PREFACE

The present thesis deals with the studies on "Dielectric and spectroscopic investigations on multi component lithium aluminium zirconium silicate glasses mixed with TiO₂ and WO₃ & Spectroscopic features of Pr³⁺ and Er³⁺ ions in Li₂O–ZrO₂–SiO₂ glass matrices mixed with some sesquioxides". 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 Li₂O–Al₂O₃–ZrO₂–SiO₂ glass systems doped with varying concentration of TiO₂ and WO₃ and also the spectroscopic properties Li₂O–Al₂O₃/Y₂O₃/Sc₂O₃–ZrO₂–SiO₂ glasses doped with Pr³⁺ and Er³⁺ ions.

SiO₂ serves as the prototype of a glass. Its structure is the simplest of all glass structures. The structural unit consists of slightly distorted SiO₄ 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 β and the torsion angles and only to a minor extent 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.

Glass 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. As a result, glasses are likely to have outstanding mechanical, optical, electrical and thermal characteristics.

Normally, the ions of titanium, exist in the glass in Ti$^{4+}$ state and participate in the glass network forming with TiO$_4$, TiO$_6$ and some times with TiO$_5$ (comprising of trigonal bipyramids) structural units. However, there are reports suggesting that these ions may also exist in Ti$^{3+}$ valence state in some of the glass matrices and acts as modifiers; such variation in the coordination and valence of titanium ions are expected to cause the structural modifications and local field variations in the glass network and expected to influence the physical properties to a large extent.
The presence of tungsten ions in silicate glasses especially, is expected to influence their physical properties to a large extent since the these ions exist in different valence states viz., $W^{6+}$, $W^{5+}$ and $W^{4+}$, as per the following thermo reversible disproportionate reaction regardless of the original oxidation state of the ion in the starting glass batch.

$$W^{5+} + W^{5+} \leftrightarrow W^{4+} + W^{6+}.$$ 

$W^{6+}$ ion participates in the glass network with different structural units like $WO_4$ ($T_d$) and $WO_6$ ($O_h$) where as $W^{5+}$ ions form the complexes of the type $W^{5+}O_3^-$ and occupy octahedral positions. Some recent studies on $WO_3$ containing glass networks like phosphate, borate, silicate etc., have indicated that the increase of $WO_3$ causes a progressive breaking of the tetrahedral linkages of the host glass network.

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 $Al_2O_3$, $Y_2O_3$ and $Sc_2O_3$ to offer suitable environment for hosting lasing ions like $Pr^{3+}$ and $Er^{3+}$ 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 $Pr^{3+}$ and $Er^{3+}$ ions that exhibit high
efficiency in visible and NIR regions, in Li$_2$O–ZrO$_2$–SiO$_2$ glasses mixed with Al$_2$O$_3$, Y$_2$O$_3$ and Sc$_2$O$_3$, 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 Al$_2$O$_3$, Y$_2$O$_3$ and Sc$_2$O$_3$ 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 titanium ions on structural aspects of Li$_2$O–Al$_2$O$_3$–ZrO$_2$–SiO$_2$ glasses by investigating the dielectric properties, optical absorption, ESR, IR, luminescence spectra.

- To have a broad perceptive over the role of tungsten ions on the structure of Li$_2$O–Al$_2$O$_3$–ZrO$_2$–SiO$_2$ glass system from a systematic study of various dielectric properties coupled with spectroscopic studies.

- To investigate the luminescence efficiencies of Pr$^{3+}$ and Er$^{3+}$ ions doped Li$_2$O–ZrO$_2$–SiO$_2$ glasses mixed with Al$_2$O$_3$, Y$_2$O$_3$ and Sc$_2$O$_3$.

The compositions of the glasses used for the present study are

1. (30-x) Li$_2$O-10 Al$_2$O$_3$-5ZrO$_2$-55 Si$_2$O$_2$: x TiO$_2$ (0 ≤ x ≤ 5)

2. (30-x) Li$_2$O-10 Al$_2$O$_3$-5ZrO$_2$-55 Si$_2$O$_2$: x WO$_3$ (0 ≤ x ≤ 5)
3. 30 Li$_2$O-9 Al$_2$O$_3$/Y$_2$O$_3$/Sc$_2$O$_3$-5 ZrO$_2$-55 SiO$_2$: 1 Pr$_2$O$_3$/Er$_2$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 $^\circ$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 TiO$_2$ and WO$_3$ mixed samples at room temperature.

5) Infrared spectra of transition metal oxide mixed glasses and glass 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.

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–Al$_2$O$_3$–ZrO$_2$–SiO$_2$: TiO$_2$/WO$_3$ glasses and spectroscopic properties of Pr$^{3+}$/Er$^{3+}$ doped Li$_2$O–ZrO$_2$–SiO$_2$ glasses mixed with Al$_2$O$_3$, Y$_2$O$_3$ and Sc$_2$O$_3$. 
CHAPTER-II gives the description of experimental methods employed in the preparation and characterization of Li$_2$O–Al$_2$O$_3$–ZrO$_2$–SiO$_2$: TiO$_2$/WO$_3$ and Li$_2$O–Al$_2$O$_3$/Y$_2$O$_3$/Sc$_2$O$_3$–ZrO$_2$–SiO$_2$: Pr$_2$O$_3$/ Er$_2$O$_3$.

The details of the apparatus used and the techniques adopted for characterization and for measuring dielectric properties, optical absorption, ESR, IR, and photoluminescence are also described in detail in this chapter.

The differential thermal analysis studies (DTA) of all the samples exhibit endothermic change due to the glass transition followed by multiple exothermic effects due to the crystal growth have been observed for all the glass samples. The 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, photoluminescence) and dielectric properties of Li$_2$O–Al$_2$O$_3$–ZrO$_2$–SiO$_2$ glasses with different concentrations of TiO$_2$ have been presented and are discussed in the light of principal role of the titanium valence states and its co-ordination number in the valence state.

The detailed compositions of the glasses used in the present study are as follows:

- $T_0$: 30 Li$_2$O–10Al$_2$O$_3$–5ZrO$_2$–55SiO$_2$
- $T_1$: 29 Li$_2$O–10Al$_2$O$_3$–5ZrO$_2$–55SiO$_2$: 1.0TiO$_2$
- $T_2$: 28 Li$_2$O–10Al$_2$O$_3$–5ZrO$_2$–55SiO$_2$: 2.0TiO$_2$
Our visual examination of the samples, absence of peaks in the X-Ray diffraction, the presence of exothermic and endothermic effects in the thermograms clearly suggest that the samples prepared are of amorphous in nature. The IR spectrum of TiO₂ free Li₂O–Al₂O₃–ZrO₂–SiO₂ glass has exhibited conventional bands due to Si–O–Si asymmetric and symmetric vibrations at about 1016 cm⁻¹ and at about 820 cm⁻¹ respectively. In ZrO₂ containing silicate glasses the asymmetrical band was considered due to the vibrations of Si–O–Zr linkages. The symmetrical band is in fact identified as bending mode of bridging oxygen perpendicular to Si–Si axis with in the Si–O–Si plane. In this region, the band due to vibrations of AlO₄ structural units is also expected. The vibrational band due to AlO₆ structural units is located at about 452 cm⁻¹; in this region the band due to Si–O–Si rocking motion is also reported. Hence the linkages of the type Al–O–Si is predictable in the glass network.

Two other bands at about 535 and 740 cm⁻¹ corresponding to the Zr–O–Zr vibrations of ZrO₄ structural units are also located in the spectra of this glass. With the gradual introduction of TiO₂ in the glass network, all the symmetrical bands are observed to grow at the expense of asymmetrical bands; additionally
a prominent band at about 630 cm\(^{-1}\) attributed to the vibrations of TiO\(_6\) structural units is also located in these spectra. The band due to Ti–O–Ti symmetric stretching vibrations of TiO\(_4\) units is also expected at about 740 cm\(^{-1}\); in the spectra of the studied glasses this band seems to have merged with the band due to tetrahedral zirconia. Hence the band observed at about 740 cm\(^{-1}\) can be considered as due to the vibrations of Zr–O–Ti units.

The optical absorption spectra for Li\(_2\)O–Al\(_2\)O\(_3\)–ZrO\(_2\)–SiO\(_2\): TiO\(_2\) glass samples recorded at room temperature in the wavelength region 300-900 nm. The absorption edge observed at 376.6 nm for the glass sample T\(_2\) exhibited blue shift with increase in the concentration of TiO\(_2\). Additionally, the spectrum of glass T\(_2\) exhibited two clearly resolved absorption bands at 544 and 700 nm. As the concentration of TiO\(_2\) is continued to increase the half width and intensity of these two bands are observed to decrease with the slight shift in the peak positions towards lower wavelength. The optical band gaps (E\(_o\)) of these glasses were evaluated from Urbach plot and the value of E\(_o\) is found to increase with the increase in the content of TiO\(_2\).

Luminescence emission spectra of Li\(_2\)O–Al\(_2\)O\(_3\)–ZrO\(_2\)–SiO\(_2\): TiO\(_2\) glasses recorded at room temperature of excited at a wavelength corresponding to their absorption edge. The spectrum of the sample T\(_2\) exhibited a broad emission band with the meta-center at about 508 nm with a large Stoke’s shift.
As the concentration of TiO$_2$ is increased, the luminescence output is observed to increase.

ESR spectra of Li$_2$O–Al$_2$O$_3$–ZrO$_2$–SiO$_2$ glasses doped with different concentrations of TiO$_2$ recorded at room temperature are shown in. The spectrum of glass T$_2$ sample consists of an intense asymmetric spectral line centered at about $g = 1.990$. The half width and the intensity of this signal exhibited gradual decrease with the concentration of TiO$_2$.

From the dielectric studies of Li$_2$O–Al$_2$O$_3$–ZrO$_2$–SiO$_2$: TiO$_2$ glasses; the dielectric constant and loss variation with the concentration of TiO$_2$ have been explained on the basis of space charge polarization mechanism. The dielectric relaxation effects exhibited by these samples have been analyzed by a pseudo Cole–Cole plot method and the spreading of dielectric relaxation has been established. The relaxation effects are attributed to Ti$^{3+}$ ($d^1$) ions. A.C. conductivity in the high temperature region seems to be connected both with electronic transfer and ionic movements, but conduction due to such processes seems to be hampered with the entry of titanium ions into the network forming positions. The low temperature (or the nearly temperature independent) part of conductivity could be explained on the basis of quantum mechanical tunneling model.
The objective of the **CHAPTER-IV** is to synthesize Li$_2$O–Al$_2$O$_3$–ZrO$_2$–SiO$_2$ glasses with different concentrations of WO$_3$. The studies taken up are DTA, spectroscopic properties (optical absorption, Raman, IR and photoluminescence) and dielectric properties.

The detailed compositions of the glasses used in the present study are as follows:

$W_0$: 30Li$_2$O–10Al$_2$O$_3$–5ZrO$_2$–55SiO$_2$
$W_1$: 29Li$_2$O–10Al$_2$O$_3$–5ZrO$_2$–55SiO$_2$: 1.0WO$_3$
$W_2$: 28Li$_2$O–10Al$_2$O$_3$–5ZrO$_2$–55SiO$_2$: 2.0WO$_3$
$W_3$: 27Li$_2$O–10Al$_2$O$_3$–5ZrO$_2$–55SiO$_2$: 3.0WO$_3$
$W_4$: 26Li$_2$O–10Al$_2$O$_3$–5ZrO$_2$–55SiO$_2$: 4.0WO$_3$
$W_5$: 25Li$_2$O–10Al$_2$O$_3$–5ZrO$_2$–55SiO$_2$: 5.0WO$_3$

DTA scans for Li$_2$O–Al$_2$O$_3$–ZrO$_2$–SiO$_2$ glasses doped with different concentrations WO$_3$ are presented; all the traces exhibited typical glass transition with the inflection point between 480–520 °C; with the growing content of WO$_3$ in the glass matrix, the glass transitions temperature is observed to increase. In the region, 975–1042 °C, an exothermic peak due to crystallization is observed in the traces of all the glasses. The value of $(T_c-T_g)$, a parameter that represents thermal stability of a glass against devitrification, is found to increase with the content of WO$_3$ in the glass matrix.

The IR spectrum of WO$_3$ free Li$_2$O–Al$_2$O$_3$–ZrO$_2$–SiO$_2$ glass exhibited bands at 1017 cm$^{-1}$ (due to Si–O–Si asymmetrical stretching vibrations), 832
cm$^{-1}$ (due to Si–O–Si symmetrical stretching vibrations perpendicular to Si–Si axis with in the Si–O–Si plane; in this region band due to AlO$_4$ vibrations is also expected) and at 458 cm$^{-1}$ (due to Si–O–Si bending and or AlO$_6$ vibrations). Two other bands at about 538 and 739 cm$^{-1}$ due to Zr–O–Zr vibrations of ZrO$_4$ structural units have also been observed in the spectrum of this glass. The spectra of the glasses containing WO$_3$, have exhibited three additional bands due to $v_1$-WO$_4$, $v_4$-WO$_4$ and $v_1$-WO$_6$ vibrations at about 926 cm$^{-1}$, 411 cm$^{-1}$ and 969 cm$^{-1}$ respectively. With the gradual introduction of WO$_3$ in the glass network, the bands due to symmetrical stretching vibrations of SiO$_4$, ZrO$_4$ and also AlO$_4$ and WO$_4$ structural units are observed to grow at the expense of bands due to asymmetrical SiO$_4$, AlO$_6$ and WO$_6$ structural units.

The Raman spectra of Li$_2$O–Al$_2$O$_3$–ZrO$_2$–SiO$_2$ glasses exhibited bands at 1050 cm$^{-1}$ and at 814 cm$^{-1}$ due to Si–O–Si stretching and bending modes of SiO$_4$ tetrahedra respectively. In the region of Si-O-Si bending modes, Al–O stretching vibrations of Al tetrahedral coordination is also possible. Additionally two other bands at 553 cm$^{-1}$ and at 475 cm$^{-1}$ attributed to the bridging oxygen breathing mode in (Si, Al) three-membered rings and four membered rings respectively have also been located in these spectra.

In the spectra of WO$_3$ doped glasses, the bands due to W–O$^-$ stretchings of WO$_4$ units and bending vibrations of W–O–W linkages of WO$_6$ units are at
about 946 cm\(^{-1}\) and 368 cm\(^{-1}\) respectively in addition to the above mentioned bands. The intensity of symmetrical SiO\(_4\) and AlO\(_4\) tetrahedral bands is increased with the concentration of WO\(_3\).

The optical absorption spectra for Li\(_2\)O–Al\(_2\)O\(_3\)–ZrO\(_2\)–SiO\(_2\): WO\(_3\) glass samples recorded at room temperature in the wavelength region 300-1000 nm. The absorption edge for the pure glass is located at 307 nm where as for the glass W\(_2\) it is observed at 329 nm. As the concentration of WO\(_3\) is increased the edge exhibited blue shift.

Additionally, the spectrum of glass W\(_2\) exhibited a broad absorption band centered at about 869 nm is attributed to \(d_{xy} \rightarrow d_{x^2-y^2}\) transition of W\(^{5+}\) ions. As the concentration of WO\(_3\) is continued to increase, the intensity of these bands is observed to decrease with a slight shift in the peak position towards lower wavelength. the value of optical band gap \(E_o\) increases with the content of WO\(_3\).

ESR spectra of Li\(_2\)O–Al\(_2\)O\(_3\)–ZrO\(_2\)–SiO\(_2\) glasses doped with different concentrations of WO\(_3\) recorded at room temperature are shown in Fig. 6. The spectra of the glasses exhibited an asymmetric signal (identified due to distorted octahedral W\(^{5+}\) ions [50] at \(g_\perp = 1.71\) and \(g_\parallel = 1.61\); the spectra also exhibited another conventional signal due to paramagnetic O\(^-\) ion defects at about \(g = 1.96\). As the concentration of WO\(_3\) is increased, a slight decay in the intensity of this
signal with increase in the concentration of WO₃ is observed; however the values of g tensors remain unaffected.

The dielectric studies of these glasses indicated that with the gradual increase of concentration of WO₃, the values of ε', tan δ and σ_ac are found to decrease at any frequency and temperature. The decreasing trend of dielectric parameters with the concentration of WO₃ suggests increasing degree of rigidity in the glass network. In other words, with increase in the concentration of WO₃, the fraction of W⁵⁺ ions that act as modifiers decreases and the tungsten ions mostly participate in the network forming with WO₄ structural units and alternate with SiO₄, AlO₄ and ZrO₄ structural units. The activation energy for ac conduction is observed to increase with the concentration of WO₃. This observation points out that there is a decreasing freedom for dipoles to orient in the field direction indicating once again the higher rigidity of the glass network. The observed relaxation effects in these glasses can also be attributed to W⁵⁺ ions. The quantitative analysis of the a.c. conductivity has indicated the dimensionality of conducting space decreases with the concentration of WO₃.

In CHAPTERS-V an attempt is made to characterize the optical absorption and the fluorescence spectra of two lanthanide ions viz., Pr³⁺ and Er³⁺ in lithium zirconium silicate glasses mixed with Al₂O₃, Y₂O₃ and Sc₂O₃. 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 Al/Y/Sc ions to glass host over the luminescence efficiencies.

From the glass-forming region of Li$_2$O– Al$_2$O$_3$– Y$_2$O$_3$–Sc$_2$O$_3$–ZrO$_2$–SiO$_2$ glass systems, the following compositions are chosen for the present study

**Pr series:**

LAiZSPr : 30Li$_2$O–9Al$_2$O$_3$–5ZrO$_2$–55SiO$_2$: 1Pr$_2$O$_3$

LScZSPr : 30Li$_2$O–9Sc$_2$O$_3$–5ZrO$_2$–55SiO$_2$: 1Pr$_2$O$_3$

LYZSPr : 30Li$_2$O–9Y$_2$O$_3$–5ZrO$_2$–55SiO$_2$: 1Pr$_2$O$_3$

**Er series:**

LAiZSER : 30Li$_2$O–9Al$_2$O$_3$–5ZrO$_2$–55SiO$_2$: 1Er$_2$O$_3$

LScZSER : 30Li$_2$O–9Sc$_2$O$_3$–5ZrO$_2$–55SiO$_2$: 1Er$_2$O$_3$

LYZSER : 30Li$_2$O–9Y$_2$O$_3$–5ZrO$_2$–55SiO$_2$: 1Er$_2$O$_3$

The optical absorption spectra of Al$_2$O$_3$, Y$_2$O$_3$ and Sc$_2$O$_3$ mixed Li$_2$O–ZrO$_2$–SiO$_2$: Pr$^+$ and Er$^{3+}$ 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:

**Pr$^{3+}$:** $^3$H$_4$ $\rightarrow$ $^3$P$_2$, $^3$P$_1$, $^3$P$_0$, $^1$D$_2$, $^3$F$_4$, $^3$F$_3$ and $^3$F$_2$

**Er$^{3+}$:** $^4$I$_{15/2}$ $\rightarrow$ $^4$G$_{9/2}$, $^4$G$_{11/2}$, $^2$H$_{9/2}$, $^4$F$_{3/2}$, $^4$F$_{5/2}$, $^4$F$_{7/2}$, $^2$H$_{11/2}$, $^4$S$_{3/2}$, $^4$F$_{9/2}$, $^4$I$_{9/2}$, $^4$I$_{11/2}$

and $^4$I$_{13/2}$

By performing least square fitting analysis the J-O parameters for these samples are computed and are found to show the following order for the Pr$^{3+}$
doped glasses: $\Omega_6 > \Omega_4 > \Omega_2$ and for Er$^{3+}$ the order is $\Omega_2 > \Omega_4 > \Omega_6$ for all the three sets of samples.

The luminescence spectra of all the three glasses doped with Pr$^{3+}$ and Er$^{3+}$ ions recorded at room temperature in the visible and NIR regions are shown in Figs. 5.3 (a and b) and 5.4 (a and b) respectively; the spectra exhibited the following prominent emission bands:

Pr$^{3+}$ ($\lambda_{\text{exc}} = 442$ nm): $^3\text{P}_0 \rightarrow ^3\text{F}_2, ^3\text{H}_6, ^3\text{H}_4, ^3\text{H}_5; ^1\text{D}_2 \rightarrow ^3\text{H}_4$ and $^3\text{P}_1 \rightarrow ^3\text{H}_5, ^3\text{F}_3$

Er$^{3+}$ glass ($\lambda_{\text{exc}} = 379$ nm): $^2\text{H}_{9/2} \rightarrow ^4\text{I}_{15/2}, ^4\text{F}_{5/2} \rightarrow ^4\text{I}_{15/2}, ^4\text{F}_{7/2} \rightarrow ^4\text{I}_{15/2}, ^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}, ^2\text{G}_{9/2} \rightarrow ^4\text{I}_{13/2}, ^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}, ^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$

and $^2\text{G}_{9/2} \rightarrow ^4\text{I}_{11/2}$

The comparison of branching ratios $\beta$ and quantum efficiencies of $^3\text{P}_0 \rightarrow ^3\text{H}_4$ (Pr$^{3+}$) and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ (Er$^{3+}$) emissions for both the series of the glasses showed the largest values for glass mixed with Y$_2$O$_3$.

The comparison table of radiative life times and quantum yields for glasses and glass ceramics containing Pr$^{3+}$ and Er$^{3+}$ samples are given in Tables 1
Table 1 Data related to quantum efficiencies of the principal lines for the Li$_2$O – Al$_2$O$_3$/Y$_2$O$_3$/Sc$_2$O$_3$–ZrO$_2$–SiO$_2$ : Pr$^{3+}$/Er$^{3+}$ glasses

<table>
<thead>
<tr>
<th></th>
<th>Pr$^{3+}$ ($^3P_0$)</th>
<th>Er$^{3+}$ ($^4S_{3/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LAIZS</td>
<td>LScZS</td>
</tr>
<tr>
<td>Measured  ($\tau_m$) (µs)</td>
<td>3.9</td>
<td>7.3</td>
</tr>
<tr>
<td>Calculated ($\tau$) (µs)</td>
<td>26.0</td>
<td>26.6</td>
</tr>
<tr>
<td>Quantum yield (η%)</td>
<td>15.0</td>
<td>27.4</td>
</tr>
</tbody>
</table>

The higher values of these parameters for Y$_2$O$_3$ mixed glasses among the three glasses studied are 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 Ln$^{3+}$ ion with the high-energy phonons in case of Y$_2$O$_3$ mixed glasses and relatively higher degree of this coupling with low-energy phonons for Sc$_2$O$_3$ and Al$_2$O$_3$ mixed glasses.

**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– Al$_2$O$_3$–ZrO$_2$–SiO$_2$ glass systems doped with varying concentration of TiO$_2$ and WO$_3$ and also the spectroscopic properties Li$_2$O– Al$_2$O$_3$/Y$_2$O$_3$/Sc$_2$O$_3$–ZrO$_2$–SiO$_2$ glasses doped with Pr$^+$ and Er$^{3+}$ ions.
References closely related to the present work have been compiled to the extent possible and given at the end of the relevant chapter.