Chapter 6

# SUMMARY AND CONCLUSIONS

***This chapter contains a brief outline and conclusions drawn from the investigation carried out on (a) dielectric properties and (b) spectroscopic properties of $Pbo-Sb_2o_3-As_2O_3$ glasses crystallized with different concentrations of $MoO_3$, MnO and nio as nucleating agents.***

# Summary and Conclusions

## 6.1 Summary

$PbO$-$Sb_2O_3$-$As_2O_3$ glass ceramics with three nucleating agents viz., $MoO_3$, MnO and NiO have been synthesized. A systematic investigation on characterization (viz., XRD, SEM, EDS & DSC studies) and physical properties (viz., dielectric properties, infrared, optical absorption, ESR and luminescence spectra) have been carried out.

The compositions of the samples used for the present study are

1. $40PbO$- $(20-x)Sb_2O_3$-$40As_2O_3$: x $MoO_3$ ($0 \leq x \leq 1.0$)

2. $40PbO$- $(20-x)Sb_2O_3$-$40As_2O_3$: x MnO ($0 \leq x \leq 5.0$)

3. $40PbO$- $(20-x)Sb_2O_3$-$40As_2O_3$: x NiO ($0 \leq x \leq 1.0$)

The glasses were prepared by the usual melting, quenching and subsequent annealing techniques. Later they were crystallized at different temperatures. The samples were crystallized at the temperature corresponding to the crystallization temperature identified from the DTA pattern.

The samples were characterized by X-ray diffraction, scanning electron microscopy, EDS and DTA techniques.

The following measurements were taken:

1) Dielectric constant ($\varepsilon^{l}$), loss (tan $\delta$) and ac conductivity $\sigma_{ac}$ in frequency range $10^2$ to $10^5$ Hz and in the temperature range 30-250$^{o}$C.
2) Optical absorption and photoluminescence in the UV, visible and NIR regions.
3) Electron spin resonance spectra of $MoO_3$ and MnO doped glass ceramics at room temperature.
4) Infrared spectra of all these glasses in the region 400 to 4000 $cm^{-1}$.

**6.2 Conclusions**

The main conclusions drawn form the results of above studies are summarized below:

1. The **scanning electron microscopic** (SEM) pictures of the pre-heated samples containing different concentration of transition metal oxides do not show any significant crystallinity. The pictures of the crystallized $PbO-Sb_2O_3-As_2O_3$ glasses with different concentrations nucleating agents exhibit well defined and randomly distributed crystals entrenched in glassy matrix. **The EDS analysis** of the glass ceramic materials indicate the presence of Pb, Sb, As, O and Mo/Mn/Ni elements in the samples. The X-ray maps of the glass

ceramics indicated the reasonably uniform distribution of dopant ions in the entire glass ceramic material.

2. The **X-ray diffraction** (XRD) patterns of the pre-heated $PbO-Sb_2O_3-As_2O_3$: Mo/Mn/Ni samples showed that the samples are of amorphous in nature.

    i. X-ray diffraction patterns of $MoO_3$ mixed glass ceramic samples exhibited micro-structural changes. $Pb_5Sb_2O_8$, $PbSb_2O_6$, $SbAsO_4$, $Sb_2MoO_6$, $Sb_4Mo_{10}O_{31}$, $As_4Mo_3O_{15}$ and $Pb_5Sb_4O_{11}$ are the some of the crystalline phases observed in these samples.

    ii. The X-ray diffraction studies of MnO mixed glass ceramics have revealed the presence of $Pb_5Sb_2O_8$, $PbSb_2O_6$, $SbAsO_4$, $Mn_2Sb_2O_7$, $Mn_3Sb_2O_6$, $Mn_2O_3$, $MnAsO_4$ and $Pb_5Sb_4O_{11}$ crystalline phases in these samples.

    iii. The X-ray diffraction studies of NiO mixed glass ceramics have indicated the presence of $NiSb_2O_6$, $NiAs_2O_4$, $Ni_2As_2O_7$, $Pb_5Sb_2O_8$, $PbSb_2O_6$, $Pb_5Sb_4O_{11}$ crystalline phases in these samples.

3. The **differential thermal analysis patterns** (DTA) of all the crystallized samples exhibited endothermic change due to the glass

transition followed by multiple exothermic effects due to the crystal growth and an endothermic peak due to re-melting of the samples have been observed for all the glass ceramic samples indicating the presence of different crystalline phases in the samples. The DTA data could further be explained in terms of surface and bulk crystallization in all the series of the samples.

4. The **infrared spectrum** of dopant free $PbO\text{-}Sb_2O_3\text{-}As_2O_3$ glass ceramic sample exhibited band due to $\nu_1$ vibrations of $SbO_3$ structural groups at about 939 $cm^{-1}$ and the band related to $\nu_2$ vibrations of these units at 617 $cm^{-1}$. The $\nu_1$ band due to $AsO_3$ structural groups is appeared at 1040 $cm^{-1}$. The $\nu_2$ and $\nu_3$ bands of $SbO_3$ and $AsO_3$ structural groups are merged and exhibited common meta-centres at 617 and 765 $cm^{-1}$, respectively.

After the crystallization with $MoO_3$, the spectra exhibited two new bands due to $v_1$ and $v_3$ vibrational modes of $MoO_4^{2-}$ tetrahedral units at 890 and 835 $cm^{-1}$. With the rise in the concentration of the crystallizing agent, the intensity of the bands due to $MoO_4^{2-}$ ($v_1$) tetrahedral units is observed to decrease and is found to be shifted towards slightly higher frequency side whereas the $v_3$ vibrational band of these groups is observed to be shifted towards lower frequency.

Further, the intensity of bands due to symmetric stretching and symmetric bending vibrations of $SbO_3$ and $AsO_3$ structural groups is also observed to decrease gradually with increase in the concentration of $MoO_3$. From these results, it is concluded that there is a gradual transformation of molybdenum ions from tetrahedral positions to octahedral positions with increase in the concentration of crystallizing agent $MoO_3$.

The IR spectra of MnO mixed glass ceramics have also exhibited conventional $AsO_3$, $SbO_3$, structural units. The IR spectral studies of these samples have further indicated the decreasing concentration of symmetrical structural vibrational groups with increase in the concentration of MnO.

The IR spectral studies of NiO mixed samples have pointed out the glass ceramic network is composed of conventional $AsO_3$ and $SbO_3$ structural units; these studies have further indicated that the decreasing concentration of symmetrical vibrations of above structural groups with increase in the concentration of NiO beyond 0.8 mol%.

5. The **optical absorption spectra** of $MoO_3$ mixed $PbO\text{-}Sb_2O_3\text{-}As_2O_3$ glass ceramic samples exhibited a broad absorption band (with the meta centre falling in the region of 670-690 nm) due to the excitation

of $Mo^{5+}$ ($4d^1$) ion. The optical activation energy associated with this band has been found to be of about 1.70–1.85 eV for these samples and this variation is predicted as a characteristic signal of inter valence transfer ($Mo^{5+} \Leftrightarrow Mo^{6+}$) or a polaronic type of absorption.

The optical absorption spectra of MnO mixed glass ceramic samples exhibited a band at about 520 nm assigned to $^6A_{1g}(S) \rightarrow {}^4T_{1g}$ (G) ($O_h$) transitions. Another broad band at 422 nm ascribed to $^6A_1(S) \rightarrow {}^4T_2(G)$ transition of tetrahedral $Mn^{2+}$ ions is also observed. With increase in the concentration of MnO, the octahedral band is observed to grow at the expense of tetrahedral band; from this observation, it is concluded that there is a gradual decrease of tetrahedrally positioned $Mn^{2+}$ ions in the glass ceramic. A well resolved broad band at about 495 nm is also detected especially in the spectra of the glasses crystallized with higher concentrations of MnO; this band is attributed to spin allowed $^5E_g \rightarrow {}^5T_{2g}$ transition. The presence of this band suggested that a part of manganese ions exist in $Mn^{3+}$ ($d^4$) that occupy octahedral positions in the glass ceramic.

The absorption spectra NiO mixed samples exhibited, four clearly resolved bands in the visible and NIR regions at 1274 nm ($O_h1$), 792 nm ($O_h2$) and 471 nm ($O_h3$) and 595 nm (tetrahedral

band) attributed respectively to $^3A_2$ (F) → $^3T_2$ (F) ($Oh_1$), $^3T_1$ (F) ($Oh_2$), $^1T_2$ (D) ($Oh_3$) and $^3A_2$ (F) → $^3T_1$ (P) transitions. As the concentration of NiO is increased up to 0.8 mol %, the intensity of the octahedral bands is observed to increase with a shift towards slightly higher wavelength; in this concentration range the intensity of the tetrahedral band ($T_d$ band) is observed to decrease with a slight shift towards higher wavelengths. With the raise of NiO content from 0.8 to 1.5 mol %, the tetrahedral band is observed to grow at the expense of octahedral band. The observed enhancement of the absorption in the octahedral bands with increase in the content of NiO up to 0.8 mol% suggested the increasing presence of octahedrally positioned nickel ions and the increasing trend of tetrahedral band beyond 0.8 mol% of NiO indicated that the nickel ions prefer tetrahedral positions in this concentration range.

6. The **ESR spectra** of PbO-$Sb_2O_3$-$As_2O_3$: $MoO_3$ glass ceramics recorded at room temperature exhibited a signal consisting of an intense central line surrounded by smaller satellites (at $g_\perp$ ~ 1.933 and $g_{ll}$ ~ 1.883). The intensity of the signal is observed to increase with the gradual increase in the concentration of crystallizing agent $MoO_3$ The highest intensity of the signal observed in the spectrum of the

sample $M_{10}$, suggested the presence of the highest concentration of $Mo^{5+}O_3^-$ complexes. The values of $g_\perp$ and $g_{ll}$ of these spectra have been found to be dependant on the concentration of crystallizing agent; the structural disorder arising from the site-to-site fluctuations of the local surroundings of the paramagnetic $Mo^{5+}$ ions found to be responsible for such variations.

The ESR spectra of $PbO\text{-}Sb_2O_3\text{-}As_2O_3$ glass crystallized with different concentrations of MnO exhibited six-line hyperfine structure centered at g ~ 2.001 and another signal at g ~ 4.3; the relative intensity of these two signals is observed to increase with increase in the concentration of manganese ions in the samples.

The hyperfine interaction parameter A evaluated from these spectra increases gradually from 9.02 to 9.88 mT with the concentration of the nucleating agent. This observation suggested the increasing ionic nature of the bonding between $Mn^{2+}$ ions and its ligands and ions occupy octahedral positions. The deviation of g from $g_e$ is observed to become gradually negative with increase in the content of MnO, this observation also indicated the increasing concentration of octahedral positioned $Mn^{2+}$ ions. The larger values of 'g' observed for the samples $Mn_2$ and $Mn_3$ are ascribed partly due to

the contribution of orbital angular momentum to the magnetic moment of $Mn^{2+}$ ions. The single resonance without hyperfine splitting observed for the samples crystallized with low content of MnO is attributed to spin-spin interaction between $Mn^{2+}$ ions and its ligands.

The ESR spectra of NiO mixed glass ceramic samples did not exhibit any ESR signal at room temperature.

7. The value of **magnetic susceptibility** $\chi$ of $PbO\text{-}Sb_2O_3\text{-}As_2O_3$: $MoO_3$ glass ceramics is found to increase gradually with the increase in the concentration of $MoO_3$. From the measured values of $\chi$, the concentration of $Mo^{5+}$ ions (N') is estimated; the redox ratio c, evaluated from this N', is observed to increase significantly with increase in the concentration of crystallizing agent; from this observation it is concluded that there is a gradual increase in the reduction of molybdenum ions from $Mo^{6+}$ state to $Mo^{5+}$ state with the increase in the concentration of $MoO_3$ in the glass ceramic matrix.

The analysis of the data on magnetic susceptibility of $PbO\text{-}Sb_2O_3\text{-}As_2O_3$: MnO glass ceramics indicated that there is a significant presence of $Mn^{3+}$ ions in the samples crystallized with higher content of MnO.

The effective magnetic moment evaluated from magnetic susceptibility of NiO mixed glass ceramics indicated gradual increase from 3.33 $\mu_B$ (for sample $N_8$) to 4.05 $\mu_B$ (for sample $N_{15}$); from this observation, it is concluded that there is a gradual transformation of $Ni^{2+}$ ions from the octahedral sites to the tetrahedral sites as the concentration of crystallizing agent is increased beyond 0.8 mol %.

8. The **emission spectra** of all the MnO mixed $PbO\text{-}Sb_2O_3\text{-}As_2O_3$ glass ceramic samples (recorded at room temperature) when excited at 449 nm exhibited two prominent emission bands at about 550 nm (green emission) due to $^4T_1(^4G) \rightarrow {}^6A_l(^6S)$ tetrahedral transition of $Mn^{2+}$ ions and 650 nm (orange emission) due to $^4T_{1g}(^4G) \rightarrow {}^6A_{lg}(^6S)$ octahedral transition of $Mn^{2+}$ ions. As the concentration of crystallizing agent is increased, the orange emission band is observed to grow at the expense of green emission band. From this observation it is concluded that there is a gradual transformation of $Mn^{2+}$ ions from tetrahedral to octahedral positions and the samples crystallized with 5 mol% of MnO exhibited highest luminescence efficiency.
9. With the gradual increase of the crystallizing agent $MoO_3$ from 0 to 1.0 mol%, in $PbO\text{-}Sb_2O_3\text{-}As_2O_3$ glass ceramics the values of the **dielectric parameters** viz., $\varepsilon'$, tan $\delta$ and $\sigma_{ac}$ are found to increase at

any frequency and temperature and activation energy for a.c. conduction is observed to decrease with respect to those of pre-crystallized samples; this is attributed to an increase in the space charge polarization due to the growing presence of $Mo^{5+}$ ions that act as modifiers in these samples. The detailed analysis of the dielectric properties suggested an increasing semiconducting character of these samples with increase in the concentration of the $MoO_3$

The values of dielectric parameters viz., $\varepsilon'$, tan $\delta$ and $\sigma_{ac}$ of MnO mixed $PbO\text{-}Sb_2O_3\text{-}As_2O_3$ glass ceramics are found to increase with temperature and activation energy for a.c. conduction is observed to decrease with increase in the content of nucleating agent MnO; this observation indicated an increase in the space charge polarization attributed to the increasing concentration of octahedrally positioned $Mn^{2+}$ ions that act as modifiers in these samples. Further analysis, of these results suggested that there is a decrease in the insulating character of these samples with increase in the concentration of crystallizing agent MnO.

The dielectric studies of NiO mixed $PbO\text{-}Sb_2O_3\text{-}As_2O_3$ glass ceramics have indicated the growing degree of disorder in the glass network with increase in the concentration of crystallizing agent NiO

up to 0.8 mol%; from these results it is concluded that within the concentration range of 0.2 to 0.8 mol%, the nickel ions mostly occupy octahedral positions and induce bonding defects and lead to the enhancement of the values of dielectric parameters.

Summing up the entire work presented in this thesis, it is felt that the study of various electrical and spectroscopic properties of $PbO{-}Sb_2O_3{-}As_2O_3$ glasses crystallized with different concentrations of $MoO_3$, MnO and NiO has yielded some valuable information which will be useful for the practical applications of these materials.