PREFACE

The present thesis deals with the studies on “Dielectric dispersion and electrical conductivity studies on Fe$_2$O$_3$ mixed lithium yttrium silicate glasses and up-conversion and NIR luminescence studies of Ce$^{3+}$–Yb$^{3+}$ and Tm$^{3+}$–Yb$^{3+}$ co-doped lithium silicate glass system influence of yttrium ions”. 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, studies on electric properties of Li$_2$O–Y$_2$O$_3$–SiO$_2$ glass systems doped with varying concentration of Fe$_2$O$_3$ and also up-conversion and NIR luminescence studies Ce$^{3+}$–Yb$^{3+}$ and Tm$^{3+}$–Yb$^{3+}$ co-doped Li$_2$O–Y$_2$O$_3$–SiO$_2$ glasses.

Lithium silicate glasses mixed with sesquioxides like Y$_2$O$_3$, Al$_2$O$_3$, Sc$_2$O$_3$ etc., were considered as excellent materials for integrated optics, photonic and biomedical applications because of their high thermo-physical, chemical and mechanical stability. The presence of yttrium ions in silicate glasses is proved to diminish the phonon energies, to broaden the spectral range of transparency and to enhance the refractive indices.

The addition of transition metal ions like iron to the stable lithium silicate glasses is expected to improve their electrical and dielectric features. Regardless of the original oxidation state of the iron in the starting glass batch, the final glass contains Fe$^{3+}$ (in both tetrahedral and octahedral coordination
environments) and Fe	extsuperscript{2+} ions in octahedral coordination. The concentration of Fe	extsuperscript{2+} (or Fe	extsuperscript{3+}) which will have a strong bearing on electrical properties of the glasses depends upon the melting temperature and time and other constituents of the glass.

In view of this we have devoted initial part of the thesis to investigate the influence of Fe	extsubscript{2}O	extsubscript{3} on electrical properties of Li	extsubscript{2}O–Y	extsubscript{2}O	extsubscript{3}–SiO	extsubscript{2} glasses. The studies cover electrical conductivity and dielectric dispersion (dielectric constant $\varepsilon'$ and loss tan $\delta$) over a wide frequency range from 40 Hz to 2 MHz and in temperature range from 100 to 360 K. To have some pre-structural understanding for explaining the conduction phenomenon, we have also included the data on optical absorption, ESR and IR spectral studies on these glasses.

Y	extsubscript{2}O	extsubscript{3} mixed lithium silicate glasses were considered as excellent host materials for rare earth ion doping and proved to be efficient both in continuous wave operation as well as in pulsed regimes. Yb	extsuperscript{3+} doped laser materials are of interest for the next generation nuclear fusion and are being used as gain media in the microchip laser at sufficiently high doping levels. Energy level structure of Yb	extsuperscript{3+} ion is exceptionally simple, consisting of a ground state manifold, $^2F_{7/2}$, Stark-split into four sublevels and an excited-state manifold, $^2F_{5/2}$, Stark-split into three sublevels. Thus, excited state absorption (ESA) for both the pump and signal wavelengths is absent for this ion. The
upper manifold lies approximately 10500 cm\(^{-1}\) above the ground level. This large energy gap favors significant reduction of multi-phonon non radiative decay. The broad absorption spectrum due to Stark-splitting of this ion provides a wide choice of pump wavelengths. Further, the broad emission spectrum of Yb\(^{3+}\) ion and its large saturation fluencies enable to achieve lasing inverse level occupation and corresponding laser generation over a wide range of lasing region (\(~1–1.2\ \mu\text{m}\)). Such interesting features of this rare earth ion make its host as an attractive medium for the generation and amplification of ultra-short pico-and femtosecond laser pulses.

Ce\(^{3+}\) ions are being extensively used as activators in various fluoride and oxide materials due to their intra-center optical transitions of 4f \(\rightarrow\) 5d (allowed by the Laporte parity selection rules. The allowed electric dipole transition from 4f ground state to 5d excited state of Ce\(^{3+}\), with very high absorption cross section \(~10^{-18}\ \text{cm}^2\) in the UV region makes Ce\(^{3+}\) ion as promising broad band sensitizer for Yb\(^{3+}\) ions. Moreover, the back energy transfer from Yb\(^{3+}\) to Ce\(^{3+}\) is relatively small and the energy transition of Ce\(^{3+}\): 4f \(\rightarrow\) 5d can be spectrally tuned by host materials. All these factors indicate the probable strong NIR emission with high quantum efficiency when Yb\(^{3+}\) activator ions are sensitized by Ce\(^{3+}\) ions. In view of such interesting features of these two rare earth ions a part of the thesis is devoted to study the fluorescence features of Ce\(^{3+}\) and Yb\(^{3+}\) ions and the energy transfer from Ce\(^{3+}\)
to Yb$^{3+}$ in Li$_2$O–Y$_2$O$_3$–SiO$_2$ glass host matrix with the gradual increase of Y$_2$O$_3$ content at the expense of Li$_2$O. Such variation in the concentration of Y$_2$O$_3$ in the glass network may inculcate the structural modifications and local field variations.

Among different rare-earth ions doped glasses, the Tm$^{3+}$ ions activated glasses have gained much attention because of the fact that, Tm$^{3+}$ ion possesses two meta-stable excited levels viz., $^1$D$_2$ and $^1$G$_4$, in its energy-level structure for displaying blue emission either from its normal emission or by up-conversion luminescence process. Yb$^{3+}$ ion, in particular, is considered as a promising sensitizer for Tm$^{3+}$ ions in glass matrices due to its significantly high absorption cross section in the NIR region and favourable energy level structure. In fact, efficient energy transfer processes from Yb$^{3+}$ to Tm$^{3+}$ ions when excited at 900 nm (corresponding to $^2$F$_{7/2}$→$^2$F$_{5/2}$ transition of Yb$^{3+}$ ion) intense R, G and B emissions were reported in different kinds of glass matrices. In view of these facts, It is felt worth to devote a part of the thesis to study the fluorescent features of Tm$^{3+}$ and Yb$^{3+}$ ions and the up-conversion phenomenon involved in the Li$_2$O–Y$_2$O$_3$–SiO$_2$ glass system co-doped with Tm$^{3+}$ and Yb$^{3+}$ ions as a function of Y$_2$O$_3$ concentration.

The compositions of the glasses used for the present studies are:

1. $(40-x)$ Li$_2$O–10 Y$_2$O$_3$–50 SiO$_2$: x Fe$_2$O$_3$ ($0 \leq x \leq 1.5$ mol%)
2. $(49-x)$ Li$_2$O– x Y$_2$O$_3$–50 SiO$_2$: 1.0 Ce$_2$O$_3$/Yb$_2$O$_3$ and
(49−x) Li$_2$O−xY$_2$O$_3$−50SiO$_2$: 0.5Ce$_2$O$_3$+0.5Yb$_2$O$_3$ (0 ≤ x ≤ 15.0 mol%)

3. (49−x) Li$_2$O− x Y$_2$O$_3$−50 SiO$_2$: 1.0 Yb$_2$O$_3$/Tm$_2$O$_3$ and

(49−x) Li$_2$O−xY$_2$O$_3$−50SiO$_2$: 0.5Yb$_2$O$_3$+0.5Tm$_2$O$_3$ (0 ≤ x ≤ 5.0 mol%)

The glasses were prepared by the usual melting, quenching and subsequent annealing techniques and the following studies were carried out:

(i) infrared spectral studies in the wavenumber range 400–1600 cm$^{-1}$ and the study of the effect of concentration of iron ion and rare earth ions on the position and intensity of various vibrational bands.

(ii) optical absorption studies in the wavelength range 300–1800 nm, identification of various electronic transitions of iron and rare earth ions.

(iii) electron spin resonance measurements and the identification of the positions and valence states of iron ions in the glass network.

(iv) dielectric properties viz., dielectric constant $\varepsilon'$, dielectric loss tan $\delta$ and ac conductivity $\sigma_{ac}$ and impedance spectra in the frequency range 40 Hz to 2 MHz and in temperature range from 100 to 360 K of Fe$_2$O$_3$ doped glasses.

(v) Photoluminescence spectra of the rare earth doped glasses in the visible and NIR regions 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–Y$_2$O$_3$–SiO$_2$: Fe$_2$O$_3$ and spectroscopic properties of Li$_2$O–Y$_2$O$_3$–SiO$_2$: Ce$^{3+}$/Tm$^{3+}$/$\text{Yb}^{3+}$ glasses are presented systematically.

**CHAPTER – II** gives the description of experimental methods employed in the preparation and characterization of Li$_2$O–Y$_2$O$_3$–SiO$_2$. The details of the apparatus used and the techniques adopted for characterization and for measuring electrical properties, optical absorption, ESR, IR, and photoluminescence are described in detail in this chapter.

**CHAPTER – III** is devoted to the studies on electrical properties (dielectric constant, loss, electric moduli, impedance spectra and ac conductivity) of Li$_2$O–Y$_2$O$_3$–SiO$_2$ glasses doped with different concentrations of Fe$_2$O$_3$ over a wide continuous frequency range (viz., 40 Hz to 2 MHz) and also dc conductivity in the low temperature region (100 K to 360 K). The results were explained using structural information obtained from IR, optical absorption and ESR spectral measurements.

Dielectric constant, $\varepsilon'(\omega)$, of Li$_2$O–Y$_2$O$_3$–SiO$_2$:Fe$_2$O$_3$ glasses at higher frequency approaches a constant value, $\varepsilon'_{\infty}(\omega)$, which results in rapid polarization processes occurring in the glasses under applied field. With
decreasing frequency dielectric constant reaches higher value, $\varepsilon'(\omega)$. The behaviour of dielectric constant with temperature and frequency for all the other glasses has demonstrated similar behaviour. Further, at any frequency and temperature these parameters are found to increase with increase in the content of Fe$_2$O$_3$ beyond 0.5 mol% in the glass matrix. The results have been analysed on the basis of different polarization mechanisms and space charge polarization is found to be responsible for the increase of dielectric constant with the temperature. The space charge polarization is attributed mainly due to Fe$^{2+}$ ions that act as modifiers in the glass network. The decrease of dielectric parameters with the concentration of dopant is understood due to decrease in the concentration of such modifying ions. At higher frequency, the charge carriers will no longer be able to rotate sufficiently rapidly, so their oscillation will begin to lay behind this field leading to a decrease of dielectric permittivity, $\varepsilon'(\omega)$.

The variation of dielectric loss, tan $\delta$, with temperature of Fe$_2$O$_3$ mixed glasses have exhibited dielectric relaxation character; these effects are attributed to Fe$^{2+}$ complexes. The activation energy for the dipoles is found to decrease with increase in concentration of dopant beyond 0.5 mol %; this is attributed to decreasing degree of augmented cross-links in the glass network.

The a.c. conductivity and also d.c. conductivity have exhibited increasing trend with the raise of Fe$_2$O$_3$ concentration from 0.5 to 1.5 mol%. These Fe$^{2+}$
ions are assumed to act as modifiers and create more dangling bonds and free charge carriers in the glass network and are found to be responsible for the increase of conductivity. Both quantum mechanical tunneling (QMT) and correlated barrier hopping models (CBH) were used for understanding the origin of ac conductivity and the corresponding analysis has indicated that CBH model is more appropriate for this glass system. For the better understanding of relaxation dynamics of the electrical properties we have drawn the scaling plots for ac conductivity and also electric moduli. The plots indicated that the relaxation dynamics is independent on temperature but depends on concentration of Fe$_2$O$_3$. The dc conductivity is analyzed using small polaron hoping model. The increase of conductivity with the concentration of Fe$_2$O$_3$ beyond 0.5 mol% is explained in terms of variations in the redox ratio of iron ions in the glass network.

The IR spectra of Fe$_2$O$_3$ doped Li$_2$O–Y$_2$O$_3$–SiO$_2$ glasses have exhibited conventional vibrational band due to Si–O–Si asymmetric vibrations at about 1083 cm$^{-1}$ and another band at about 787 cm$^{-1}$ due to Si–O–Si symmetric vibrations or due to bending mode of bridging oxygen situated perpendicularly to Si–Si axis within the Si–O–Si plane. The octahedral band of yttrium ions (YO$_6$) is also located in these spectra at about 482 cm$^{-1}$. With the addition of Fe$_2$O$_3$ to the glass matrix, the spectra exhibited three additional bands due to FeO$_4$ structural units (at about 652 cm$^{-1}$) and due to $\nu_1$ and $\nu_3$ vibrations of
FeO$_6$ structural units at about 566 and 440 cm$^{-1}$, respectively. As the concentration of Fe$_2$O$_3$ is increased beyond 0.5 mol%, all asymmetrical bands are observed to grow at the expense of symmetrical bands. The intensity of the band due to FeO$_4$ structural units and also Si–O–Si symmetric vibrational band is found to be maximal in the glass doped with 0.5 mol% of Fe$_2$O$_3$. Such variations in the IR spectra have been explained based on viewpoint that there is an increasing concentration of Fe$^{2+}$ ions that act as modifiers in the glasses containing Fe$_2$O$_3$ beyond 0.5 mol%.

The optical absorption spectra of Li$_2$O–Y$_2$O$_3$–SiO$_2$ glasses doped with different concentrations of Fe$_2$O$_3$ recorded in the wavelength region 300–1100 nm. When the concentration of Fe$_2$O$_3$ is raised from 0.3 to 0.5 mol%, the absorption edge exhibited spectrally blue shift from 336 to 329 nm. For further increase in the concentration of Fe$_2$O$_3$, the absorption edge shifted spectrally towards higher wavelength side. From the observed absorption edges, we have evaluated the optical band gaps ($E_g$). The spectrum of glass F$_3$ exhibited three feeble absorption kinks due to the excitation Fe$^{3+}$ ions at about 372, 392 and 419 nm wavelengths are assigned to $^6A_{1g}(S) \rightarrow ^4T_{1g}(P)$, $^4A_{1g}(G) + ^4E_g(G)$ and $^4T_{1g}(G)$ octahedral (no spin allowed) transitions of Fe$^{3+}$ ions, respectively. The absorption band observed at about 530 nm is identified due to $^6A_1(e^2t_2^2) \rightarrow ^4T_1(e^3t_2^2)$ tetrahedral transition of Fe$^{3+}$ ions. The decreasing intensity this band with the content of Fe$_2$O$_3$ suggests the decrement in the
concentration of tetrahedral iron ions that cross–link with SiO₄ structural units. The broad spectral peak observed at around 993 nm is due to $^5T_{2g} \rightarrow ^5E_g$ intra–octahedral transition of Fe$^{2+}$ ions. The gradual growth of this Fe$^{2+}$ band with increasing content of Fe₂O₃ beyond 0.5 mol% suggests an increase in the concentration of Fe$^{2+}$ in the glass matrix. These Fe$^{2+}$ ions similar to Li$^+$ ions act as modifiers and create more non–bridging oxygens and dangling bonds inside the glass network.

The ESR spectra of Fe₂O₃ doped Li₂O–Y₂O₃–SiO₂ glasses exhibited two signals at $g \approx 2.01$ (signal-1) and at $g \approx 4.5$ (signal-2). The signal-2 is identified due to the isolated Fe$^{3+}$ ions in the low symmetry orthorhombic crystal field sites of either tetrahedral or octahedral coordination. The signal-1 is due to the isolated Fe$^{3+}$ in slightly distorted structural units in samples with a low Fe₂O₃ content and due to Fe$^{3+}$–O–Fe$^{3+}$ cluster formations in the samples containing higher content of Fe₂O₃. We have observed a slight narrowing of the signal with decreasing intensity as the concentration of Fe₂O₃ is increased. The narrowing process seems to be influenced by increase in network disordering and interaction between multivalent iron ions (viz., Fe$^{2+}$ and Fe$^{3+}$). The decrease in the line width of the signal–1 with Fe₂O₃ content beyond 0.5 mol% shows the dominance of the exchange mechanisms which in turn indicates a gradual increase in the concentration of Fe$^{2+}$ ions that act as modifiers.
The overall analysis indicated that Li$_2$O–Y$_2$O$_3$–SiO$_2$ glasses containing more than 0.5 mol% of Fe$_2$O$_3$ are more suitable for achieving good electrical conductivity in these glasses.

**The main objective of CHAPTER – IV** is devoted to studies on the fluorescence features of Ce$^{3+}$ and Yb$^{3+}$ ions and the energy transfer from Ce$^{3+}$ to Yb$^{3+}$ in Li$_2$O–Y$_2$O$_3$–SiO$_2$ glass host matrices with the gradual increase of Y$_2$O$_3$ content at the expense of Li$_2$O. Such variation in the concentration of Y$_2$O$_3$ in the glass network may inculcate the structural modifications and local field variations around Ln$^{3+}$ ion embedded in the glass network and influence various luminescence transitions of lanthanide ions. The results of IR spectral studies also have been included so as to have comprehensive information concerning the structural changes in the glass network caused by variations in the concentrations of Y$_2$O$_3$ at the vicinity of rare earth ions.

Optical absorption and photoluminescence spectra of Ce$^{3+}$ and Yb$^{3+}$ co-doped Li$_2$O–Y$_2$O$_3$–SiO$_2$ glasses mixed with different concentrations of Y$_2$O$_3$ (from 5 to 15 mol %) have been studied. The PL spectra of Ce$^{3+}$ doped glasses excited at 360 nm exhibited two broad parity allowed 5d ($^2$D) $\rightarrow$ 4f ($^2$F$_{5/2}$, 7/2) bands in the blue spectral region, whereas the spectra of Yb$^{3+}$ doped glasses excited at 900 nm exhibited a broad emission band centered at about 980 nm due to $^2$F$_{5/2}$ $\rightarrow$ $^2$F$_{7/2}$ transition. A significant enhancement in the intensity of NIR emission is observed due to the sensitization with Ce$^{3+}$ ions. The increase in the rate of energy transfer
from Ce$^{3+}$ to Yb$^{3+}$ could be observed with increasing Y$_2$O$_3$ content. The reasons for such enhancement have been discussed within a frame work of structural modifications taking place in the vicinity of Yb$^{3+}$ ions in the glass network due to varying concentrations of Y$_2$O$_3$.

The goal of the CHAPTER V is to study the fluorescent features of Tm$^{3+}$ and Yb$^{3+}$ ions and the up-conversion phenomenon involved in the Li$_2$O–Y$_2$O$_3$–SiO$_2$ glass system co-doped with Tm$^{3+}$ and Yb$^{3+}$ ions as a function of Y$_2$O$_3$ concentration.

Tm$^{3+}$ doped Li$_2$O–Y$_2$O$_3$–SiO$_2$ glasses mixed with different concentrations of Y$_2$O$_3$ recorded at room temperature in the wavelength range 400–1800 nm, have exhibited the following absorption bands: $^3$H$_6$ → $^1$G$_4$, $^3$F$_2$, $^3$F$_3$, $^3$H$_4$, $^3$H$_5$ and $^3$F$_4$. The optical absorption spectra of Yb$^{3+}$ doped Li$_2$O–Y$_2$O$_3$–SiO$_2$ glasses have exhibited an absorption band with a degeneracy corresponding to localized $^2$F$_{7/2}$ → $^2$F$_{5/2}$ transition of Yb$^{3+}$ ion spreading over a spectral range covering 900–1000 nm.

In the absorption spectra of co-doped glasses, the bands due to transitions of both the ions are present. However, with the increase in the concentration of Y$_2$O$_3$, a significant increase in the intensity of all absorption bands is observed.

The luminescence spectra of Tm$^{3+}$ doped glasses excited at 400 nm exhibited the following prominent emission bands:
\[ \text{As the concentration of } Y_2O_3 \text{ is increased the intensity of these bands is observed to increase. When } Tm^{3+} \text{ and } Yb^{3+} \text{ are present together in the glass, the incident radiation } ^2F_{5/2} \rightarrow ^2F_{7/2} \text{ (980 nm) is understood to excite both the ions. For } Tm^{3+} \text{ ion, the excitation takes place from } ^3H_6 \text{ to } ^1G_4 \text{ level by absorbing three photons and transitions takes place to } ^3H_6, ^3H_4 \text{ and } ^3F_4 \text{ levels giving rise to blue, green and red emission. The observed decreasing trend of } \Omega_2 \text{ parameter with the increase in the content of } Y_2O_3 \text{ is attributed to the decreasing interaction of rare earth ions with the ions of the host materials due to increasing distortion or structural change (owing due to the increasing presence of octahedral yttrium ions) in the vicinity of rare earth ions. The } ^3H_4 \text{ level of } Tm^{3+} \text{ ions is populated due to the non radiative relaxation from } ^3F_2 \text{ or } ^3F_3 \text{ levels and de-excited to } ^3F_4 \text{ level. In view of these, more intense } ^3H_4 \rightarrow ^3F_4 \text{ transitions are observed.} \]

\[ \begin{align*}
^1D_2 & \rightarrow ^3F_4, ^3H_{4,5}, ^1G_4 & \rightarrow ^3H_{5,6}, ^3F_4, \text{ in the visible region and} \\
^3H_5 & \rightarrow ^3H_6, ^3H_4 & \rightarrow ^3F_4, ^3F_4 & \rightarrow ^3H_6 \text{ in the NIR region.}
\end{align*} \]
(~1.5 µm) NIR emission in the co-doped samples is observed in the glasses mixed with higher concentration of Y$_2$O$_3$.

**CHAPTER-VI** reports brief summary and conclusions drawn from the investigation carried out on a variety of properties viz., dielectric and spectroscopic properties of Li$_2$O–Y$_2$O$_3$–SiO$_2$ glasses doped with different concentrations of Fe$_2$O$_3$ and also the spectroscopic properties Li$_2$O–Y$_2$O$_3$–SiO$_2$ glasses doped with Ce$^{3+}$, Tm$^{3+}$ and Yb$^{3+}$ ions.

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