PREFACE

The present work concerns with the "CHARACTERIZATION AND PHYSICAL PROPERTIES OF MO (M= Zn, Ca, Pb)-Sb₂O₃-B₂O₃ GLASS SYSTEMS DOPED WITH SOME TRANSITION AND IIIA GROUP METAL IONS". This work has been carried out in the Department of Physics, Acharya Nagarjuna University Post-Graduate Centre, Nuzvid. The dissertation reports important results of the investigations carried out on a variety of properties viz., electrical, spectroscopic and magnetic properties of ZnO-Sb₂O₃-B₂O₃: MnO, PbO-Sb₂O₃-B₂O₃: MoO₃, ZnO-Sb₂O₃-B₂O₃: CrO₄²⁻, CaO-Sb₂O₃-B₂O₃: M₂O₃ (M= Al, Ga, In).

Sb₂O₃ based glasses, have attracted extensive investigation in recent years; these glasses possess large non-linear optical susceptibility (χ³) coefficient that makes them suitable for potential applications in non-linear optical devices (such as ultra fast optical switches and power limiters), broad band optical amplifiers operating around 1.5 µm and in a number of solid state ionic devices. Antimony oxide participates in the glass network with SbO₃ structural units and can be viewed as tetrahedrons with the oxygen at three corners and a lone pair of electrons of antimony (Sb³⁺) at the fourth corner localized in the third equatorial direction of Sb atom; the deformability of this pair probably could make these glasses to exhibit non-linear optical susceptibility. Further, Sb₂O₃ based glasses are known due to their significant
transmission potential in the infrared region and possess high refractive index. Attempts were made previously, to improve the physical characteristics of these glasses by the addition of alkali oxides (like Li$_2$O), alkali halides (like NaCl, NaI) and alkali sulphides (like Na$_2$S, K$_2$S) to Sb$_2$O$_3$ glass matrices. Among different Sb$_2$O$_3$ glass systems, the alkali free ZnO-Sb$_2$O$_3$-B$_2$O$_3$, PbO-Sb$_2$O$_3$-B$_2$O$_3$ and CaO-Sb$_2$O$_3$-B$_2$O$_3$ glasses are however anticipated to be relatively moisture resistant and are observed to possess low rates of crystallization.

The transition metal ions such as manganese, molybdenum, chromium and other metal oxides like aluminium, gallium, indium etc., dissolved in glass matrices even in very small quantities are likely to inculcate strong bearing on the insulating character and the optical transmission. Recently, much attention has been paid to the research in inorganic glasses doped with a variety of transition metal ions because of their technological importance in the development of tunable solid state lasers, new luminescence materials, solar energy converters and fiber optic communication devices. Though, a few studies on certain physical properties of some antimony based glasses are available in recent years, a thorough survey of the literature on these glasses show detailed investigations on dielectric, and spectroscopic properties of transition metal ions doped MO-Sb$_2$O$_3$-B$_2$O$_3$ glasses in particular are not available.
Study on the dielectric properties helps in estimating the insulating strength of these glasses and also helps in understanding the structural aspects of the glasses to a large extent. Detailed studies on spectroscopic properties viz., optical absorption, infrared, Raman and ESR spectra of transition and IIIA group metal oxide doped MO-Sb$_2$O$_3$-B$_2$O$_3$ glasses are expected to throw some light on the possible use of these glasses as optical materials.

Thus the objective of the present investigation is to report in detail the above-mentioned properties of i) ZnO-Sb$_2$O$_3$-B$_2$O$_3$ doped with MnO and CrO$_4^{2-}$ ions, PbO-Sb$_2$O$_3$-B$_2$O$_3$ doped with MoO$_3$ and CaO-Sb$_2$O$_3$-B$_2$O$_3$ glasses doped with Al$_2$O$_3$, Ga$_2$O$_3$ and In$_2$O$_3$.

The glasses are synthesized by melt quenching technique and are characterized by X-Ray diffraction, scanning electron microscopy and differential thermal analysis techniques.

The following are the physical properties studied:

1) Dielectric constant ($\varepsilon'$), loss (tan $\delta$) and a.c conductivity $\sigma$ in the frequency range $10^2$ to $10^5$ Hz and in the temperature range 30-350 °C

2) Optical absorption in the UV, visible and NIR regions

3) Infrared spectra of all these glasses in the region 400 to 4000 cm$^{-1}$

4) Raman spectra of all the glasses in the region 100 to 2000 cm$^{-1}$

5) ESR spectra of transition metal oxides doped glasses

6) Magnetic susceptibility of these glasses containing transition metal oxides.
For the sake of convenience the present thesis is divided into seven chapters.

**CHAPTER - I** presents the general introduction, scope, contents and the aim of the present work. In this chapter the basic theory related with dielectric, magnetic properties and also spectroscopic properties of transition and IIIA group metal oxides doped MO-Sb$_2$O$_3$-B$_2$O$_3$ glasses is presented systematically.

**CHAPTER - II** gives the description of experimental methods employed in the preparation and characterization of MO-Sb$_2$O$_3$-B$_2$O$_3$ glasses mixed with different dopants. The apparatus used and the techniques adopted for measuring dielectric and magnetic properties have been described. The details of the apparatus used for recording the optical absorption, IR, Raman and ESR spectra of the glasses have also been discussed in this chapter.

**Chapter III** reports the study on influence of manganese ions on optical and dielectric properties of the following composition: (20-x) ZnO-40Sb$_2$O$_3$-40B$_2$O$_3$: x MnO with (0 ≤ x ≤ 1.0) and the samples are labeled as M$_0$ (pure), M$_2$ (x = 0.2), M$_4$ (x = 0.4), M$_6$ (x = 0.6), M$_8$ (x = 0.8)and M$_{10}$ (x = 1.0).

Scanning electron microscopy and differential thermal analysis studies of these glasses indicated the highest glass forming ability for the glass M$_6$ (glass containing 0.6 mol % of MnO) among all MnO doped ZnO-Sb$_2$O$_3$-B$_2$O$_3$ glasses.
The optical absorption spectra of MnO doped glasses exhibited three absorption bands of Mn$^{2+}$ ions at 512, 420 and 403 nm respectively corresponding to the transitions $^6A_{1g}(S) \rightarrow ^4T_{1g}(G)$, $^6A_{1g}(S) \rightarrow ^4T_{2g}(G)$ and $^6A_{1g}(S) \rightarrow ^4A_{1g}(G)$. With the increase in the concentration of MnO up to 0.6 mol %, no detectable changes in the position of these bands are observed; however, the intensity of these bands is noticed to increase. When the concentration of MnO is increased beyond 0.6 mol %, these Mn$^{2+}$ ion bands appeared to be obscured with the presence of a broad absorption band with a peak at 494 nm. This band is identified due to $^5E_g \rightarrow ^5T_{2g}$ transition of Mn$^{3+}$ ions. The analysis of the data on optical absorption spectra point out that when MnO is present in lower concentrations (up to 0.6 mol %), majority of manganese ions exist in Mn$^{2+}$ state, occupy substitutional Zn$^{2+}$ ion sites and may also form Zn-O-Mn linkages making the glass network more rigid. Nevertheless, when the concentration of MnO is $> 0.6$ mol %, the manganese ions seem to subsist mostly in Mn$^{3+}$ state and occupy modifying positions with octahedral coordination.

The infrared spectra of all the three modifier oxide (PbO, ZnO, CaO) -Sb$_2$O$_3$- B$_2$O$_3$ glasses, have exhibited two conventional bands due to trigonal BO$_3$ units (at about 1390 cm$^{-1}$) and the tetrahedral BO$_4$ units at 1015 cm$^{-1}$. An additional band is also observed at about 710 cm$^{-1}$ due to the bending of B-O linkages in the borate network. In the infrared spectra of all the glasses, out of 4 expected fundamental absorption bands viz., $v_1$ (at about 1000 cm$^{-1}$) -
due to symmetric stretching vibrations, $v_2$ (at about 600 cm$^{-1}$) - due to symmetric bending vibrations, $v_3$ (at about 710 cm$^{-1}$) - due to doubly degenerate stretching vibrations and $v_4$ (at about 485 cm$^{-1}$) - due to doubly degenerate bending vibrations ($v_4$) of SbO$_3$ structural units, the bands due to $v_2$ vibrations seemed to be missing. In MnO doped glasses, in the spectrum of glass $M_6$, the band due to $v_1$ vibrations of SbO$_3$ structural groups appeared to be merged with the vibrational band of tetrahedral BO$_4$ units and a band observed at 1015 cm$^{-1}$ has been considered as a common vibrational band due to B-O-Sb linkages. In the region of $v_4$ vibrations, the band due to vibrations of ZnO$_4$ structural units is also expected and hence the band observed at about 500 cm$^{-1}$ is assumed to be due to the vibrations of Zn-O-Sb linkage groups. When the concentration of MnO is greater than 0.6 mol %, a gradual decrease in the intensity of common vibrational band due to B-O (of BO$_4$ units)-Sb linkages and a simultaneous increase in the intensity of band due to BO$_3$ structural units is observed. From this observation it is concluded that there is an increasing disorder in the glass network with increase in the concentration of MnO beyond 0.6 mol %.

Raman spectra of MO-Sb$_2$O$_3$-B$_2$O$_3$ glasses have exhibited a band at about 1040 cm$^{-1}$, identified due to diborate groups consisting of six membered rings containing two BO$_4$ tetahehedra and another band centered at 805 cm$^{-1}$, ascribed due to the boroxil ring oxygen breathing in which the boron coordinate atom is three. Additionally, a significant band at about 600
cm\(^{-1}\) assigned to the anti-symmetric stretching vibrations of Sb-O-Sb bridges is also observed. A weak but definite band at about 400 cm\(^{-1}\) (recognized due to the symmetric stretching vibrations of SbO\(_3\) pyramids could also be detected in the spectra of all the glasses.

The spectra of ZnO-Sb\(_2\)O\(_3\)-B\(_2\)O\(_3\) glass system have exhibited two weak bands, at 500 cm\(^{-1}\) and at about 200 cm\(^{-1}\) identified due to the vibrations of ZnO\(_4\) and ZnO\(_6\) units. With the introduction of MnO (up to 0.6 mol %) the intensity of the bands due to BO\(_4\) tetrahedra, symmetric stretching vibrations of SbO\(_3\) pyramids and that of ZnO\(_4\) units is observed to increase gradually, where as that of the bands due to anti-symmetric stretching vibrations of Sb-O-Sb bridges and ZnO\(_6\) octahedral band, is observed to decrease. Beyond this concentration the intensity of these bands has exhibited a reversal trend. From this observation it has been concluded that there is a higher degree of disorder in the network of the glasses containing MnO > 0.6 mol %.

The ESR spectra of MnO doped ZnO-Sb\(_2\)O\(_3\)-B\(_2\)O\(_3\) glasses exhibited a six-line hyperfine structure centered at g ~ 2.01; a considerable increase in the effective value of g is observed with increase in the concentration of MnO in the glass matrix up to 0.6 mol %; beyond this concentration the intensity and resolution of the sextet pattern is observed to decrease. The signal is identified due to the interaction of electron spin of manganese ions with its own nuclear spin of I = 5/2. The observed increase in the value of g
of this signal is ascribed to the contribution of orbital angular momentum to the magnetic moment of Mn$^{2+}$ ions. Another weak signal observed at $g = 4.3$ line, is considered as an indicative of a distorted crystalline field in the vicinity of some Mn$^{2+}$ ions and presumably due to magnetically isolated Mn$^{2+}$ ions in tetragonal sites of octahedral symmetry.

The magnetic properties of MnO doped glasses arise from the paramagnetic Mn$^{2+}$ (3d$^5$) and Mn$^{3+}$ (3d$^4$) ions. The value of the effective magnetic moment for glass M$_6$ is found to be 5.90 $\mu_B$. From this observation it is concluded that the presence of the highest concentration of manganese ions in Mn$^{2+}$ state in this glass. From the observed decrease in the value of $\mu_{\text{eff}}$ from 5.90 $\mu_B$ to 4.85 $\mu_B$ (for glass M$_{10}$), it has been concluded that the glass M$_{10}$ consists of manganese ions predominantly in Mn$^{3+}$ state.

The dielectric parameters viz., $\varepsilon'$, loss tan $\delta$ and a.c. conductivity $\sigma$ of ZnO-Sb$_2$O$_3$-B$_2$O$_3$: MnO, are found to increase with increase in the concentration of MnO from 0.6 to 1.0 mol %. Such an increase (which is a consequence of an increase in the space-charge polarization) has been attributed to the increase in the degree of disorder in the glass network due to the growing modifying action of Mn$^{3+}$ ions.

Finally, the analysis of various studies viz. optical absorption, IR, Raman, ESR and magnetic susceptibility coupled with dielectric studies of ZnO-Sb$_2$O$_3$-B$_2$O$_3$ glasses doped with different concentration of MnO indicate that manganese ions mostly exist in Mn$^{2+}$ state if the concentration
of MnO is $\leq 0.6$ mol % and there is a possibility for these ions to exist in Mn$^{3+}$ state if the concentration of MnO $> 0.6$ mol % and act as modifiers.

CHAPTER -IV is devoted to the study on molybdenum ion as a structural probe in PbO-Sb$_2$O$_3$-B$_2$O$_3$ glass system by means of dielectric and spectroscopic investigations. The following is the composition chosen for the present study: (20-x) PbO-40Sb$_2$O$_3$-40B$_2$O$_3$: x MoO$_3$ with $(0 \leq x \leq 5.0)$ and the samples are labeled as Mo$_0$ (pure), Mo$_{0.4}$ ($x = 0.4$), Mo$_{0.6}$ ($x = 0.6$), Mo$_1$ ($x = 1.0$), Mo$_2$ ($x = 2.0$), Mo$_3$ ($x = 3.0$), Mo$_4$ ($x = 4.0$) and Mo$_5$ ($x = 5.0$).

Scanning electron microscopy and differential thermal analysis studies on MoO$_3$ doped PbO-Sb$_2$O$_3$-B$_2$O$_3$ glasses have indicated that the glass Mo$_{0.6}$ (glass containing 0.6 mol% of MoO$_3$) has the highest glass forming ability and more resistant against devitrification.

The optical absorption spectra of MoO$_3$ doped glasses have exhibited a broad absorption band in the region 500-650 nm; there is a noticeable increase in the intensity of this band with the increase in the concentration of MoO$_3$ from 1 to 5 mol %. This band is attributed to the excitation of Mo$^{5+}$ (4d$^1$) ion. More precisely this is predicted as the superposition of the two optical excitations, starting from $b_2$ ($d_{xy}$) ground state to ($d_{xz,yz}$) and ($d_{x^2-y^2}$) with $\delta=15000$ cm$^{-1}$ and $\Delta=23000$ cm$^{-1}$. The highest intensity of this band is observed in the spectrum of glass Mo$_5$ and it is ascribed to the presence of the highest concentration of molybdenum ions in Mo$^{5+}$ state in these glasses.
In the IR spectra of MoO$_3$ doped PbO-Sb$_2$O$_3$-B$_2$O$_3$ glasses, in the region of $\nu_4$ vibrations of SbO$_3$ structural groups, the band due to vibrations of PbO$_4$ structural units is also present and hence the band observed at about 470 cm$^{-1}$ is attributed to the vibrational groups of Pb-O-Sb linkages in the glass network. In addition to the bands due to BO$_3$, BO$_4$ and SbO$_3$ structural units, in the spectra of these glasses two well resolved bands attributed to $\nu_1$ and $\nu_3$ vibrational modes of $\text{MoO}_4^{2-}$ tetrahedral units have also been observed at 885 and 820 cm$^{-1}$. The detailed analysis of these results indicated that molybdenum ions occupy both tetrahedral and octahedrally positions in the glass network and the concentration of octahedral positioned molybdenum ions increases with increase in the concentration of MoO$_3$ beyond 0.6 mol %.

In the Raman spectra of MoO$_3$ doped glasses, the intensity of the band due to antisymmetric stretching vibrations of Sb-O-Sb bridges is observed to increase with increase in the concentration of MoO$_3$ beyond 0.6 mol %; the band due to symmetric stretching vibrations of SbO$_3$ pyramidal structural units is observed to be more prominent only in the spectrum of glass Mo$_{0.6}$. These observations suggest an increasing disorder in the PbO-Sb$_2$O$_3$-B$_2$O$_3$ glass network with increase in the concentration of MoO$_3$ beyond 0.6 mol %. Additionally, the spectra of these glasses have exhibited two new bands identified due to $\nu_1$ and $\nu_2$ vibrations of tetrahedral $\text{MoO}_4^{2-}$ (orthomolybdate) structural units with the highest intensity in the spectrum of glass Mo$_{0.6}$. With increase in the concentration of MoO$_3$ (beyond 0.6 mol %) the $\nu_1$ vibrational
band is shifted towards higher wavenumber whereas, the band due to \( v_2 \) vibrations is shifted towards lower wavenumber region. In these regions, the bands due to MoO\(_6\) groups are expected. From these results, it is therefore, concluded that there is a gradual transformation of molybdenum ions from tetrahedral positions to octahedral positions with increase in the concentration of MoO\(_3\) from 0.6 to 5 mol %. The analysis of these results also suggested the formation of condensed molybdate anions viz., \((\text{Mo}2\text{O}_7)^{2-}\) in the glass network when the concentration of MoO\(_3\) is increased beyond 0.6 mol % in the glass matrix.

The glasses containing MoO\(_3\) (\( \geq 1.0 \) mol %) have exhibited an ESR signal consisting of a central line surrounded by smaller satellites (with \( g_\perp =1.930 \) and \( g_\parallel =1.872 \)). This signal is identified due to the paramagnetic Mo\(^{5+}\) ions and the two components of the \( g \) values are assumed due to the result of structural disorder arising from the site-to-site fluctuations of the local surroundings of the paramagnetic Mo\(^{5+}\) ions. The intensity and the half width of the central line are observed to increase with increase in the concentration of MoO\(_3\) from 1.0 to 5.0 mol % indicating a gradual increase in the concentration of Mo\(^{5+}\) ions in this concentration range.

The magnetic properties of MoO\(_3\) doped glasses are ascribed to Mo\(^{5+}(4d^1)\) paramagnetic ions. From magnetic susceptibility measurements, an increase in the value of redox ratio C with increase in the concentration of MoO\(_3\) (from 1.0 to 5.0 mol %) has been observed. From this observation, it is
envisaged that there is a gradual increase in the reduction of molybdenum ions from Mo$^{6+}$ state to Mo$^{5+}$ state in the glass matrix in this composition range.

The dielectric parameters viz., $\varepsilon'$, tan$\delta$ and $\sigma_{a.c}$ of these glasses are found to increase and the activation energy for a.c. conduction is found to decrease with the increase in the concentration of MoO$_3$ beyond 0.6 mol %; this behaviour has been attributed to the increasing presence of Mo$^{5+}$ ions that act as modifiers. The high temperature part of the conductivity is explained on the basis of mixed conduction mechanism whereas the quantum mechanical tunneling model seems to be appropriate for the low temperature part (temperature independent part) of the conductivity in these glasses.

In conclusion, the analysis of the results of various studies viz., optical absorption, ESR, IR and Raman spectra, magnetic susceptibility and dielectric properties of PbO-Sb$_2$O$_3$-B$_2$O$_3$ glasses doped with different concentrations of MoO$_3$, indicated that there is a possibility of conversion of a part of Mo$^{6+}$ ions into Mo$^{5+}$ ions, especially when the concentration of MoO$_3$ is approximately more than 0.6 mol %. Such ions mostly act modifiers and weaken the glass network. However, in the glasses containing low concentrations of MoO$_3$, molybdenum ions seemed to exist mostly in Mo$^{6+}$ state, occupy network forming positions with MoO$_4^{2-}$ structural units and predicted to increase the rigidity of the glass network.
In Chapter-V, the results of the investigations on valence and coordination of chromium ions in ZnO-Sb$_2$O$_3$-B$_2$O$_3$ glass system by means of spectroscopic and dielectric relaxation studies have been reported. Within the glass-forming region of ZnO-Sb$_2$O$_3$-B$_2$O$_3$ glass system, the composition (20-x) ZnO-40 Sb$_2$O$_3$-40 B$_2$O$_3$: x CrO$_{4}^{2-}$ (introduced as ammonium dichromate) with the values of x ranging from 0 to 1.0 mol % in steps of 0.2) is chosen for the present study. Based upon the values of x, the samples are labeled as C$_0$ (pure), C$_2$ (x = 0.2), C$_4$ (x = 0.4), C$_6$ (x = 0.6), C$_8$ (x = 0.8) and C$_{10}$ (x = 1.0).

The characterization techniques, viz., scanning electron microscopy and differential thermal analysis, indicate that among different chromium doped glasses, the glass forming ability is observed to be the maximum for the glasses containing 0.2 mol % of CrO$_{4}^{2-}$.

In the optical absorption spectra of these glasses, it is observed that the spectrum of glass C$_2$ to exhibit an intense absorption band at 370 nm identified due to the excitation of CrO$_{4}^{2-}$ (Cr (VI)) group. With increase in the concentration of chromium ions from 0.2 to 0.4 mol %, the intensity of this band is observed to decrease and a new broad band at about 469 nm has been observed; the new band is identified due to the excitation of CrO$_{4}^{3-}$ (Cr(V)) group. For further increase in the concentration of chromium ions, the band due to Cr (VI) ions slowly disappeared and the intensity of the band due to Cr (V) is gradually decreased. Additionally at about 0.6 mol % of chromium
ion concentration, two new bands with absorption peaks at 430 and 660 nm have appeared. The intensity of these two bands is observed to increase at the expense of first two bands with increase in the chromium content. The bands are identified due to the $^4A_2 \rightarrow ^4T_1(F)$, $^4A_2 \rightarrow ^4T_2$ transitions of Cr$^{3+}$ ions respectively. Further more, two kinks at 690 and 702 nm have been located on 660 nm band in the spectra of the glasses C_8 and C_{10}. These bands have been identified due to $^4A_2 \rightarrow ^2T_1$ and $^4A_2 \rightarrow ^2E$ (spin and parity forbidden) transitions of Cr$^{3+}$ ions respectively. The detailed analysis of the results of the optical absorption spectra of CrO$_2^{2-}$ doped ZnO-Sb$_2$O$_3$-B$_2$O$_3$ glasses indicated a gradual conversion of chromium ion from Cr$^{6+}$ state into Cr$^{3+}$ ions with increase in the concentration of CrO$_2^{2-}$ in the glass network.

The IR spectra of chromium ions doped glasses, have exhibited a new band (in addition to the conventional bands due to BO$_3$, BO$_4$ and SbO$_3$ structural groups) at about 885 cm$^{-1}$; this band is identified due to the v$_3$ vibrations of CrO$_2^{2-}$ structural units. In the spectrum of glass C$_2$, this v$_3$ vibrational band exhibited degeneracy with two closed distinct bands at 888 and 860 cm$^{-1}$. With a gradual increase in the chromium content, the degeneracy is slowly disappeared and in the spectrum of glass C_{10}, the v$_3$ vibrational band itself appeared to be very feeble. Such splitting has been explained in terms of site symmetry and local lattice interactions on chromium ion.
The Raman spectra of these glasses exhibited a new band identified due to the vibrations of $CrO_4^{2-}$ structural units at 860 cm$^{-1}$. The intensity of this band is observed to decrease with increase in the concentration of chromium ion concentration beyond 0.2 mol %. The analysis of Raman and IR spectral studies indicated that there is a gradual conversion of chromium ions from $Cr^{6+}$ state (that take part tetrahedral positions) into $Cr^{3+}$ that occupy octahedral positions and induce non-bridging oxygens in the glass network.

The ESR spectrum of chromium doped ZnO-Sb$_2$O$_3$-B$_2$O$_3$ glasses recorded at liquid nitrogen temperature exhibited an asymmetric weak signal at $g = 1.98$ when the concentration of $CrO_4^{2-}$ is about 0.4 mol %. This signal is identified due to $Cr^{5+}$ ions connected with the spin lattice relaxation which in turn is governed by the ground state of the unpaired electron in unperturbed tetrahedral $CrO_4^{2-}$ ion. As the concentration of chromium ions is increased, the signal due to $Cr^{5+}$ ions is slowly faded away. The reason for such a decreasing intensity of this signal is assumed to be either due to a large anisotropy arising from the highly distorted $CrO_4^{2-}$ complex or due to the reduction in the concentration of $Cr^{5+}$ ions itself. With increase in the concentration of chromium ions $> 0.4$ mol %, another strong signal at $g = 1.97$ identified due to the exchange coupling between $Cr^{3+}$ - $Cr^{3+}$ ion pairs and a weak signal at $g = 4.7$ identified due to the isolated $Cr^{3+}$ ions are also observed. The final analysis of ESR spectral results of the ZnO-Sb$_2$O$_3$-B$_2$O$_3$:
CrO$_4^{2-}$ glasses predict that, with increase in the content of chromium ions, a gradual conversion of these ions from 6+ state to 3+ state; additionally these results also suggest a decreasing covalent environment of chromium ions in the network with increase in the content of chromium ions.

For ZnO-Sb$_2$O$_3$-B$_2$O$_3$: CrO$_4^{2-}$ glasses, the dielectric parameters are found to increase and the activation energy for a.c. conduction is found to decrease with the increase in the concentration of chromium content beyond 0.2 mol %, this has been attributed to the increasing presence of chromium ions in Cr$^{3+}$ state in the glass network that act as modifiers. The dielectric relaxation effects exhibited by these glasses could successfully be analyzed by Cole-Cole plot and graphical methods. The spreading of relaxation effects has been established and the relaxation effects were identified due to the presence of different kinds of dipoles. The QMT model seems to be more appropriate for explaining the low temperature part of the a.c. conductivity.

The objective of Chapter -VI is, to explore the structural influence of Al$_2$O$_3$, Ga$_2$O$_3$ and In$_2$O$_3$ on CaO-Sb$_2$O$_3$-B$_2$O$_3$ glass system through a detailed investigation on dielectric properties over a range of frequency and temperature with the aid of data on spectroscopic (optical absorption, Raman, IR) studies.

The following five particular compositions of the CaO-Sb$_2$O$_3$-B$_2$O$_3$: M$_2$O$_3$ glass system with different concentration of M$_2$O$_3$ (Al$_2$O$_3$, Ga$_2$O$_3$ and In$_2$O$_3$) are chosen for the present study: The details of the composition are
Series-A: 20 CaO-(40-x) Sb$_2$O$_3$-40 B$_2$O$_3$: x Al$_2$O$_3$

Series G: 20 CaO-(40-x) Sb$_2$O$_3$-40 B$_2$O$_3$: x Ga$_2$O$_3$

Series I: 20 CaO-(40-x) Sb$_2$O$_3$-40 B$_2$O$_3$: x In$_2$O$_3$

all in mol %, with five values of x values ranging from 0 to 5. The samples are labeled as M$_1$ (x = 1 mol %), M$_2$ (x = 2 mol %), M$_3$ (x = 3 mol %), M$_4$ (x = 4 mol %), M$_5$ (x = 5 mol %), where M stands for A, G & I.

The scanning electron microscopy and differential thermal analysis studies on these glasses, indicated that glass forming ability to increase up to 4.6 mol % and 2.0 mol % of Al$_2$O$_3$ and Ga$_2$O$_3$ respectively and to decrease for further increase in the concentration of these oxides. However, for In$_2$O$_3$ mixed glasses, glass forming ability parameter is observed to decrease up to 1.0 mol % (with respect to those of pure glasses) and found to increase when this oxide is increased beyond this concentration.

For M$_2$O$_3$ free glasses, the optical absorption edge is observed at 380 nm; for Al$_2$O$_3$ and Ga$_2$O$_3$ doped glasses the edge is shifted towards lower wavelength side with increase in their concentrations up to 4.0 and 2.0 mol % respectively; beyond these concentrations, the edge is shifted towards higher wavelength. When In$_2$O$_3$ (1.0 mol %) is mixed in these glasses, the cut-off wavelength is decreased from 380 nm to 370 nm; for further increase of In$_2$O$_3$, it is shifted towards lower side. From the observed absorption edges, we have evaluated the optical band gaps ($E_0$) of these glasses by drawing Urbach plot. The value of optical band gap ($E_0$) determined from
these plots is found to be the highest for the glasses A4, G2 and I5 in their respective series.

In the spectra of various IIIA group metal ions mixed CaO-Sb2O3-B2O3 glasses, the spectra of the glasses A4, G2 and I5 have exhibited maximum intensity of the bands due to BO4 and symmetrical SbO3 structural units. Additionally, the spectra of Al2O3 mixed glasses have exhibited an absorption band at about 780 cm⁻¹ attributed to AlO4 structural units; this band is observed to be more intense in the spectrum of glass A4. Similarly, the Ga2O3 mixed glasses have exhibited an additional band at about 610 cm⁻¹ identified due to the vibrations of GaO4 structural units. The maximum intensity of this band is observed in the spectrum of glass G2. There is no clear evidence from the IR spectra to show that the indium ions occupy either octa or tetrahedral units.

The Raman spectra of Al2O3 and Ga2O3 mixed glasses did not reveal any additional information other than that provided by the IR spectra. However, The spectra of In2O3 mixed glasses have exhibited band at 200 cm⁻¹ (in addition to conventional bands due to borate groups) identified due to the vibrations of substitutionally positioned octahedral indium ions. The intensity of this band goes on increasing with increase in the concentration of In2O3.

The analysis of detailed studies of the dielectric properties CaO-Sb2O3-B2O3: M2O3 glasses indicated that if the concentration of M2O3 is
increased up to 4.0 mol % (Al₂O₃), 2.0 mol % (Ga₂O₃) and 5.0 mol % (In₂O₃), Al³⁺, Ga³⁺ and In³⁺ ions occupy substitutional positions in the glass network and increase in the insulating strength of the glasses.

CHAPTER-VII reports brief summary and conclusions drawn from the measurements of various physical parameters of glass systems under investigation. References closely related to the present work have been compiled to the extent possible and given at the end of the relevant chapter.