages. The charge stability of sample has been investigated using these two techniques. It was concluded that they have shown that the polypropylene electrets of improved stability was obtained by corona charging at elevated temperatures.

Khare and Srivastava (1993) have recorded thermally stimulated depolarization current (TSDC) of polarized samples of ethyl cellulose (EC) as a function of doping concentrations, heating rates and storage times. Two current maxima in positive direction are found around 60°C and 110°C for pure
EC samples, while for doped samples with ferrocen, an additional current maxima around $152 \pm 2^\circ C$ is observed in negative direction. For doped samples with iodine one peak was found around $68 \pm 2^\circ C$ in positive direction and the other peak around $135 \pm 2^\circ C$ in the opposite direction. The magnitude of peak current increases with heating rate and decreases with storage time.

Khare et al (1993) have preformed polarization and depolarization studies in polymethylmethacrylate and polyvinyl pyrrolidone polyblend films. The occurrence of single peak and enhancement of peak current for polymer blends have been explained on the basis of induced dipoles created because of the piling up of charge carriers at the phase boundary of heterogeneous structure of blend and increase in mobility of charge carriers due to plasticisation effect.

Khare et al (1993) have carried out the study of thermally stimulated discharge currents in iodine doped polyvinyl pyrrolidone films. They have found the mechanism of charge production, and its persistence in vacuum metallized pure and iodine doped polyvinyl pyrrolidone (PVP) films of about 20μm in thickness. The TSDC spectra of pure and iodine-doped PVP have been found to be characterized with two prominent peaks located at $106 \pm 6^\circ C$ for Al-Al electrode system. Various characteristics of thermograms indicated the injection of charge carriers from electrodes with their subsequent localization in surface and bulk traps. On iodine doping there was an increase in current, which is attributed to the formation of charge transfer complexes.

Khare and Srivastava (1994) have measured thermally stimulated discharge current in polymethylmethacrylate film as a function of polarizing fields for
different electrode systems. The effect of polarity reversal of the polarizing field on TSDC was also studied. The values of various parameters have been reported.

Khare et al (1995) have reported the study of absorption currents in polymethylmethacrylate (PMMA): polyvinyl acetate (PVAc) blend films. These have been found to follow Curie-von Schweilder law, characterized with two slopes in short and long time regions. The curves become steeper at longer times. Isochronals characteristics constructed from these data seemed to reveal a broad peak observed at 353K. The activation energy values are found to increase with PVAc content and also with time of observation. The various observed characteristics are considered to be due to space charge origin along with contribution from dipolar groups.

Sangawar and Adgaonkar (1995) carried out the dc electrical conductivity study of benzoic acid doped polystyrene thin film thermoelectrets. The results showed the semiconducting property of the thermo electret sample, probably owing to the formation CT complexes.

Sawarkar et al (1997) have measured thermally stimulated discharge current in lead borate glass system for samples polarized at various polarizing temperatures and fixed polarizing field. The various TSDC parameters such as activation energy; characteristics relaxation time, attempt to escape frequency, capture cross section and charge released during the relaxation process calculated by using Garlick and Gibson’s method have been reported. The various observed peaks in the thermogram were discussed on the basis of space charge polarization and distribution of trap level of charges inside the thermoelectret.
Mishra et al (1998) have studied the bioelectret state in glycine using the thermally stimulated discharge current (TSDC) technique. The TSDC spectrum was characterized by a large peak at temperature around 265K. The spectrum has been analyzed by varying various poling parameters and the source of the polarization storage is identified as the rotation of the polar amino acid molecule. The results of the present investigation indicate the possible role of polarization storage in amino acids for the bioelectret state in biopolymer.

Belsare and Deogaonkar (1998) have carried out TSDC study of iodine doped polyblends of polystyrene (PS) and polymethylmethacrylate (PMMA). The TSDC studies of undoped and doped polyblends of thickness of about 68 m have been carried out at the various poling fields viz 6kV/cm, 9kV/cm, 12kV/cm and 18kV/cm using constant value of poling temperature \(T_p\) 348K. In general it has been observed that the TSD current \(I_m\) at given poling temperature \(T_p\) increases with the magnitude of poling field strength and at the given poling field \(I_m\) increases with the iodine doping concentration. Activation energy (E) and characteristics relaxation time \(\tau_o\) have been evaluated.

Mogus-Malankoric et al (1999) have performed thermally stimulated current and dc conductivity studies in calcium iron phosphate glasses.

Khare et al (2000) have performed TSDC studies on solution grown cellulose acetate films doped with different concentrations of acrylic acid (AA) prepared at the poling temperature (40-75°C) with poling fields (10-15kV/cm). The TSD spectra of pure and acrylic acid doped cellulose acetate films reveal two relaxation peaks at 80°C and 180 ± 2°C having activation energies centered around...
0.25 and 0.55eV. The phenomena of the existence of these current maxima have been analysed and discussed in terms of the molecular motion of the polarized group and release of the remaining part of the frozen dipoles by their cooperative motion with adjoining segments of the main polymer chain. The peak currents, released charge and activation energies associated with the peaks are affected by acrylic acid (AA) doping. The effect of doping with acrylic acid on the discharge current indicates the formation of molecular aggregates.

Khare et al (2000) have measured electrical current arising from unpolarized polyvinyl fluoride (PVF) film in a sandwich configuration, in the temperature range 30-110°C. The maximum value of the current during first heating is found to be of the order of 10^{-10} AU and its thermograms exhibit one transition (i.e. current peak) at around 60°C. The position of the current peak in thermal spectrum shifts with the heating rate. A temperature dependence of the open circuit is also observed. The activation energy of the process responsible for the current is determined. The magnitude of the current is more in the case of dissimilar electrode systems. It is proposed that the electric current arising from unpolarized metal-polymer-metal system is a water activated phenomenon, which is influenced by the transitional changes of the polymer.

Khare et al (2001) have also reported charging and discharging transient current in PVF measured as a function of temperature (40°C-80°C), poling fields (9.0 \times 10^3 - 9.0 \times 10^4 V/cm) and electrode combinations (Al-Al, Au-Al, Zn-Al, Bi-Al, Cu-Al and Ag-Al). The current time characteristics have different values of slope lying between 0.42 to 0.56 and 1.42-1.63. The polarization is considered to
be due to dipolar reorientation associated with structural motions and space charge relaxation due to trapping of injected charge carriers in energetically distributed traps.

Burghate et al (2003) have been reported the measurements of thermally stimulated discharge current (TSDC) and dielectric constant of semiconducting glasses in the temperature range 30°C-300°C. The thermoelectret 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.

Gour et al (2006) have studied the charge decay behaviour of polystyrene (PS) samples, 40μm in thickness, investigated by means of transients (in charging and discharging mode) and thermally stimulated discharge current (TSDC) measurements as a function of polarizing fields, and temperatures. The order of currents has been found to increase with increasing these parameters. The current time characteristics have different values of slopes lying between 0.45 to 0.65 and 1.66-1.99. The TSDC thermograms of PS consist of a peak located around 60-85°C. Comparative studies of the isochronal characteristics (i.e. current-temperature plots at constant time) with the TSDC, indicated a strong resemblance between two techniques. It is suggested that both the dipolar orientation due to molecular mechanism of motions with the side chains and space charges due to trapping of injected charge carriers in energetically distributed traps may be responsible for the observed currents.
2.4 Review of Optical Properties:

Amorphous solid is not an ordinary electronic material. Polymer composites have steadily gained growing importance during the past decade the optical parameters *i.e.* refractive index is an important parameter for the design of optical components such as prisms, windows and optical fibers (*Ma et al* 1993). The study of the optical absorption spectra in solids provides essential information about the band structure and the energy gap in the crystalline and non-crystalline materials. Analysis of the absorption spectra in the lower energy part gives information about atomic vibrations, while the higher energy part of the spectrum gives knowledge about the electronic states in the atom (*Abd et al* 1993).

Hirde and Tembhurkar (1990) have studied the optical and structural properties of thin films of \( \text{Cd}_x \text{Zn}_{1-x} \text{S} \) deposited by spray pyrolysis. From reflectance and transmittance studies the band gap energy \( (E_g) \) was calculated for different composition parameter \( x \).

Band gap and structural parameter variation of \( \text{CulnSe}_{2(1-x)} \text{S}_{2x} \) solid-solution in the form of thin films was reported by Tembhurkar and Hirde (1992). Optical band gap \( (E_g) \) was determined for the composition parameter ‘\( x \)’ from the transmittance study at room temperature. Variation of \( E_g \), lattice constant ‘\( a \)’ and ‘\( c \)’ with ‘\( x \)’ was found to be linear.

The refractive index measurements of the tellurium halide (TeX) (where \( X \) is the halide elements) based glasses as a function of temperature and wavelength has been studied by *Ma et al* (1993), showing that a small modification of glass composition can lead to an important change of the refractive index.
Tembhurkar and Hirde (1993) have studied structural, optical and electrical properties of spray pyrolytically deposited thin films of CulnS$_2$. From the X-RD pattern the chalcopyrite structure of these films was confirmed. Resistivity of the thin film was measured for temperatures ranging from 77 to 473K. Band gap values were determined from optical transmission data.

Canioni et al (1994) have reported experimental and theoretical investigation of highly non-linear optical properties of Na$_2$O-TiO$_2$-P$_2$O$_5$ glass system with a high sensitivity absolute interferometeric technique.

Burghate et al (1995) have recorded the optical transmission and absorption spectra (UV-VIS) in the wave length range 350-800 nm for different composition of lead-bismuth-titanate glasses. The optical properties such as absorption coefficient ($\alpha$), optical energy gap ($E_{\text{opt}}$), refractive index ($n_o$), optical dielectric constant ($\varepsilon'$) and width of the tail of localized state in the normal forbidden gap ($\Delta E$) have been reported. The effect of composition of glasses on these parameters has been discussed. The nonlinear behaviour for all the parameters has been investigated.

The optical properties of PbO glass containing small amount of silica have been studied by Dayanand et al (1995). The optical band gap (2.56 eV) of PbO glass was determined.

Burghate et al (1999) have studied the optical transmission and absorption spectra in (UV-VIS) in the wavelength range 350-800 nm for different composition of lead-bismuth glasses. The various optical parameters such as absorption coefficient ($\alpha$), optical energy gap ($E_{\text{opt}}$), refractive index ($n_o$), optical
dielectric constant at infinite frequency ($\varepsilon_x$), measurement of extent of band tailing ($\Delta E$), constant $B$ and ratio of carrier concentration to the effective mass ($N/m^*$) have been evaluated. It is indicated that a small modification of the glass composition can lead to important changes in all the optical properties.

Electro-optical studies of chemically deposited Sm/Pr doped (Cd-Pb) films have been reported by Mukherjee et al (2001). Band-gaps have been determined from optical absorption. The direct band-gap is found for mixed films. X-RD studies show crystalline nature.

Pujari et al (2002) have carried out, the structural and optical studies of perylene-doped polymer thin films. The results of X-ray diffraction analysis reveal the crystalline nature of the film. The band gap energy of perylene in polymer films was calculated from absorption curves.

Optical properties of SnTe$_x$Se$_{1-x}$ thin films have been studied by Soliman and Farag (2003). The optical constants (the refractive index $n$, the absorption coefficient $\alpha$, the absorption index $k$, the dielectric constants $\varepsilon_1$ and $\varepsilon_2$) were determined for different thickness in the spectral range 500-2500 nm. The optical absorption results indicate that the fundamental absorption edge for SnTe$_x$Se$_{1-x}$ ($0 \leq n \leq 0.6$) films was due to an allowed, direct and indirect transition energy gaps and only two direct energy gap for $0.8 \leq x \leq 1$.

Rao (2004) studied optical and electrical properties of indium-tin-oxide films. In this investigation, indium-tin-oxide films have been deposited by reactive electron beam evaporation of In and Sn alloy both in neutral and ionized oxygen environments. As deposited film on substrate with very low resistivity obtained by evaporation, are very significant.
Electrical and optical properties of polyvinyl alcohol thin films doped with metal salts have been discussed by Abd-El-Kader et al (2004). X-ray diffraction, dc electrical conductivity and temporal variation of conduction current were used to characterize PVA and its composite systems. The UV visible spectra of all samples under investigation showed that the shoulder like band at 280 nm becomes a pronounced peak with increasing dopant concentration. The direct and indirect energy gaps together with the band tail for the two composite systems under investigation have been estimated.

Optical and thermal properties of mixed semiconducting alloy, $\text{Sn}_{1-x}\text{Ge}_x\text{Te}$ is studied by Sivabharathy et al (2005) for various Ge concentrations and phase transition for a particular concentration is also studied by the same method. The results are compared with the available literature and discussed.

Ahmed and Hanaty (2005) have reported optical absorption and electrical properties of polyvinyl alcohol (PVA)-gelatin blend. The optical absorption (real and imaginary parts of the) dielectric constant, dc-conductivity and I-V characteristics of PVA-gelatin blend were investigated in the temperature range of 250 to 460 K.

Optical and electrical properties of RF and AC plasma polymerized aniline thin film have been studied by Sajeev et al (2006). The structural properties of these films were evaluated by FTIR spectroscopy and the optical band gap was estimated from UV-vis-NIR measurements. They found that the optical band gap of the polyaniline thin films prepared by RF and AC
plasma polymerization techniques differ considerably and the band gap was further reduced by \textit{in situ} doping of iodine.

Mohammad and Dariush (2006) have performed the study of optical absorption and optical band gap determination of thin amorphous TeO$_2$-V$_2$O$_5$-MoO$_3$ blown films. The optical absorption coefficient of amorphous thin films was determined in a spectral range 190-1100nm at room temperature. The fundamental optical absorption edge was sharp. The optical gap generally increases as the proportion of MoO$_3$ in the mixed films increases. The width of the tail of the localized states in the band gap was determined for different compositions, which is because of the lack of long range order. The results of the usual density of state models of amorphous materials were presented.

Electrical and optical properties of Zn doped tin oxide films prepared using sol-gel spin coating process have been investigated by Bhat \textit{et al} (2006). The absorption edge lies in the range of 3.489-3.557eV depending upon the Zn doping concentration. The direct and indirect transitions and their dependence on dopant concentration and number of coatings are presented.

Optical structure and electrical properties of Mn doped tin oxide thin films have been studied by Brahma \textit{et al} (2006).

Structural, optical, electrical and photovoltaic electrochemical studies of cobalt molybdate thin films have been investigated by Pandey \textit{et al} (2006). X-ray diffraction (X-RD) studies confirm the microcrystalline, single-phase nature of the sintered thin films. Scanning electron microscope (SEM) images clearly show the aggregate of crystallites of dimension 1.5\textmu m. The optical absorption studies of
the sintered thin film in the wavelength range 350-850nm show direct as well as indirect optical transitions in the material. The direct and indirect band gap values are found to be 1.75 and 1.40eV respectively.

Patidar et al (2006) have recorded reflection spectra of covered and uncovered CdS sintered film over the wavelength range 300-700nm. The energy band gaps of these films have been calculated from reflection spectra. It is found that the energy band gap of both films was same as 2.41eV. It was indicated that energy band gap of these films does not change.
References


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