PREFACE:

Since the beginning of human civilization, glass has been considered to be one of the oldest man made material. The glasses were first made by man about 4000 years ago in ancient Egypt. Initially, used as an aesthetic appeal, glass has slowly encroached into our daily life in a variety of forms with the passage of time.

Glass can be recognised by its transparency, hardness, shining, form and often by beautiful colours. For a long time, glass remained to household, potteries, lens, windows etc. and no technological uses were explored. After 1800, various compositions were studied to use them as optical glass. Scientific & technological progress continued, when borosilicate glass composition was developed and later, glass of various refractive index, thermally & chemically resistant, photoresistive , photochromatic glasses were developed. Other glasses like laminated glass, glass in vehicles and bullet proof purposes, optical glass fibres, semiconducting glasses, glass ceramics for missile cones and glass lasers to generate power as high as few terrawatts were investigated. Some of the other important applications in the field of optics are the use of laser range finder, infrared transmission glasses for night vision, special glass coatings for selective transmission or reflection of light and remote sensing through optical fibres. In the field of composites, glass fibre reinforced plastics (FRP) are already having thousand of applications. Glass fibre reinforced gypsum (GRG) can be used as a substitute of wood while glass fibre reinforced cement possess sufficient strength and toughness for various constructional applications replacing conventional reinforced concrete.

For glass making, the rate of cooling is very important during the solidification. A slower cooling rate brings the liquid into crystalline and faster converts into amorphous or non-crystalline state. A non-crystalline state of a solid is also known as polycrystalline or glassy states. Various types of glasses like inorganic oxide glasses, chalcogenide glasses, halides glasses, metallic glasses, spin glasses, organic glasses etc. can be formed.

The National Research Council Ad Hoc Committee on infrared transmission materials suggests that a glass is an X-ray amorphous solid, which exhibits the glass transition. Whereas according to Morey , "glass is an inorganic substance in a condition, which is continues with, and analogous to, the liquid state of the substance but which as a result of having been cooled from fused condition, has attained so high a degree of viscosity as to be for all practical purposes rigid. "

Inorganic oxide glasses are the oldest well known non-crystalline materials. These glasses have a great technical importance due to its versatile structure. Present inorganic oxide glasses have much importance due to their well known electronic and thermal switching and semiconducting nature. Most of the borate glasses are insulating in nature. The addition of transition metal oxides (TMO) such as V_2O_5, Fe_2O_3, CuO etc. makes these glasses semiconducting in nature. The semiconducting glasses have attracted scientific interest and technical applications.

In the present work Potassium-Boro-Vanadate-Iron glasses have been studied and attempt has been made to understand the effect of glass modifier K_2O by using a various techniques like Mössbauer Spectroscopy, IR-spectroscopy, conductivity, switching properties and characterisation of glasses using X-ray, DSC, density measurements, thermoelectric power and chemical analysis. The following three series of glass systems have been prepared and discussed in the present thesis.

(i) xK_2O :(95-x)($2V_2O_5$: B_2O_3): $5Fe_2O_3$, where x= 0,5, . . . 30 in step of 5.

(ii) $20K_2O$: yV_2O_5: $(75-y)B_2O_3$: $5Fe_2O_3$, where y= 40 to 75 in step of 5.

(iii) xK_2O : $(100-x-y)[(1+n)V_2O_5 : B_2O_3]$: y Fe_2O_3 ,where x= 0,5, . . . 20 in step of 5. y= 5,7.5, . . 15 in step of 2.5 and n = 0.2, 0.4, . . 1 in step of 0.2.

The thesis has been divided into the following chapters.

Chapter one gives introduction about glasses and their different types.

Chapter two presents the theoretical background of various techniques used for characterisation and structural study. It elaborates essential features of Mössbauer spectroscopy and its parameters which are generally considered necessary for analysis and interpretation of Mössbauer spectra of semiconducting oxide glasses. IR, dc conductivity, switching, thermoelectric power and DSC techniques have also been included.

Electrical properties of semiconducting oxide glass are based mainly on the small polaron theory of Sir Nevile Mott and Austin & Mott. Some basic concept of electrical & thermal switching phenomena have also been included. Thermoelectric power has been discussed on the basis of Heikes & Mott formula.

Theoretical background of characterisation studies like X-ray, IR, DSC, density measurement and chemical analysis have also been included in this chapter.

Chapter three deals with the experimental details of all studies undertaken to pursue the present work. Experimental set-up of Mössbauer spectrometer has been discussed using Wissvl Mössbauer Spectrometer (Germany).

An indigenous design of two probe electrical conductivity measurement, electronic design of constant current source upto 10^{-9} Amp. and digital ammeter for current measurement has been described. The method used for observing I-V characteristics for switching phenomena has been discussed.

An indigenously designed set-up with two heaters for thermoelectric power measurement has been discussed. A temperature gradient of 5 °C has been maintained across sample using Cr-Al thermocouples as sensor and microvoltmeter for measuring thermo e.m.f. DSC thermograms have been taken using DSC-2910 TA Instruments (USA) in the temperature range of 50- 600 °C. Density of all glass samples has been measured using a "Archemidies principle" and FTIR spectra have been taken using standard " Bomem Michelson Series" spectrometer.

Chapter four discusses the characterisation studies. Sample prepared by splat quenching technique are characterised by different studies like X-ray, IR, DSC, density measurement and chemical analysis.

IR spectroscopy is a fingerprint for the identification of functional group and types of bond formation. Vibrational groups present in the glass have been used to discuss the structural details. DSC thermograms provide the valuable information about the glass transition temperature, crystallisation and melting temperature of these glasses.

Density measurements are used to get the information about number of charge carriers, polaron radius, distance between transition metal ions etc. Chemical analysis of a present glass system are undertaken using a photometric titration in $KMnO_4$ as a self indicator to get the number of reduced charge carriers (V^{+4}) and total charge carrier of vanadium.

Chapter five deals with the results of Mössbauer spectroscopy. The Mössbauer parameters like quadrupole splitting, isomer shift, line width are calculated. The structure of Potassium Boro-Vanadate glasses with reference to Fe^{+3} ions has been discussed. Its results also support electrical properties of the present glass systems. The effect of modifier and former in the glass has been discussed.

Chapter six contains the results of conductivity, switching and thermoelectric power and are correlated to the other results from Mössbauer, IR , DSC, density and chemical analysis.

The electrical conduction on the basis of Mott's theory for V_2O_5 based glasses is discussed in the present chapter. The activation energy, adiabatic type of conduction, disorder energy etc. are analysed. A model has been presented for electrical and thermal switching phenomenon for the present glass system.

In thermoelectric power studies, invariance of thermoelectric power with temperature is observed. Change in thermoelectric power with V^{+4}/V^{+5} ratio provides information about hopping process and type of charge carriers have been interpreted using this technique.