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General Introduction

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1.4: INTRODUCTION

The twenty years in the recent past have seen a remarkable growth in the subject of structure and properties of condensed disordered systems such as liquid metals and glasses of microscopic levels. This is because of novelty of physics, mainly relating to the particular nonperiodicity in their atomic arrangements, and also because of the technological potential of some of these disordered materials for almost immediate use as functional materials, for example, soft magnetic materials and electronic devices. The methods of structural analysis for crystalline systems have been well established for a long time. However the understanding of liquids and amorphous solids has lagged behind that of the crystalline state, even though much of the data on thermodynamic and electronic properties are available.

A glass can be defined as a non-crystalline solid formed by undercooling of liquids. Glasses can be defined as anion conducting glasses and cation conducting glasses. Cation conducting glasses can again be varied as depending on type of glass former and type of glass modifier used at the time of glass preparation. Glasses are coming out to be very useful materials recently. Their room temperature resistivity can range from 100 ohm-cm to $10^{20}$ ohm-cm. They can conduct both ionically and electronically. The solid materials, which exhibit high ionic conductivity comparable to those of liquid electrolytes, are known as solid electrolytes. The ionic conductors in non-crystalline solids are called as glassy or vitreous electrolytes.

The glasses are characterized by networking oxides (Glass formers), which gives rise to random linked tetrahedral arrangement broken at some places by the network modifier (Glass modifier). The conventional technique of glass preparation involves melting of the thoroughly mixed ingredients and quenching of the homogeneous melt. The current interest in the field of glasses is to enhance the electrical conductivity for making them suitable for specific application.

The ionic / electronic conductivity in the glasses was established a century ago. High ionic conductivity in the glasses was found in 1973 by Kunze. There has been a revival of interest in this field over last two decades and as a result, by now, many glass systems have been known which exhibits high ionic / electronic conductivity. The structure of the glass was proposed by Zachariasen. Semiconducting glasses possess a
structure that is disordered to some extent. Mott\(^2\) and Borland\(^3\) showed that in a completely disordered Kronig-Penney model, all the solutions of the wave equations are localized and no band formation occurs. A general conclusion had been that in a disordered system with short-range order. Similar conclusions were also arrived at, empirically, by Ioffe and Regel\(^4\).

In glass, mostly polyvalent cations are not only immobile, even at room temperature, but they have different valence states, makes possible electronically conduction in glass. Exploitation of glass semiconductors as active semiconductors is still in its infancy. But it appears that oxide-glass semiconductors could make good temperature and pressure transducers and that other glasses can be made in to switching and active but non-volatile memory components. Many oxide glass semiconductors have large Seebeck coefficient, a measure of thermoelectric conversion efficiency. The Seebeck coefficient is relatively stable over wide range of temperatures. Thus, these glasses might make good, low cost temperature sensors. The electronic conductivity of some semiconductor glasses increases with physical pressure. The resistivity change can be remarkably linear. Such a transducer could make good pressure sensors. Thin film cell based on Li\(_2\)O – P\(_2\)O\(_5\) solid electrolyte and amorphous V\(_2\)O\(_5\) film as cathode can also be of interest.

1.2: USE OF GLASSES IN VARIOUS FIELDS

Transport properties of semiconducting glasses are very interesting and provide useful information about conduction mechanism. Now-a-days glasses have a prominent role in the field of electronics and have wide applications in industry, space research and computer memories.

Perovskite lead zirconate titanate, Pb (Zr\(_x\)Ti\(_{1-x}\))O\(_3\) or PZT ceramics are well known materials which have very interesting ferroelectric properties for non-volatile memory applications\(^5\).

Amorphous solid is not an ordinary electronic material. Many kinds of composition, from switching and memory diodes to computer memories, might be cheaply produced with glass if recent discoveries by glass scientists were exploited by electronic engineers. Glasses can now be made as semiconductors, photoconductors, magnets, transducers, optical switches, memory materials and superior insulators and dielectrics\(^6\).
The optical parameter like refractive index is an important parameter for the design of optical components such as prism, windows and optical fibers\(^7\).

Vanadium pentoxide may have potential use in optical switches and write-erase media as well. Vanadium pentoxide is especially interesting in thin film form because of possibility of integration in to microelectronic circuitry\(^8,9\).

**Batteries:**

Ambient temperature Li battery using Li metal anode and TiS\(_2\) cathode with glassy solid electrolyte was developed by Union carbide in USA. Voltage around 2 volts and current densities between 0.1 and 1 mA/cm\(^2\) have been obtained. The target applications include self-contained microprocessor power supplies for electronic and time devices. For electrode applications the glasses should posses mixed (electronic and cationic) conduction. For this purpose, the glasses containing transition metal oxides are quite appropriate. V\(_2\)O\(_2\) -containing glasses has been used for Li battery in France, Britain and Japan.

**Gas sensors:**

Oxygen gas sensors are developed based on AgI-Ag\(_2\)O-WO\(_3\) glass with the configuration Ag/glass/LaF\(_3\) film/Pt. The Ag/glass reference electrode has good reversibility and low impedance useful for stable, fast response at ambient temperature. This potentiometric sensor responded to changes in oxygen partial pressure from 0.01 to 1 atm with 90 % response time of less than 12 minutes. A new type of chemical sensor has been developed using polythiophene (PT) film and silver ion conducting glass with the configuration Ag film / glass/ ClO\(_4\) doped PT film. This sensor was found to be sensitive to acetic acid gas. The sensor is selective and sensitive to protons and to those organic solvents, which acts as proton donors.

**Smart windows:**

One important potential application for thin film solid state ionic materials is 'electrochromic smart window'. It can be used to improve the energy efficiency of buildings and vehicles by electrically controlling the radiant energy transfer through them. The smart window glass structure consists of two transparent conducting layers sandwiching an electrochromic layer and counter electrode layer which are separated by an ion-conducting layer. The three inside layers essentially comprise an electro-optically active battery.
Glass ceramics:

Uncontrolled crystallization in glass is undesirable because it makes the physical properties uncontrollable. However, in recent years the controlled crystallization of glass has become a highly successful technology with electronic implications far wider than the present use of the technique to produce supporting materials.

New magnetic materials:

Glass ceramics containing ferrite crystals of controlled composition and distribution, creates exciting possibilities in development of microelectronic magnetic devices. Thin films of barium-titanate ferroelectric have already been made an achievement that makes possible the manufacture of thin-film capacitors with high dielectric constant.

Optoelectronic switches and memories:

Controlled crystallization has also led to the invention of phototropic or photochromic glasses—materials that change color when irradiated by light of one wavelength and then revert it to their original color under light of another wavelength. Scientists at the Corning glass works discovered that silicate glasses containing about 0.5% of silver halide crystals retain their phototropy for more than 300,000 cycles. Corning is studying the feasibility of using such glasses in optical displays, temporary data storage and data processing systems, as well as ophthalmic, automotive and architectural applications.

Nonoxide glasses:

A group of glasses known as chalcogenides now used for infrared transmissions. The constant hunt for better infrared transmitters that are more stable at high temperatures led to the discovery of many such nonoxide or elemental glassy systems. Some typical glass systems and applications are: As-S-Se, an insulator that melts at low temperature; As-Te-I, electronic switches and memory devices; As-Se-Te, photoconductor; and As-Ge-Si-Te, an infrared transmitter that withstands high temperatures with wavelengths as long as 20 microns.

Elemental glass switches:

Current-voltage characteristics of some elemental glasses indicate that they can be used as switching and memory devices. A variation in applied voltage switches the
device from an insulating to a highly conducting state. The switching can occur in less than a microsecond and is reversible. The diode would remain in given state, even under zero bias, and could remember which state it was in for many days.

*Photoconducting glasses:*

Glasses based on selenium, tellurium and arsenic are photoconductors. In contrast to crystalline materials, the conductivity of the glasses is insensitive to impurity contents. This means electronic properties are easier to control during manufacture. Silicon and germanium are rendered in the amorphous-or glassy-state by vacuum evaporation and show higher conductivity and other interesting variations in semiconducting properties.

The ionically conducting glasses have numerous advantages over their crystalline counterparts like, the lack of grain boundaries, wide choice of chemical composition, ease of thin film formation and low electronic conductivity. They have wide applications viz; separators in solid state batteries, timers, high-density polarizable dielectrics, glass bonded ferroelectric materials etc.¹⁰

Semiconductor glasses are superior to conventional silicate glasses for all direct current applications. An immediate and important application is improving the long-term performance of image-orthicon tubes. Targets made of new semiconducting glass give the tubes long life.

The field of glasses is very exiting for technical application. Thus there is a tremendous scope to develop these materials in future, owing to the lack of structural knowledge.¹¹

For the preparation of solid state batteries, fast ion-conducting solids in the form of glasses, polymers, thin films have been used by many research workers. For this, electrolytes based on the silver, copper, lithium and sodium have been tried in the fabrication of solid state batteries. To achieve the better thermal stability and high electrical conductivity, the ion conducting glasses plays a very important role.

1.3: PRESENT POSITION OF GLASS IN RESEARCH AND NECESSITY OF INVESTIGATION

The general concept of glass as an auxiliary material is actually very narrow in contrast with the capabilities of hundreds of new glasses. Device designers can’t really
be faulted for not having exploited these and other potentially significant features of glass. Materials scientists have still not thoroughly probed all the inherent electronic properties of glass and some of the glasses that enhance such properties are new and untried. But it is apparent that glass is enjoying a technological renaissance certain to make it an increasingly electronic device material in the coming decade. Some of the recent discoveries are already been converted into practical hardware.

Much work on the semiconducting glasses has been done by research workers. A review of the compositions investigated up to 1964 has been given by Mackenzie\textsuperscript{12}, while more recent reviews of the conduction process are those of Mott\textsuperscript{13}, Austin and Mott\textsuperscript{14}, and Oven\textsuperscript{15}. Ghosh and Chaudhary\textsuperscript{16} discussed the dc conductivity of semiconducting vanadium bismuth oxide glasses containing 80 – 95 % \( V_2O_5 \) in the temperature range 300-500 K, observed adiabatic hopping conduction and discussed the results on the basis of polaron hopping conduction mechanism. Mackenzie\textsuperscript{17} and Higgins \textit{et al.}\textsuperscript{18} have used thick film for studying switching in semiconducting glasses. The glassy alloys of the form AS-Ge-Te are an important class of amorphous semiconductor because of their memory switching property. The glasses of chalcogenide group show the memory switching as well as the intrinsic conduction. It has been observed that the electrical properties of the semiconducting oxide glasses depends on the annealing temperature, annealing time, field, frequency, temperature, humidity, pressure environment etc. As regards to these the various applications of these glasses are present and the investigations along these lines are going on. Many references are available in the literature about the various applications and the uses. The gas and humidity sensors are also a growing field today and most of the research workers are doing research on these lines. The solid state batteries in which ionic conducting solid electrolytes plays important role.

Similarly the superconductivity is also a growing field today. The ceramic materials which are good insulators at room temperature shows the superconducting property at low temperature. The optical switches and optical devices are also fabricated with glassy materials because of their photoconductive property. As the field of amorphous materials is not new for research workers but still looking to their potential it is a growing one and many investigations are remaining to carry out. Therefore it has been decided to measure the various electrical properties of \( V_2O_5 – P_2O_5 \) glass doped with PbS and CdS together with photoconductive property.
1.4 : FABRICATION OF GLASS SAMPLES

Amorphous solids are prepared in general by two ways 1) by condensation from the vapor phase as in thermal evaporation, sputtering, glow discharge decomposition of glass or other methods of deposition 2) by cooling from the melt. The first method produces thin films and the second bulk materials. If a material can be prepared in the amorphous phase from a melt, it is generally also possible to prepare it by deposition. However there will inevitably be some structural differences between the samples of same material prepared by different methods, which must be taken in to consideration in any comparative study of physical properties. Other methods include electrolytic deposition from solution and prolonged irradiation of crystalline materials with high-energy particles such as neutrons or ions. A general review describing these methods of preparing amorphous solids has been reported by Owen.

Several transition metal oxides when heated with glass forming oxides like P₂O₅, TeO₂, GeO₂, Bi₂O₃ etc form semiconducting glasses on quenching the melt below the glass transition temperature.

For the preparation of glasses, muffle furnace (Quality instruments & equipment’s, kadal-Make) used was reaching up to 1250 °C ± 10 °C, having automatic temperature controlled system.

For the present work, glasses were prepared from Analar-R grade chemicals such as CdS (BDH Chemicals Ltd. Poole, England Make), PbS (Burgoyne urbidges & co. Bombay Make), V₂O₅ (Loba chemie, Bombay Make) and P₂O₅ (Sd fine Chem. Ltd. Boiser make). Three series of oxide glasses were prepared.

For the first series of samples, only two chemicals V₂O₅ and P₂O₅ are taken in different ( mol % ) , general formula for this series is

\[ X \text{V}_2\text{O}_5 - (100-X) \text{P}_2\text{O}_5. \]

In the second series mol % of P₂O₅ at 10 % was kept constant and that of V₂O₅ and CdS was changed. General formula for this series is

\[ X \text{V}_2\text{O}_5 - (90-X)\text{CdS} - 10\text{P}_2\text{O}_5. \]

In the third series mol % of P₂O₅ at 10 % was kept constant and that of V₂O₅ and PbS was changed. General formula for this series is

\[ X \text{V}_2\text{O}_5 - (90-X)\text{PbS} - 10\text{P}_2\text{O}_5. \]
<table>
<thead>
<tr>
<th>Sr. no</th>
<th>Nomenclature</th>
<th>Composition (mol %)</th>
<th>% Crystallinity (From XRD data)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>V1</td>
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<td>20</td>
</tr>
<tr>
<td>2</td>
<td>V2</td>
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</tr>
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</tr>
<tr>
<td>4</td>
<td>V4</td>
<td>50</td>
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</table>

**Table 1.1(b)** Series 2: \( [X \cdot V_2O_5 - (90-X) \cdot CdS - 10P_2O_5] \)

<table>
<thead>
<tr>
<th>Sr. no</th>
<th>Nomenclature</th>
<th>Composition (mol %)</th>
<th>% Crystallinity (From XRD data)</th>
</tr>
</thead>
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</tr>
<tr>
<td>6</td>
<td>VX6</td>
<td>30</td>
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</table>

**Table 1.1(c)** Series 3: \( [X \cdot V_2O_5 - (90-X) \cdot PbS - 10P_2O_5] \)

<table>
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<tr>
<th>Sr. no</th>
<th>Nomenclature</th>
<th>Composition (mol %)</th>
<th>% Crystallinity (From XRD data)</th>
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<td>VY6</td>
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<td>60</td>
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</table>

The three series of glasses of various compositions were prepared in the laboratory by mixing appropriate amounts in mol % of different chemicals (AR-grade) in powder form. The constituents were weighed on K-Roy monopanel balance having accuracy ± 0.00001 gm. Repeated grinding of the mixtures was done to ensure homogeneity. Homogeneous mixture was transferred to silica crucible which was then subjected to melting in automatically controlled muffle furnace at temperature ranging from 700 °C to 1200 °C ±10 °C. The duration of melting was generally two hours. The homogeneous molten glass was cast on steel plate. After quenching all samples were immediately transferred to annealing furnace. Samples were annealed at 100 °C for about two hours. The effect of annealing is to remove the air bubbles or cavities, which are formed by sudden quenching.

All samples after annealing were subjected to finishing processes such as cleaning and polishing. Four to five pieces each were formed from one and the same melt of all samples. This was necessary for their characterization by different methods and also using for their electrical, thermoelectric and optical measurements.

For attaining exact parallel and plane surfaces of the glasses, a fine lapping paper is used (300 no.). A conducting silver paint is applied to the plane surfaces of
the glass samples. All samples were backed at 150 °C for two hours, for removal of mechanical stresses, if any, developed during polishing. These samples were used for electrical characterization.

1.5: PRESENT LINE OF INVESTIGATION IN THE THESIS

Much work on the V₂O₅ – P₂O₅ glass system has been done by various research workers²⁰–²⁵. The electrical as well as dielectric properties of this system have been studied but less attention seems to have been given when it is doped with CdS and PbS. CdS and PbS are the photosensitive materials used for the preparation of light dependent resistors (LDR) individually. Similarly the electrical properties of vanadate phosphate system after doping with the CdS and PbS could be interesting, as CdS and PbS are photosensitive. The resistivity range of V₂O₅ – P₂O₅ glass system is of the order of 10³ to 10⁷ (ohm-cm.) which is quite useful for electronic semiconductors.

The glass samples (bulk) can be prepared by conventional technique, involving mixing of the thoroughly mixed ingredients. The quenching can be done in metallic blocks. In all these techniques quenching rate is high.

Many research workers²⁶–³¹ have studied dc conductivity of transition metal oxide glasses. The mechanism of conduction process in oxide glasses is different from the crystalline solids, liquids and disordered materials. In most of the glass systems it is observed that, the activation energy for electrical conduction plays a dominant role. It has greater influence on the electrical properties. In phosphate glasses, the electron overlap integral between sites is of significance.

Generally the glasses can be prepared by sudden quenching method. Various methods of glass formation are available but the rapid quenching of melt method is easy and can be very easily adopted in a conventional laboratory.

The samples are studied for the following properties,

1. Dc conductivity:

By measuring the current flowing through the specimen, by ohms law method, over the temperature range RT (room temperature 30 °C) to 250 °C, conductivity and activation energy are calculated. Similarly conduction mechanism is studied.

2. Thermoelectric effect:

If the metal contacts are applied to the two ends of the sample under investigation and if
one junction is maintained at a higher temperature than the other, a potential difference will be developed across the two electrodes. From the sign of thermoelectric voltage, it is thus possible to deduce whether a specimen exhibit n-type or p-type conductivity. Further from the magnitude of the thermoelectric voltage, one can determine the concentration of charge carriers in the chosen specimen.

3. *Photoconductivity*:

The photoconductivity and dark conductivity are important parameters as regard to their photoconductive applications. Most of the glasses are photoconductive and show photoconducting behavior. In the present glasses PbS and CdS are the photosensitive materials individually. The effect of these materials on V2O5 – P2O5 system is studied.

4. *Optical properties*:

The optical transmission and absorption spectra in (UV-VIS) is studied for different compositions of the glass samples. The optical properties such as absorption coefficient ($\alpha$), optical energy gap ($E_{opt}$), refractive index ($n_0$), optical dielectric constant ($\varepsilon$) and width of the tail of localized states in the normal forbidden gap (E) is calculated. The effect of composition of glasses on these parameters is studied. The optical parameter like refractive index is an important parameter for the design of optical components, such as prism, windows and optical fibers. Optical absorption edge characteristic yields information about the fundamental nature of the films.

The physical, optical and electrical properties provide a probe to make an in-depth study and to observe the characteristic behavior of glass.

The X-ray pattern is useful in determining the local structure of the glasses. The general idea of structure can also be known from the density and molar volume of the glass. While using the photosensitive materials in the glass as a dopant, the photoconductivity is also seemed to be a good parameter for device applications.

With the above investigations, good amount of results are expected, which are due to amorphous behavior of CdS and PbS with V2O5 – P2O5. The conduction mechanism and the structure are discussed.

**1.6 : X-RAY CHARACTERIZATION**

The characterization of the material is the most important factor to ascertain the amorphous nature of the sample and to determine the conditions of its isolation. In the
absence of the above information, a justified understanding of the electrical behavior of the glasses under consideration is rather difficult.

An important feature of several oxide glasses is the presence of an extensive network structure of the type A-O-B, where A and B are described as the network formers. Glass formation in oxides is generally consistent with the Zachariasen rule, according to which the co-ordination number of A and B are small (3 or 4). The structure of such oxide glasses characterized by the presence of extensive, two and three-dimensional network is modified by the addition of ionic alkali and alkaline earth oxides. To characterize the materials, X-ray diffraction technique has been used.

Sometimes X-ray diffraction shows existence of small percent of crystallinity (Mott et al 1979). In amorphous materials the crystallinity should always be less than 15 to 20 %. The percent crystallinity which is produced in the sample may be calculated from the intensity versus 2θ plot (Fig 1.1), by using following relation given by Kaelbel (1967)

The percentage crystallinity of the sample is determined by using following relation

\[ \%\text{crystallinity} = \frac{I_c}{I_c + KI_A} \times 100 \]

Where \( I_c \) = crystalline area

\( I_A \) = amorphous area

K = constant equal to unity

The X-ray diffraction technique has been used for all the glasses to check the amorphous nature. The large angle X-ray curves were recorded using the philips X-ray
Diffractometer type PW 1710 BASED and target CuKα radiation. The experimental conditions are as follows.

KV and mA – 35 kV, 20 mA
Scanning angle – 20
Range – 10 to 99.99

The X-ray diffraction patterns are obtained to check the amorphous nature of the samples. It has been observed that the glasses are formed with some percent of crystallinity in some glass samples [Fig 1.2 (a), (b) and (c)]. In series I (V₂O₃-P₂O₅) glasses, the percent crystallinity observed is found in the range of 11 to 19% (Table 1.1) and the phase of VPO₃ is formed. But the percent crystallinity is very small hence the major role is due to amorphous behavior. In series II (V₂O₅-CdS-P₂O₅) glasses, no peak is seen but due to the short range order the d values are obtained. Which shows that the minor phase of β Cd V₂O₅ is formed. The percent crystallinity shows that the sample is amorphous in nature. Similarly in series III (V₂O₅-PbS-P₂O₅), no peak is observed hence no d values. Therefore the samples are completely amorphous.

*Fig 1.2 (a) XRD pattern for V₂O₅-P₂O₅ glass series*
Fig 1.2 (a) XRD pattern for V$_2$O$_5$ – P$_2$O$_5$ glass series.
Fig 1.2 (f) XRD pattern for Y$_2$O$_3$ - Cds:PyO$_2$ glass series.
Fig 1.2 (c) XRD pattern for $\text{V}_2\text{O}_3 - \text{PbS-PbO}_2$ glass series.
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