PREFACE

The present thesis deals with the studies on “Microstructural, dielectric and spectroscopic properties of Li$_2$O–Nb$_2$O$_5$–ZrO$_2$–SiO$_2$ glass system crystallized with CuO and V$_2$O$_5$ & Emission features of Nd$^{3+}$ and Ho$^{3+}$ ions in Li$_2$O–Nb$_2$O$_5$/Ta$_2$O$_5$/La$_2$O$_3$–ZrO$_2$–SiO$_2$ glass systems”. 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 including photo-induced second order susceptibility studies of Li$_2$O–Nb$_2$O$_5$–ZrO$_2$–SiO$_2$ glass systems crystallized with varying concentration of CuO and V$_2$O$_5$ and also the spectroscopic properties Li$_2$O–Nb$_2$O$_5$/Ta$_2$O$_5$/La$_2$O$_3$–ZrO$_2$–SiO$_2$ glasses doped with Nd$^{3+}$ and Ho$^{3+}$ ions.

SiO$_2$ serves as the prototype of a glass. Its structure is the simplest of all glass structures. The structural unit consists of slightly distorted SiO$_4$ tetrahedra with all BOs. Hence a strongly connected three-dimensional network is established. The disorder in the structure is caused mainly by variations in the bond angles $\beta$ and the torsion angles and only to a minor extend by the distortion of the tetrahedra. There is a wide glass forming range in the binary alkali silicate system (alkali ions M = Li, Na, K, Rb, Cs). The network modifiers (alkali ions) enter the glass as singly charged cations and occupy interstitial sites. Their charge is compensated by NBOs created by breaking bridges between adjacent SiO$_4$ tetrahedra. The creation of NBOs reduces the connectivity of the glass.
network, and hence the thermal expansion coefficient, the fluidity, diffusion, electrical conduction, and chemical corrosion all increase with increasing modifier content.

Further, thermally poled silica based glasses and glass ceramics under electrical fields are the materials of choice for applications in optoelectronics because of their excellent optical properties; recently for some of the silicate based glasses, the value of $\chi^{(2)}$ is reported to be $\sim 0.30 \text{ pm/V}$. For applications like modulators, routers or switches, the amplitude of the electric field $E_{DC}$ recorded in the material has to be strong and stable at the place of the optical waveguides.

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 transition metal ions, copper ion is a very interesting ion to probe in the glass ceramic material. In the silicate glass matrices this ion is expected to exist as metallic Cu, cuprous Cu\(^+\), or cupric Cu\(^{2+}\) ions as per the following redox reaction

\[
4\text{Cu}^{2+} + 2\text{O}_2^- \leftrightarrow 4\text{Cu}^+ + \text{O}_2.
\]

It is known that the valence state in copper affects not only optical, chemical, electrical and mechanical properties but also the glass-forming ability of the system. Due to the crystallization, there is a possibility for the formation of copper nanoclusters in glasses; such nano crystals are expected to exhibit absorption bands at characteristic surface plasma resonance in the visible region and optical nonlinearity. In view of these qualities, the glass ceramics containing copper ions in different oxidation states are highly useful for consideration of the materials to use in electrical memory switching devices. There are also reports suggesting that copper ions in some glass ceramics containing alkali ions like lithium do exist in Cu\(^{3+}\) state and form LiCuO\(_2\) crystal phases with Li-layered structures. Li–Cu–O containing systems have attracted great interest as cathode material for an advanced lithium ion batteries.

Similarly another interesting transition metal ion viz., V\(_2\)O\(_5\) for the simple reason that the presence of vanadium ions makes the material to exhibit semiconducting behavior with the electrical conductivity >10\(^{-3}\) to 10\(^{-5}\) (ohm cm\(^{-1}\)) due to electron hopping between V\(^{4+}\) to V\(^{5+}\) ions. V\(_2\)O\(_5\) containing glasses are being extensively used in memory and switching devices. The crystallization of
these materials, further leads to the formation of Li$_2$V$_2$O$_5$ crystal grains in which vanadium ions present in V$^{4+}$ state. Presence of such complexes facilitate to accelerate the rate of hopping of electron between V$^{4+}$ and V$^{5+}$ ions which ultimately lead to the enhancement of conductivity. The process of hopping of the electrons between V$^{4+}$ and V$^{5+}$ ions in the presence of larger concentrations of mobile cations like lithium ions is highly interesting and useful to investigate in the multi component glass ceramic systems like Li$_2$O–Nb$_2$O$_5$–ZrO$_2$–SiO$_2$ in view of huge technological importance of this material.

Further, the lithium zirconium silicate glasses are more stable against the pumping light, possess relatively high refractive index and are transparent up to the far infrared wavelengths and allow to incorporating the rare earth dopants in the desired site positions. These factors favor lithium zirconium silicate glasses mixed with Nb$_2$O$_5$, La$_2$O$_3$ and Ta$_2$O$_5$ to offer suitable environment for hosting lasing ions like Nd$^{3+}$ and Ho$^{3+}$ to give out high luminescence efficiency in the NIR region. Hence, a part of the thesis is devoted to study the fluorescence characteristics of two rare earth ions Nd$^{3+}$ and Ho$^{3+}$ ions that exhibit high efficiency in visible and NIR regions, in Li$_2$O–ZrO$_2$–SiO$_2$ glasses mixed with Nb$_2$O$_5$, La$_2$O$_3$ and Ta$_2$O$_5$, in particularly their fluorescence time decays, which are crucial for the optical triggers and laser gain media. This study is further intended to compare the probabilities of principal luminescence transitions of rare earth ions, determining their intensities in amorphous matrices and to explore the advantage of addition of Nb$_2$O$_5$, La$_2$O$_3$ and Ta$_2$O$_5$ on luminescence efficiency.
Thus the clear objectives of the present study are to prepare, characterize and

- To have a comprehensive understanding over the influence of copper ions on structural aspects of Li$_2$O–Nb$_2$O$_5$–ZrO$_2$–SiO$_2$ glass ceramics by investigating the dielectric properties, optical absorption, ESR, IR, luminescence spectra and photoinduced second order susceptibility.

- To have a broad perceptive over the role of vanadyl ions on the structure of Li$_2$O–Nb$_2$O$_5$–ZrO$_2$–SiO$_2$ glass ceramic system from a systematic study of various dielectric properties coupled with spectroscopic studies.

- To investigate the luminescence efficiencies of of Nd$^{3+}$ and Ho$^{3+}$ ions doped Li$_2$O–ZrO$_2$–SiO$_2$ glasses mixed with Nb$_2$O$_5$, Ta$_2$O$_5$ and La$_2$O$_3$.

The compositions of the glasses used for the present study are

1. (30-x) Li$_2$O-10 Nb$_2$O$_5$-5ZrO$_2$-55 Si$_2$O$_2$: x CuO (0 ≤ x ≤ 0.3)
2. (30-x) Li$_2$O-10 Nb$_2$O$_5$-5ZrO$_2$-55 Si$_2$O$_2$: x V$_2$O$_5$ (0 ≤ x ≤ 1.0)
3. 30 Li$_2$O-9 Nb$_2$O$_5$/Ta$_2$O$_5$/La$_2$O$_5$-5 ZrO$_2$-55 SiO$_2$: 1 Nd$_2$O$_3$/Ho$_2$O$_3$

The details of the studies carried out are

1) Dielectric constant ($\varepsilon'$), loss (tan $\delta$) and a.c conductivity $\sigma_{ac}$ in frequency range $10^2$ to $10^5$ Hz and in the temperature range 30- 250 °C.
2) Optical absorption in the UV, visible and NIR regions at room temperature.
3) Photoluminescence spectra in the visible and NIR regions at room temperature.
4) Electron spin resonance spectra at room temperature for CuO and V$_2$O$_5$ mixed samples at room temperature.
5) Infrared spectra of transition metal oxide mixed glasses and glass ceramic samples in the region 400 to 4000 cm\(^{-1}\).

6) Raman spectra in the region 100 to 2000 cm\(^{-1}\) at room temperature using argon laser 514 nm as the excitation source.

7) Photoinduced second order susceptibility measurements excited with Er:Glass laser at room temperature.

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

**CHAPTER–I** 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 Li\(_2\)O–Nb\(_2\)O\(_5\)–ZrO\(_2\)–SiO\(_2\): CuO/V\(_2\)O\(_5\) glasses and glass ceramics and spectroscopic properties of Nd\(^{3+}\)/Ho\(^{3+}\) doped Li\(_2\)O–ZrO\(_2\)–SiO\(_2\) glasses mixed with Nb\(_2\)O\(_5\), La\(_2\)O\(_3\) and Ta\(_2\)O\(_5\).

**CHAPTER–II** gives the description of experimental methods employed in the preparation and characterization of Li\(_2\)O–Nb\(_2\)O\(_5\)–ZrO\(_2\)–SiO\(_2\): CuO/V\(_2\)O\(_5\) and Li\(_2\)O–Nb\(_2\)O\(_5\)/Ta\(_2\)O\(_5\)/La\(_2\)O\(_3\)–ZrO\(_2\)–SiO\(_2\): Nd\(_2\)O\(_3\)/Ho\(_2\)O\(_3\) glasses. The samples were crystallized by heating the glass samples for 24 h at the crystallization temperature identified from the DSC/DTA studies. The details of the apparatus used and the techniques adopted for characterization and for measuring dielectric properties, optical absorption, ESR, IR, photoinduced second order susceptibility and photoluminescence are also described in detail in this chapter.
The scanning electron microscopic (SEM) pictures of the pre-heated samples containing different concentration of transition metal oxides/rare earth oxides do not show any significant crystallinity. The pictures of the crystallized Li$_2$O–Nb$_2$O$_5$–ZrO$_2$–SiO$_2$ 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 Li, Nb, Ta, La, Zr, Si, O and Cu/V/Ln 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 scanning calorimetric (DSC) / differential thermal analysis studies (DTA) of all the crystallized samples exhibit 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 DSC/DTA data could further be explained in terms of surface and bulk crystallization in all the series of the samples.

In CHAPTER-III the results of investigations on spectroscopic properties (optical absorption, ESR, IR, photoinduced second order susceptibility) and dielectric properties of Li$_2$O–Nb$_2$O$_5$–ZrO$_2$–SiO$_2$ glasses crystallized with different concentrations of CuO have been presented and are discussed in the light of principal role of the copper valence states and its co-ordination number in the valence state.
The detailed compositions chosen for this study are as follows:

$C_0$: 30.00Li$_2$O–10Nb$_2$O$_5$–5ZrO$_2$–55SiO$_2$

$C_5$: 29.95Li$_2$O–10Nb$_2$O$_5$–5ZrO$_2$–55SiO$_2$: 0.05CuO

$C_{10}$: 29.90Li$_2$O–10Nb$_2$O$_5$–5ZrO$_2$–55SiO$_2$: 0.10CuO

$C_{15}$: 29.85Li$_2$O–10Nb$_2$O$_5$–5ZrO$_2$–55SiO$_2$: 0.15CuO

$C_{20}$: 29.80Li$_2$O–10Nb$_2$O$_5$–5ZrO$_2$–55SiO$_2$: 0.20CuO

$C_{25}$: 29.75Li$_2$O–10Nb$_2$O$_5$–5ZrO$_2$–55SiO$_2$: 0.25CuO

$C_{30}$: 29.70Li$_2$O–10Nb$_2$O$_5$–5ZrO$_2$–55SiO$_2$: 0.30CuO

The X-ray diffraction pattern of CuO mixed ceramic samples exhibit peaks due to Li$_6$CuO$_4$, CuSiO$_3$, Li$_6$Si$_2$O$_7$, Li$_2$Si$_3$O$_5$, Li$_8$SiO$_6$, Li$_2$Si$_2$O$_5$, Li$_4$SiO$_4$, Li$_2$SiO$_3$, Li$_2$Si$_3$O$_7$, Li$_3$NbO$_4$, Li$_{10}$Nb$_2$O$_{10}$, Li$_8$Nb$_2$O$_9$, LiNbO$_2$, Li$_{12}$Nb$_{17}$O$_{33}$, LiNb$_3$O$_8$, Li$_2$Nb$_{32}$O$_{81}$, Li$_7$NbO$_6$, LiNbO$_3$, ZrNb$_2$O$_7$, ZrNb$_{10}$O$_{27}$, ZrNb$_{14}$O$_{37}$, Zr$_6$Nb$_2$O$_{17}$, CuNb$_2$O$_6$, CuNbO$_3$ and Cu$_3$Nb$_2$O$_8$ crystal phases. The presence of LiCuO$_2$ orthorhombic crystal phases points out that there is a possibility for the copper ions to exist in Cu$^{3+}$ state.

The infrared transmission spectrum of dopant free Li$_2$O–Nb$_2$O$_5$–ZrO$_2$–SiO$_2$ glass ceramic sample exhibited the following bands (i) At 1050 cm$^{-1}$ due to Si–O–Si asymmetric vibrations (ii) 800 cm$^{-1}$ due to bending mode of bridging oxygen perpendicular to Si–Si axis within the Si–O–Si plane (symmetrical vibrational band) (iii) 980 cm$^{-1}$ due to Si–O–Zr linkages (iv) 850 and 600 cm$^{-1}$ due to Nb=O, Nb–O–Nb stretching vibrations (v) 530 and 700 cm$^{-1}$ due to Zr–O–Zr vibrations of ZrO$_4$/v$_3$-NbO$_6$ structural units and (vi) 475 cm$^{-1}$ due to Si–O–Si /
O–Si–O bending modes. As the concentration of CuO is increased, the bands due to asymmetrical vibrations of silicate and other structural units are observed to grow at the expense of symmetrical bands with a slight shift towards lower energies. A slight reversal trend in the intensities of these bands could be visualized when the concentration of CuO is raised beyond 0.20 mol%.

The optical absorption spectra of Li$_2$O–Nb$_2$O$_5$–ZrO$_2$–SiO$_2$: CuO glass ceramics recorded at room temperature have exhibited a broad band with a meta center between 800-850 nm and is assigned to $^2B_{1g} \rightarrow ^2B_{2g}$ transition of Cu$^{2+}$ ions. With increase in the concentration of CuO (at least up to 0.20 mol%), the half width at full maximum and peak height of this broad band is observed to increase. Further, a considerably larger increase in the cut-off wavelength (from 321 to 380 nm) is observed due to increasing concentration of CuO. The optical band gaps ($E_o$) of these glasses were evaluated from Urbach plot and the value of $E_o$ is found to decrease with the increase in the content of CuO.

Luminescence emission spectra recorded at room temperature of Li$_2$O–Nb$_2$O$_5$–ZrO$_2$–SiO$_2$: CuO glass ceramics recorded at room temperature at the excitation wavelength corresponding to the absorption edge. Emission spectra exhibited emission band in the yellow region centered at about 552 nm and a weak blue emission centered at about 440 nm. These bands are more intense in the spectra of the samples C$_{25}$ and C$_{30}$. The spectrum of the amorphous samples exhibited very feeble kinks at about the same wavelength. Since these bands are charge transfer bands of the copper ions, it may be noted here that the spectrum of
either amorphous or crystallized samples free of CuO does not exhibit any emission bands.

The photoinduced second order susceptibility versus applied dc field is measured for Li$_2$O–Nb$_2$O$_5$–ZrO$_2$–SiO$_2$: CuO glass ceramics at optimal temperature 270 °C. It indicated a substantial increase of the second-order susceptibility with the increase of the field for all the samples. With the concentration of the crystallizing agent the second-order susceptibility exhibited maximal effect at about 0.2 mol% of CuO and for further increase of CuO content, a considerable decrease of second-order susceptibility could be observed. For the amorphous samples the maximal effects were observed at about 320 °C for the same pump density and dc field treatment.

ESR spectra of Li$_2$O–Nb$_2$O$_5$–ZrO$_2$–SiO$_2$: CuO glass ceramics recorded at room temperature have exhibited a strong asymmetric signal with a hyperfine structure partially resolved at $g_\perp \sim$2.08 and a shallow quadruplet at about $g_\parallel \sim$2.4. The components of g are observed to vary considerably with the concentration of CuO. The line width of parallel and perpendicular hyperfine peak is observed to increase with the order of magnetic quantum number $m_l$. As the concentration of CuO is increased beyond 0.2 mol%, a considerable decrease in the intensity of the signal is observed. For the pre-crystallized samples the intensity of this signal is found to be comparatively lower.

Dielectric studies of Li$_2$O–Nb$_2$O$_5$–ZrO$_2$–SiO$_2$: CuO glass ceramics indicated that dielectric parameters viz., $\varepsilon'$, $\tan \delta$ and $\sigma_{ac}$ at any frequency 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 CuO up to 0.2 mol%; this is an indication of an increase in the space charge polarization. Such increase is due to the increasing concentration of Cu$^{2+}$ ions that act as modifiers in these samples. The observed dielectric relaxation effects in these glass ceramics may be attributed to the association of octahedrally positioned Cu$^{2+}$ ions with a pair of cationic vacancies as observed in a number of conventional glasses, glass ceramics and crystals that contain divalent positive ions. The observed trend of increase of conductivity and decrease of activation energy for $x < 0.2$ mol% and, decrease of conductivity and increase of activation energy for $x > 0.2$ mol% of CuO content suggests switch over of predominance of conduction mechanism from ionic to electronic.

The objective of the **CHAPTER-IV** is to synthesize Li$_2$O–Nb$_2$O$_5$–ZrO$_2$–SiO$_2$ glass ceramics with different concentrations of V$_2$O$_5$ as nucleating agent, to characterize by variety of techniques viz., XRD, SEM, DTA and energy dispersive spectra (EDS). The studies taken up are spectroscopic properties (optical absorption, IR and photoluminescence) and dielectric properties.

The detailed compositions chosen for this study are as follows:

$V_0$: 30.0Li$_2$O–10Nb$_2$O$_5$–5ZrO$_2$–55SiO$_2$

$V_1$: 29.9Li$_2$O–10Nb$_2$O$_5$–5ZrO$_2$–55SiO$_2$: 0.1V$_2$O$_5$

$V_3$: 29.7Li$_2$O–10Nb$_2$O$_5$–5ZrO$_2$–55SiO$_2$: 0.3V$_2$O$_5$

$V_5$: 29.5Li$_2$O–10Nb$_2$O$_5$–5ZrO$_2$–55SiO$_2$: 0.5V$_2$O$_5$
V_8: 29.2Li_2O–10Nb_2O_5–5ZrO_2–55SiO_2: 0.8V_2O_5
V_{10}: 29.0Li_2O–10Nb_2O_5–5ZrO_2–55SiO_2: 1.0V_2O_5

The X-ray diffraction studies of V_2O_5 glass ceramic samples exhibit peaks due to the formation of Li_2V_2O_5, Nb_6V_2O_19, Nb_2V_2O_9 crystalline phases detected from the XRD studies emphasizes the presence of vanadium ions in V^{4+} state in addition to V^{5+} state in these glass ceramics. The relative increase in the intensity of the diffraction peaks due to these crystallites indicates an increasing concentration of vanadyl complexes with the increase in the concentration of nucleating agent in the glass matrix.

Infrared spectra of these V_2O_5 doped glass ceramics have exhibited bands at 980 cm\(^{-1}\), 800 cm\(^{-1}\) can be considered as common vibrational modes due to Si–O–V stretchings where as the band at 600 cm\(^{-1}\) can be considered as common vibrations due to Nb–O–V chains. As the concentration of V_2O_5 is increased in the glass ceramics gradually, the bands due to asymmetrical vibrations of silicate and other structural units are observed to grow at the expense of symmetrical bands.

The optical absorption spectra of Li_2O–Nb_2O_5–ZrO_2–SiO_2: V_2O_5 glass ceramics recorded at room temperature in the wavelength region 400–1200 nm. For the vanadium free glass ceramic the absorption edge is observed at 368 nm. With the gradual inclusion of crystallizing agent V_2O_5, the absorption edge exhibited red shift. From the observed absorption edges, the optical band gaps (E_\text{g}) of these glass ceramics are evaluated by drawing Urbach plots. The value of E_\text{g} is found to be the lowest for the glasses crystallized with 1.0 mol\(\%\) of V_2O_5. The
The spectrum of glass ceramic sample V_1 exhibited two broad absorption bands with the meta-centers at 634 and 1040 nm attributed to ^2B_2→^2B_1 and ^2B_2→^2E transitions of VO^{2+} ions. A continuous increase of absorption under these bands is observed with the content of V_2O_5 in the glass ceramic.

The photoluminescence spectra of V_2O_5 doped glass ceramics recorded at room temperature at the excitation wavelength corresponding to the transition ^2B_2→^2B_1 in the absorption spectra exhibited a broad emission band peaking in the region 750-850 nm. This band is identified due to ^2E→^2T_2 transition of vanadyl ion; the band shows signs of a slight asymmetry in the higher wavelength region. With the growing content of crystallizing agent V_2O_5, the half width of the peak is observed to increase with shifting of meta-centre towards higher wavelength.

The ESR spectra of V_2O_5 mixed glass ceramic samples recorded at room temperature are observed to be complex made up of resolved hyperfine components arising from unpaired 3d^1 electron of ^{51}V isotope. As the concentration of nucleating agent V_2O_5 is increased, an increasing degree of resolution and the intensity of the signal have been observed. The values of g and g⊥ evaluated from these spectra are observed to increase with increase in the concentration of V_2O_5.

The dielectric studies of these glass ceramics indicated that with the gradual increase of crystallizing agent V_2O_5, the values of ε', tan δ and σ_{ac} are found to increase at any frequency and temperature and the activation energy for ac
conduction is observed to decrease; this observation indicates an increase in the space charge polarization owing to the enhanced degree of disorder in the glass network. The value of the effective activation energy associated with the dipoles is observed to decrease with increase in the content of vanadyl ions in the glass ceramic network; from this observation it is concluded that there is an increasing freedom for dipoles to orient in the field direction due to increasing degree of disorder in glass ceramic network. These studies also reveal that there is a decrease in the dielectric breakdown strength with increase in the concentration of crystallizing agent V$_2$O$_5$.

In **CHAPTER-V** an attempt is made to characterize the optical absorption and the fluorescence spectra of two lanthanide ions viz., Nd$^{3+}$ and Ho$^{3+}$ in lithium zirconium silicate glasses mixed with Nb$_2$O$_5$, Ta$_2$O$_5$ and La$_2$O$_3$. The study is further intended to throw some light on the relationship between the structural modifications and luminescence efficiencies and to explore the influence of addition of Nb/Ta/La ions to glass host over the luminescence efficiencies.

From the glass-forming region of Li$_2$O–Nb$_2$O$_5$/Ta$_2$O$_5$/La$_2$O$_3$–ZrO$_2$–SiO$_2$ glass systems, the following compositions are chosen for the present study

**Nd$^{3+}$ series:**

LNZSN : 30Li$_2$O–9Nb$_2$O$_5$–5ZrO$_2$–55SiO$_2$: 1Nd$_2$O$_3$

LTZSN : 30Li$_2$O–9Ta$_2$O$_5$–5ZrO$_2$–55SiO$_2$: 1Nd$_2$O$_3$

LLZSN : 30Li$_2$O–9La$_2$O$_3$–5ZrO$_2$–55SiO$_2$: 1Nd$_2$O$_3$

**Ho$^{3+}$ series:**
LNZSN : 30Li₂O–9Nb₂O₅–5ZrO₂–55SiO₂: 1Hod₂O₃
LTZSN : 30Li₂O–9Ta₂O₅–5ZrO₂–55SiO₂: 1Ho₂O₃
LLZSN : 30Li₂O–9La₂O₃–5ZrO₂–55SiO₂: 1Ho₂O₃

The optical absorption spectra of Nb₂O₅, La₂O₃ and Ta₂O₅ mixed Li₂O–ZrO₂–SiO₂: Nd³⁺ and Ho³⁺ doped glasses recorded at room temperature in the wavelength region 300-2000 nm exhibited several absorption bands these levels are assigned to the following appropriate electronic transition:

Nd³⁺: \(4I_{9/2} \rightarrow 2P_{1/2}, 2D_{3/2}+4G_{11/2}, 4G_{9/2}+4G_{7/2}, 4G_{5/2}, 2H_{11/2}, 4F_{9/2}, 4F_{7/2}, 4F_{5/2}, 4F_{3/2}\)

Ho³⁺: \(5I_8 \rightarrow 5G_6, 5G_5, 5F_1, 5F_3, (5F_4+5S_2), 5F_5, 5I_5, 5I_6, 5I_7\)

By performing least square fitting analysis the J-O parameters for these samples are computed and are found to show the following trend:

Nd³⁺: \(\Omega_2 > \Omega_6 > \Omega_4\) (for all the three series)

Ho³⁺: \(\Omega_2 > \Omega_4 > \Omega_6\) (for Nb₂O₅ series)

\(\Omega_2 > \Omega_6 > \Omega_4\) (for Ta₂O₅ and La₂O₃ series)

The luminescence spectra recorded at room temperature for these glass have exhibited the bands corresponding to the following transitions:

Nd³⁺: \(4F_{3/2} \rightarrow 4I_{9/2}, 11/2, 13/2\)

Ho³⁺: \(5F_3 \rightarrow 5I_8, 5S_2 \rightarrow 5I_8, 5G_4 \rightarrow 5I_6, 5K_8 \rightarrow 5I_7, 5F_5 \rightarrow 5I_8, 5G_5 \rightarrow 5I_6, 5F_4 \rightarrow 5I_7, 5G_5 \rightarrow 5I_5, 5F_2 \rightarrow 5I_6, 5F_3 \rightarrow 5I_6, 5I_5 \rightarrow 5I_8, 5I_7 \rightarrow 5I_8\)
Emission bands exhibited by Ta$_2$O$_5$ and Nb$_2$O$_5$ mixed glasses in the region 480–505 nm are considered as superposition of emission due to Ta$^{5+}$ and Nb$^{5+}$ ions and $^5F_3 \rightarrow ^5I_8$, $^5S_2 \rightarrow ^5I_8$ transitions of Ho$^{3+}$ ions.

Branching ratio ‘$\beta$’ of $^4F_{3/2} \rightarrow ^4I_{11/2}$ of Nd$^{3+}$ ion and $^5S_2 \rightarrow ^5I_8$ transition of Ho$^{3+}$, among various transitions originated from $^4F_{3/2}$ and $^5S_2$ of Nd$^{3+}$ and Ho$^{3+}$ ions respectively are found to be the highest for the glass mixed with La$_2$O$_3$, indicating that these glasses exhibit better lasing action among all three glasses under investigation.

The comparison table of radiative life times and quantum yields for glasses and glass ceramics containing Nd$^{3+}$ and Ho$^{3+}$ samples are given in Tables 1 and 2. The comparison shows the highest value of $\eta$ for La$_2$O$_3$ mixed glasses. Such high value is connected not only with the higher radiative relaxation probability but also with a reduction of the non-radiative transition probability. This is possibly due to the low electron–phonon coupling of the rare earth ions with the high-energy phonons in case of La$_2$O$_3$ mixed glasses and relatively higher degree of this coupling with low-energy phonons for Nb$_2$O$_5$ and Ta$_2$O$_3$ mixed glasses.
Table 1
Radiative lifetime of $^{4}F_{3/2}$ level and quantum efficiency for the transition $^{4}F_{3/2} \rightarrow ^{4}I_{11/2}$ of Nd$^{3+}$ ion in Li$_2$O–Nb$_2$O$_5$/La$_2$O$_3$/Ta$_2$O$_5$–ZrO$_2$–SiO$_2$ glasses.

<table>
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<th>LNZSN</th>
<th>LTZSN</th>
<th>LLZSN</th>
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<tr>
<td>Measured ($\tau_m$) (µs)</td>
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<td>95.5</td>
<td>106.4</td>
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<td>Calculated ($\tau$) (µs)</td>
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<td>161</td>
<td>177</td>
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<td>Quantum yield ($\eta$%)</td>
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<td>59.3</td>
<td>60.1</td>
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</table>

Table 2
Radiative lifetime of the level $^5S_2$ and quantum efficiency for $^5S_2 \rightarrow ^5I_8$ transition of Ho$^{3+}$ ion in Li$_2$O–Nb$_2$O$_5$/La$_2$O$_3$/Ta$_2$O$_5$–ZrO$_2$–SiO$_2$ glasses.

<table>
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<th>LNZSH</th>
<th>LTZSH</th>
<th>LLZSH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured ($\tau_m$) (µs)</td>
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<td>60.5</td>
<td>68.0</td>
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<tr>
<td>Calculated ($\tau$) (µs)</td>
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<td>195</td>
<td>199</td>
</tr>
<tr>
<td>Quantum yield ($\eta$%)</td>
<td>29.3</td>
<td>31.0</td>
<td>34.2</td>
</tr>
</tbody>
</table>

CHAPTER-VI reports brief summary and conclusions drawn from the investigation carried out on a variety of properties viz., (a) dielectric, and (b) spectroscopic properties of Li$_2$O–Nb$_2$O$_5$–ZrO$_2$–SiO$_2$ glass systems crystallized with varying concentration of CuO and V$_2$O$_5$ and also the spectroscopic properties Li$_2$O–Nb$_2$O$_5$/Ta$_2$O$_5$/La$_2$O$_3$–ZrO$_2$–SiO$_2$ glasses doped with Nd$^{3+}$ and Ho$^{3+}$ ions.
References closely related to the present work have been compiled to the extent possible and given at the end of the relevant chapter.