PREFACE

The present thesis deals with the studies on **"Synthesis, characterization, and investigations of dielectric and spectroscopic properties of PbO-Sb_2O_3-As_2O_3 glass system crystallized with MoO_3, MnO and NiO as nucleating agents**". This work has been carried out in the Department of Physics, Acharya Nagarjuna University – Dr. M.R.A.R Campus, Nuzvid. The thesis contains the methods of preparation, characterization and studies on dielectric and spectroscopic properties of PbO-Sb_2O_3-B_2O_3 glass systems crystallized with varying concentration of MoO_3, MnO and NiO.

The Sb_2O_3 heavy metal oxide based glasses have attracted extensive investigation in recent years; these glasses posses large non-linear optical susceptibility (χ^3) coefficient that makes them suitable for potential applications in non-linear optical devices (such as ultrafast optical switches and power limiters), broad band optical amplifiers operating around 1.5 μ.m and in a number of solid state ionic devices. Antimony oxide participates in the glass network with SbO_3 structural units and can be viewed as tetrahedrons with the oxygen at three corners and a lone pair of electrons of antimony (Sb^{3+}) at the fourth corner localized in the third equatorial direction of Sb atom. Sb_2O_3 based glasses are known due to their significant transmission potential in the infrared region and possess high refractive

index. The antimony oxide as such is an incipient glass network former which does not form glass on its own. The optical transparency of PbO-Sb_2O_3 glasses can further be improved in the blue region by replacing a part of Sb_2O_3 by As_2O_3. As_2O_3 is a strong network former and is found to affect the far infrared transmission of Sb_2O_3 glasses to a less extent, since the frequencies of some of the fundamental modes of vibration of As_2O_3 structural groups lie in the region of vibration of SbO_3 structural groups. Moreover, it is also expected that AsO_3 groups form a single arsenic-antimony-oxygen framework with the Sb_2O_3 structural units and may strengthen its structure. The addition of As_2O_3 to these glasses makes them suitable for long distance optical transmission with low transmission losses.

Glass ceramic materials doped by transition metal ions are expected to be promising candidates as gain media for ultra-broadband optical fiber amplifiers, tunable lasers and ultra short pulse lasers in telecommunication wavelength regions over the glass materials. This is because of the dominance of non-radiative losses over the relaxations of excited states of transition metal ions/lasing spices in these materials. The glass ceramic materials possess a fine-grained uniform structure, consisting of small crystals of irregular and distorted form, often aggregated into spherolites, with residual glass inter-layers cementing the crystalline glass ceramic

cluster. These small and strain free intertwined microcrystals hinder the crack growth inside these materials. As a result, glass ceramics are likely to have outstanding mechanical, optical, electrical and thermal characteristics.

Among various crystallizing agents MoO_3 is considered as effective mineralizer and the molybdenum ions are expected to have profound influence on the optical and electrochemical properties of $PbO–Sb_2O_3–As_2O_3$ glass ceramics, in view of the fact that the oxide of molybdenum participate in the glass network with different structural units like MoO_4 (Td) and MoO_6 (Oh) of Mo^{6+} ions and $Mo^{5+}O^{3-}$ (Oh) of Mo^{5+} ions. The presence of molybdenum ions makes the glasses to be useful for potential applications in high-density memories, light modulation; large area displays devices like smart windows and other electrochromic devices. Hence, a part of the thesis is devoted to investigate the role of molybdenum ions on the structural aspects of lead antimony arsenate glass ceramics and their influence on physical properties.

Among various conventional crystallizing agents, MnO is expected to be more effective mineralizer especially in the glass systems like antimony-arsenate. Further the inclusion of Mn ions into the antimony glass ceramic network is an added advantage to use these materials for optically operated devices, since unfilled d-shells of these ions contribute more strongly to the

non-linear polarizabilities. A considerable number of recent studies on a variety of materials with MnO as nucleating agent are available in the literature.

The manganese ions exist in different valence states with different coordinations in glass matrices, for example as Mn^{3+} in borate glasses with octahedral coordination where as in silicate and germinate glasses as Mn^{2+} with both tetrahedral and octahedral environment. Both tetrahedral and octahedral Mn^{2+} ions have been found to exhibit luminescence emission in the green and red regions respectively in several glasses. In view of such practical importance, it is felt worthwhile to devote a part of the thesis to the studies on MnO mixed PbO-Sb_2O_3-As_2O_3 glass ceramics.

Unlike many transition metal ions that exist in multivalent states, the nickel ions mostly exist in divalent state and are extremely stable and no special care is necessary during synthesis to retain nickel ions in divalent state. Further, Ni^{2+} is an ion with exceptionally large crystal stabilization energies particularly when it is in octahedral field. Ni^{2+} ions exhibit several strong absorption bands in the visible and NIR regions where the pumping sources are easily available. The octahedrally positioned Ni^{2+} ions in glass network are expected to exhibit eye safe laser emission of wavelength about 1.5 μm due to $^3T_2 \rightarrow {}^3A_2$ transition, even at room temperature, which is of

great importance in telecommunications. There have been considerable recent studies on lasing action and other physical properties of nickel ions in various glass and glass ceramic materials. Due to these reasons, the PbO-Sb_2O_3-As_2O_3 glass that exhibits far infrared transmission is considered to offer suitable environment for hosting Ni^{2+} ions and hence a part of thesis is devoted to the report the results of spectroscopic and dielectric properties of PbO-Sb_2O_3-As_2O_3: NiO glass ceramics.

Thus the clear objectives of the present study are to prepare, characterize and

- To have a comprehensive understanding over the influence of molybdenum, manganese and nickel ions on structural aspects of PbO−Sb_2O_3-As_2O_3 glass ceramics by investigating the dielectric properties, optical absorption, luminescence, ESR and IR spectra.

The compositions of the glasses used for the present study are

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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 details of the studies carried out are

1.1 Contents of the present work

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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 studies carried out are

(i) differential thermal analysis and the evaluation of glass transition temperature T_g;

(ii) infrared spectral studies in the wavenumber range 400-2000 cm^{-1} and the study of the effect of concentration of transition metal ions on the position and intensity of various vibrational bands;

(iii) optical absorption studies in the wavelength range 300-2100 nm, identification of various electronic transitions of transition metal ions;

(iv) electron spin resonance measurements and the identification of the environment and valence states of molybdenum and manganese ions in the glass network;

(v) luminescence studies of MnO doped PbO−Sb_2O_3−As_2O_3 glass ceramics.

(vi) magnetic susceptibility studies of all the three series of the glass ceramics and the evaluation of magnetic moments of the nucleating agents;

(vii) dielectric properties viz., dielectric constant ε^{l}, dielectric loss tan δ and ac conductivity σ_{ac} in the frequency range 10^{2}-10^{5} Hz and in the temperature range 30-250 ^{o}C;

For the sake of convenience, the thesis is divided into six chapters.

CHAPTER–1 presents the General Introduction, Scope, Contents and the Aim of the present work. In this chapter, the basic theory related to electrical and spectroscopic properties of $PbO{-}Sb_2O_3{-}As_2O_3$ glass ceramics mixed with varied concentrations of MoO_3, MnO and NiO.

CHAPTER–2 gives the description of experimental methods employed in the preparation and characterization of $PbO{-}Sb_2O_3{-}As_2O_3$:MoO_3/MnO/NiO glass ceramics. The samples were crystallized by heating the glass samples for 6 h at the crystallization temperature identified from the DTA studies. The details of the apparatus used and the techniques adopted for characterization and for measuring dielectric properties, optical absorption, ESR, IR and photo-luminescence are also described in detail in this chapter.

The scanning electron microscopic (SEM) pictures of the pre-heated samples containing different concentrations 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 exhibits Pb, Sb, As, O and Mo/Mn/Ni elements in various crystalline phases. The X-ray maps of the glass ceramics indicated the reasonably uniform distribution of dopant ions in the entire glass ceramic material.

The differential thermal analysis studies (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 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.

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, $Sb_4Mo_{10}O_{31}$, $As_4Mo_3O_{15}$, $Pb_5Sb_4O_{11}$ are the some of the crystalline phases observed in these samples. 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. 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.

CHAPTER-3 devoted to the studies on bulk crystallization of $PbO–Sb_2O_3–As_2O_3$ glasses in the presence of MoO_3 nucleant and the effect of the concentration of MoO_3 on the crystallization behavior and microstructure of glass ceramic products produced and their spectroscopic (optical absorption, ESR and IR), magnetic and dielectric properties.

The detailed compositions chosen for this study are as follows:

M_0: 40 PbO- 20 Sb_2O_3- 40 As_2O_3

M_2: 40 PbO- 19.8 Sb_2O_3-40 As_2O_3: 0.2 MoO_3

M_4: 40 PbO- 19.6 Sb_2O_3-40 As_2O_3: 0.4 MoO_3

M_6: 40 PbO- 19.4 Sb_2O_3-40 As_2O_3: 0.6 MoO_3

M_8: 40 PbO- 19.2 Sb_2O_3-40 As_2O_3: 0.8 MoO_3

M_{10}: 40 PbO- 19.0 Sb_2O_3-40 As_2O_3: 1.0 MoO_3

The infrared spectrum of dopant free glass ceramic sample exhibited band due to ν_1 vibrations of SbO_3 structural groups at about 939 cm^{-1} and the

band related to ν_2 vibrations of these units at 617 cm^{-1}. The ν_1 band due to AsO_3 structural groups is appeared at 1040 cm^{-1}, where as, the ν_2 bands and the ν_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 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 ESR spectra of $PbO\text{-}Sb_2O_3\text{-}As_2O_3$: MoO_3 glass ceramics recorded at room temperature exhibited a signal consisting of an intense central line surrounded by smaller satellites (at $g_\perp \sim 1.933$ and $g_{ll} \sim 1.883$). 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 value of magnetic susceptibility χ 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 χ, 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.

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., ε', tan δ and σ_{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.

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Chapter-4 of the thesis deals with the investigation of (i) bulk crystallization of $PbO\text{-}Sb_2O_3\text{-}As_2O_3$ glasses in the presence of MnO nucleant, (ii) the effect of the concentration of MnO on the crystallization behavior and microstructure of glass ceramic products produced by means of XRD, SEM,

DTA and EDS and (iii) the spectroscopic (optical absorption, photoluminescence, ESR and IR), magnetic and dielectric properties.

Within the possible glass forming region of PbO-Sb_2O_3-As_2O_3 system, a particular compositions 40PbO–20Sb_2O_3–40As_2O_3 is chosen for the present study. The crystallizing agent MnO is varied from 0 to 5.0 mol% in this glass matrix. The detailed compositions are as follows:

Mn_0: 40PbO–20Sb_2O_3–40As_2O_3

Mn_1: 40PbO–19Sb_2O_3–40As_2O_3: 1.0 MnO

Mn_2: 40PbO–18Sb_2O_3–40As_2O_3: 2.0 MnO

Mn_3: 40PbO–17Sb_2O_3–40As_2O_3: 3.0 MnO

Mn_4: 40PbO–16Sb_2O_3–40As_2O_3: 4.0 MnO

Mn_5: 40PbO–15Sb_2O_3–40As_2O_3: 5.0 MnO

The glass specimens prepared with various concentrations of MnO were heat treated in a furnace at 300 ^oC for 6 h and chilled to room temperature for the crystallization.

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

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 ESR spectra of PbO-Sb_2O_3-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 analysis of the data on magnetic susceptibility of PbO-Sb_2O_3-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 emission spectra of all the MnO mixed PbO-Sb_2O_3-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.

The values of dielectric parameters viz., ε', tan δ and σ_{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.

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Chapter-5 of the thesis is devoted to report a variety of physical properties that include dielectric studies, spectroscopic studies (IR, optical absorption) of crystallized $PbO\text{-}Sb_2O_3\text{-}As_2O_3$ glasses with varying concentrations of NiO as nucleant. The crystallization behavior and microstructure of glass ceramic products produced have also been investigated by means of XRD, SEM,

DTA and EDS. The study is also intended to comment on the suitability of these glass ceramic materials for laser emission in NIR region.

Within the possible glass forming region of $PbO\text{-}Sb_2O_3\text{-}As_2O_3$ system, a particular compositions $40PbO\text{-}(20\text{-}x)Sb_2O_3\text{-}40As_2O_3$: x NiO with the value of x ranging from 0 to 1.5 mol% is chosen for the present study; the samples are labeled as N_0 (x=0), N_2 (x=0.2), N_4 (x=0.4), N_6 (x=0.6), N_8 (x=0.8), N_{10} (x=1.0), N_{15} (x=1.5).

The glass specimens prepared with various concentrations of NiO were heat treated in a furnace at 300 ^oC for 6 h. After the heat treatment in the furnace at specified temperature, the samples were chilled in air to room temperature.

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%.

The optical 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) $\rightarrow$ $^3T_2$ (F) (O_h1), $^3T_1$ (F) (O_h2), $^1T_2$ (D) (O_h3) and

$^3A_2$ (F) $\rightarrow$ $^3T_1$ (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.

The effective magnetic moment evaluated from magnetic susceptibility of NiO mixed glass ceramics indicated gradual increase from 3.33 μ_B (for sample N_8) to 4.05 μ_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 %.

The dielectric studies of NiO mixed PbO-Sb_2O_3-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.

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References closely related to the present work have been compiled to the extent possible and given at the end of the relevant chapter.