Influence of yttrium ions on the emission transfer features of Ce$^{3+}$/Yb$^{3+}$ co-doped lithium silicate glasses

Optical absorption and photoluminescence spectra of the glasses possessing compositions (49−x) Li$_2$O−x Y$_2$O$_3$−50SiO$_2$: 1.0Ce$_2$O$_3$/1.0Yb$_2$O$_3$ and (49−x) Li$_2$O−x Y$_2$O$_3$−50 SiO$_2$: (0.5Ce$_2$O$_3$ + 0.5Yb$_2$O$_3$) with x varying from 5 to 15 mol% were studied. The PL spectra of Ce$^{3+}$ doped glasses excited at 360 nm exhibited two broad parity allowed 5d($^2$D)→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$_{5/2}$→$^2$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 improvement have been discussed within a framework of structural modifications taking place in the vicinity of Yb$^{3+}$ ions.
Influence of yttrium ions on the emission transfer features of Ce$^{3+}$/Yb$^{3+}$ co-doped lithium silicate glasses

4.1. Introduction

Lithium silicate glasses with high thermal stability, chemical durability and good optical transparency over a wide range of wavelengths are particularly useful in data busses which cover short distances. When alkali silicate glasses are mixed with some sesquioxides (e.g., Sb$_2$O$_3$, Al$_2$O$_3$, Y$_2$O$_3$, La$_2$O$_3$, Sc$_2$O$_3$ etc.,), their thermo-physical, chemical and mechanical stability will be further improved. Such glasses were proved to be high efficient luminescence materials [1-12]. Among various sesquioxides, the addition of Y$_2$O$_3$ to silicate glass systems widens the spectral range of transparency, enhances the refractive index and lowers phonon energies [8-10].

In view of these qualities, Y$_2$O$_3$ 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$^{3+}$ doped laser materials are of interest for the next generation nuclear fusion [13, 14] and are being used as gain media in the microchip laser at sufficiently high doping levels [15]. Energy level structure of Yb$^{3+}$ 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 [16]. This large energy gap favors significant reduction of multi-phonon non-radiative decay [17]. 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 \(\mu\)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 femto second laser pulses [18].

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 [19]). A strong overlap of the 5d orbital of this activator with ligand prevailingly delocalized 2p orbital of oxygen causes high sensitivity of their spectral characteristics to the local environment structure [20]. Cerium-doped silica glasses find potential applications in a variety of luminescent and phosphor devices such as phosphors for cathode-luminescence, scintillators for elementary particles, radiation detectors, UV absorbing filters and emitters as well as activators for energy transfer [21]. In practice, \(Y_2O_3\) mixed ceria glasses are the subjects of a huge interest because the addition of such oxides substantially enhances the concentration of oxygen
vacancies, which may play a very crucial role in the fluorescent emission features of rare earth ions within the glass hosts [22–26].

The allowed electric dipole transition from 4f ground state to 5d excited state of Ce$^{3+}$, with very high absorption cross section $\sim 10^{-18}$ cm$^2$ in the UV region [27] 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.

The principal goal of the present work is 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 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.

The following composition contents were chosen for the present study:
$49-x\ Li_2O\cdots x\ Y_2O_3\cdots 50SiO_2\ :\ 1.0\ Ce_2O_3$, $(49-x)\ Li_2O\cdots x\ Y_2O_3\cdots 50SiO_2\ :\ 1.0\ Yb_2O_3$ and $(49-x)\ Li_2O\cdots x\ Y_2O_3\cdots 50SiO_2\ :\ 0.5\ Ce_2O_3+0.5\ Yb_2O_3$ with $x = 5$, 10 and 15 all in mol%. The details of the composition are presented in Table 4.1.

<table>
<thead>
<tr>
<th>Oxide → Glass</th>
<th>Li$_2$O</th>
<th>Y$_2$O$_3$</th>
<th>SiO$_2$</th>
<th>Ce$_2$O$_3$</th>
<th>Yb$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeY$_5$</td>
<td>44.0</td>
<td>5.0</td>
<td>50.0</td>
<td>1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>CeY$_{10}$</td>
<td>39.0</td>
<td>10.0</td>
<td>50.0</td>
<td>1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>CeY$_{15}$</td>
<td>34.0</td>
<td>15.0</td>
<td>50.0</td>
<td>1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>YbY$_5$</td>
<td>44.0</td>
<td>5.0</td>
<td>50.0</td>
<td>0.0</td>
<td>1.0</td>
</tr>
<tr>
<td>YbY$_{10}$</td>
<td>39.0</td>
<td>10.0</td>
<td>50.0</td>
<td>0.0</td>
<td>1.0</td>
</tr>
<tr>
<td>YbY$_{15}$</td>
<td>34.0</td>
<td>15.0</td>
<td>50.0</td>
<td>0.0</td>
<td>1.0</td>
</tr>
<tr>
<td>CeYbY$_5$</td>
<td>44.0</td>
<td>5.0</td>
<td>50.0</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>CeYbY$_{10}$</td>
<td>39.0</td>
<td>10.0</td>
<td>50.0</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>CeYbY$_{15}$</td>
<td>34.0</td>
<td>15.0</td>
<td>50.0</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

4.2 Brief review of the previous work on Yb$_2$O$_3$–Ce$_2$O$_3$ co-doped glasses

Zhou et al. [28] have studied the ultraviolet to near-infrared spectral modification in Ce$^{3+}$ and Yb$^{3+}$ co-doped phosphate glasses and realized through the energy transfer from Ce$^{3+}$ to Yb$^{3+}$. The energy transfer efficiency and concentration quenching efficiency were calculated based on the decay curves of Ce$^{3+}$ 340 nm emission and Yb$^{3+}$ 976 nm emission. Nagamatsu et al. [29] have reported the fluorescence characteristics of Yb$^{3+}$:Ce$^{3+}$:Er$^{3+}$-codoped fluoride glasses. Yb$^{3+}$ co doping improved the excitation efficiency at 980 nm pumping and Ce$^{3+}$ co doping improved the branching ratio of the Er$^{3+}$ $^4I_{11/2}$–$^4I_{13/2}$ transition level, resulting in an enhancement in the fluorescence quantum
yield at 1550 nm. The energy transfer dynamics of the Yb$^{3+}$:Ce$^{3+}$:Er$^{3+}$-codoped fluoride glass was also analyzed based on a rate equation model.

Zhao et al. [30] have designed the bent waveguide structures (U- and F-bend) based on UV-sensitive Er$^{3+}$/Yb$^{3+}$ codoped germanate glass substrates to achieve high-gain C-band amplification. Voloshinovskii et al. [31] have studied spectral-kinetic characteristics of Gd$^{3+}$ and Ce$^{3+}$ luminescence from a series of Ce$^{3+}$ doped alkali gadolinium phosphates of) with in 4.2–300K temperature range using time-resolved luminescence spectroscopy techniques. An efficient reversed Ce$^{3+}$-Gd$^{3+}$ energy transfer has been revealed for the studied phosphates at 4.2 K.

Chen et al. [32] have synthesized the high efficient near-infrared (NIR) quantum cutting (QC) LuBO$_3$:Ce$^{3+}$,Yb$^{3+}$ phosphors by hydrothermal method with further heat treatment. Due to the cooperative energy transfer (CET) from one Ce$^{3+}$ to two Yb$^{3+}$ ions, an intense NIR emission around 971nm of Yb$^{3+}$: $^{2}F_{5/2} \rightarrow ^{2}F_{7/2}$ transition was obtained under 369nm excitation. Chen et al. [33] have demonstrated an efficient near-infrared (NIR) quantum cutting (QC) in Ce$^{3+}$, Yb$^{3+}$ co-doped YBO$_3$ phosphors, which involves the emission of two low-energy NIR photons (around 973 nm) from an absorbed ultra-violet (UV) photon at 358 nm via a cooperative energy transfer (CET) from Ce$^{3+}$ to Yb$^{3+}$ ions. Lou et al. [34] prepared the Er$^{3+}$/Yb$^{3+}$ co-doped transparent glass-ceramics containing Ca$_5$(PO$_4$)$_3$F nano-crystals and their upconversion
properties were investigated. Comparing with the samples before heat treatment, high efficiency upconversion luminescence of Er$^{3+}$ at 547 nm and 667 nm was observed in the glass-ceramics under 980 nm excitation and the intensity of red emission showed different tendency to that of green emission after nano-crystals precipitation.

The study of Hu et al. [35] explores a series of optical, thermal, and structural properties based on 60P$_2$O$_5$–30ZnO–10Al$_2$O$_3$ (60P) glasses that doped with varied rare earth (RE) elements Yb$_2$O$_3$ and P$_2$O$_5$ components replaced by SiO$_2$. It was found that the glasses density decrease with SiO$_2$ concentration added to replace P$_2$O$_5$, whereas they increase with increased concentration of Yb$^{3+}$ doped. Moreover, the glasses transition temperature, softening temperature and refractive index increase with Yb$^{3+}$ concentrations added, whereas the thermal expansion coefficient decreases.

Murata et al. [36] measured the fluorescence spectra of Ce$^{3+}$ ions in silicate, borate, and phosphate glasses melted in Ar environment. The relative fluorescence intensity of Ce$^{3+}$ in the ultraviolet region increased in the order of R = Ba, Ca, Sr, and Mg in the 20Li$_2$O–20RO–60SiO$_2$ glass samples and with decreasing BaO content in the BaO–B$_2$O$_3$ glass samples, respectively. In contrast, the relative fluorescence intensity of Ce$^{3+}$ did not change with varying the glass composition in phosphate glass samples. The compositional
dependence of the relative fluorescence intensity of Ce\textsuperscript{3+} is discussed in terms of redox reaction of Ce\textsuperscript{3+}–Ce\textsuperscript{4+} in oxide glasses.

Velázquez et al. [37] have synthesized 95SiO\textsubscript{2}–5LaF\textsubscript{3} nano-glass–ceramics single doped with Ce\textsuperscript{3+} or Tb\textsuperscript{3+} and co-doped with Ce\textsuperscript{3+–Tb\textsuperscript{3+}} by thermal treatment of precursor glasses. It was found that the green emission of Tb\textsuperscript{3+} ions was greatly enhanced through down shifting process, due to efficient energy transfer from Ce\textsuperscript{3+} to Tb\textsuperscript{3+} ions in the glass–ceramics, which is favored by the reduction of the interionic distances when the dopant ions are partitioned into LaF\textsubscript{3} nanocrystals. These results suggest the use of these materials to improve the efficiency of solar cells. Yang et al. [38] have prepared Pr\textsuperscript{3+}, Yb\textsuperscript{3+} co-doped Y\textsubscript{2}O\textsubscript{3} transparent ceramics by the solid state reaction and vacuum sintering. Down-conversion near infrared emission has been demonstrated upon a 482 nm excitation. The energy of the 482 nm blue photon was first absorbed by Pr\textsuperscript{3+} and then delivered to Yb\textsuperscript{3+}. Possible energy transfer mechanisms from Pr\textsuperscript{3+} to Yb\textsuperscript{3+} have been discussed. Under the 482 nm excitation, the Pr\textsuperscript{4+–Yb\textsuperscript{2+}} charge transfer state would not seriously influence the energy transfer process. The dominant one should be either the cooperative down-conversion or the two-step photon emission. The efficient down-conversion near infrared emission has potential application in enhancing the conversion efficiency of crystalline silicon solar cells.
Wienand et al. [39] have reported the measurements on the resistivity, susceptibility and ESR vs. temperature of monopnictides MZ (with M=Sc, Y, La and Z=As, Sb, Bi) which contain small amounts of Ce- or Yb-ions as doping material. Metallic conductivities are found in all of these systems. With increasing covalent character of the MZ host we observed: an increasing conductivity, a decreasing crystal-field splitting of the Ce$^{3+}$- or Yb$^{3+}$-ionic state and for both 4f-ions an increase of the negative 4f-conduction electron exchange constant.

Zhou et al. [40] have investigated Yb$^{3+}$ and Ce$^{3+}$ ions were introduced into Er$^{3+}$doped TeO$_2$–ZnO–La$_2$O$_3$–Nb$_2$O$_5$ (the composition is in mole ratio) glasses, and the effects of Yb$^{3+}$ and Ce$^{3+}$ on the infrared fluorescence properties at the 1.5 \( \mu \)m band and the visible upconversion luminescence of Er$^{3+}$ under the excitation at 975 nm.

Despite of the fact that a number of recent investigations are available on the environment of rare earth ions in a variety of inorganic glass systems [41, 42], no dedicated studies are available on the role of yttrium ions on spectroscopic properties of Ce$^{3+}$ and Yb$^{3+}$ co-doped lithium silicate glasses.
4.3 Characterization

4.3.1 Physical Parameters

From the measured values of the density and average molecular weight $\overline{M}$ of the samples, various other physical parameters such as rare earth ion concentration $N_i$, mean rare earth ion separation $r_i$ and molar volume and other related parameters were evaluated for all the glass samples and presented in Table 4.2. The dependence of density $d$ on the concentration of $Y_2O_3$ for all the titled glasses shows slight enhancement with increasing $Y_2O_3$ content. The increasing density can be related to the replacement of $Li_2O$ (molecular weight 29.88) by $Y_2O_3$ (molecular weight 225.81).

4.4 Results

4.4.1 Infrared spectra

In Fig. 4.1, the IR spectra of $Ce^{3+}/Yb^{3+}$ co-doped $Li_2O–Y_2O_3–SiO_2$ glass compounds are presented. The spectra have exhibited conventional vibrational band due to Si–O–Si asymmetric vibrations at about 1030 cm$^{-1}$ and another band due to Si–O–Si symmetric vibrations at about 780 cm$^{-1}$. More precisely the later band is identified as bending mode of bridging oxygen situated perpendicularly to Si–Si axis within the Si–O–Si plane [43]. The band originated from Y-O vibrations of YO$_6$ structural units is located at about 470 cm$^{-1}$ [44, 26]. In this region the band caused by Si–O–Si rocking motion is
also reported [43, 45]. With increasing $Y_2O_3$ content, the intensity of the asymmetrical band of Si–O–Si and also of $YO_6$ structural units is enhanced.

**Table 4.2** Physical parameters of $Li_2O–Y_2O_3–SiO_2$ glasses doped with $Ce_2O_3$ and $Yb_2O_3$

<table>
<thead>
<tr>
<th>Physical parameters</th>
<th>$Ce$&lt;sup&gt;3+&lt;/sup&gt; series</th>
<th>$Yb$&lt;sup&gt;3+&lt;/sup&gt; series</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$CeY_5$</td>
<td>$CeY_{10}$</td>
</tr>
<tr>
<td>Density $d$ (g/cm&lt;sup&gt;3&lt;/sup&gt;)</td>
<td>2.5271</td>
<td>2.8235</td>
</tr>
<tr>
<td>Dopant ion conc. $N_i$ ($x10^{20}$ ions/cm&lt;sup&gt;3&lt;/sup&gt;)</td>
<td>2.64</td>
<td>2.52</td>
</tr>
<tr>
<td>Interionic distance $R_i$ (Å)</td>
<td>15.59</td>
<td>15.83</td>
</tr>
<tr>
<td>Polaron radius $R_p$ (Å)</td>
<td>6.28</td>
<td>6.38</td>
</tr>
<tr>
<td>Field Strength $F_i$ ($10^{15}$, cm&lt;sup&gt;-2&lt;/sup&gt;)</td>
<td>7.59</td>
<td>7.37</td>
</tr>
<tr>
<td>Optical band gap (eV)</td>
<td>3.45</td>
<td>3.42</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.523</td>
<td>1.524</td>
</tr>
</tbody>
</table>
Fig. 4.1 IR spectra of $\text{Li}_2\text{O} - \text{Y}_2\text{O}_3 - \text{SiO}_2$: $\text{Ce}^{3+}/\text{Yb}^{3+}$ co-doped glasses.
4.4.2 Optical absorption spectra

Fig. 4.2 represents the optical absorption spectra of Ce$^{3+}$ (dotted lines) and also of Ce$^{3+}$/Yb$^{3+}$ co-doped (solid lines) Li$_2$O–Y$_2$O$_3$–SiO$_2$ glasses recorded at room temperature within the spectral range 400–550 nm. The spectra exhibited a broad absorption band due to $4f(2^2F_J)\rightarrow 5d(2^2A_{1g})$ transition of Ce$^{3+}$ ions at a wavelength about 445 nm [46]. Fig. 4.3 represents the optical absorption spectra of Yb$^{3+}$ (dotted lines) and Ce$^{3+}$/Yb$^{3+}$ co-doped (solid lines) Li$_2$O–Y$_2$O$_3$–SiO$_2$ glasses recorded at room temperature in the wavelength region 800–1200 nm. The spectra have exhibited an absorption band with a degeneracy corresponding to localize $^{2}F_{7/2} \rightarrow ^{2}F_{5/2}$ transition of Yb$^{3+}$ ion spreading over a spectral range covering 900-1000 nm wavelengths [47]. Moreover, these spectra unambiguously show that there is a considerable increase in the spectral intensity of both the bands (viz., $4f \ (^{2}F_J) \rightarrow 5d \ (^{2}A_{1g})$, $^{2}F_{7/2} \rightarrow ^{2}F_{5/2}$) due to co-doping.

From the observed absorption edges, we have evaluated the optical band gaps ($E_o$) of these glasses by drawing Tauc plot between $(\alpha \ \hbar \ \omega)^{1/2}$ and $\hbar \ \omega$ as per the equation:

$$\alpha(\omega) \ \hbar \ \omega = C(\hbar \ \omega - E_o)^2$$

(4.1)

The power index 2 is caused by a fact that we deal generally with the disordered system with effective quas-zone Brillouine center located in the
effective Gamma point. So deviations of these dependences may be an indicator of the states situated within the forbidden effective energy gap.

Fig. 4.2 Optical absorption spectra of Ce$_2$O$_3$ (dotted lines) and Ce$_2$O$_3$/Yb$_2$O$_3$ co-doped (solid lines) Li$_2$O–Y$_2$O$_3$–SiO$_2$ glasses mixed with different concentrations of Y$_2$O$_3$ at ambient temperature in the visible region.
Fig. 4.3 NIR Optical absorption spectra of Yb\(_2\)O\(_3\) (dotted lines) and Ce\(_2\)O\(_3\)/Yb\(_2\)O\(_3\) co-doped (solid lines) Li\(_2\)O–Y\(_2\)O\(_3\)–SiO\(_2\) glasses mixed with different concentrations of Y\(_2\)O\(_3\) recorded at room temperature.
Fig. 4.4 represents the Tauc plots of Ce\(^{3+}\) doped glasses in which a considerable part of each curve is observed to be linear. From the extrapolation of the linear portion of these curves, the values of optical band gap (\(E_o\)) are evaluated and presented in Table 4.2. The optical band gaps for the Yb\(^{3+}\) series of glasses are also evaluated in a similar way and reported in Table 4.2. The values of optical band gaps for all the three series of glasses are found to decrease with increasing \(\text{Y}_2\text{O}_3\) content.

**4.4.3 Photoluminescence spectra**

Fig. 4.5 shows the luminescence spectra of Ce\(^{3+}\) doped (dotted lines) and Ce\(^{3+}/\text{Yb}^{3+}\) co-doped (solid lines) Li\(_2\text{O}–\text{Y}_2\text{O}_3–\text{SiO}_2\) glasses recorded at ambient temperature. During excitation at 360 nm, there occur two broad luminescence bands in the visible region (375–490 nm) which are the parity allowed 5d (\(^2\text{D}\)) \(\rightarrow\) 4f (\(^2\text{F}_{5/2}, 7/2\)) transitions of Ce\(^{3+}\) ion [32]. Due to co-doping with Yb\(^{3+}\) ions the spectral intensity of these bands is substantially enhanced with spectral red shifts of meta-centers.

It is interesting to emphasize that the luminescence spectra of Yb\(^{3+}\) solely doped Li\(_2\text{O}–\text{Y}_2\text{O}_3–\text{SiO}_2\) glasses excited at 360 nm did not show any emission band (inset of Fig.4.6). However, due to excitation at 900 nm the spectra exhibited a broad luminescence band due to standard \(^2\text{F}_{5/2}\) \(\rightarrow\) \(^2\text{F}_{7/2}\) transition of Yb\(^{3+}\) ions (Fig.4.6). As the concentration of \(\text{Y}_2\text{O}_3\) is enhanced, the spectral intensity of this band is found to increase.
Fig. 4.4 Tauc plots of Ce$_2$O$_3$ doped Li$_2$O–Y$_2$O$_3$–SiO$_2$ glasses mixed with different concentrations of Y$_2$O$_3$. 

Ce$^3+$ doped glasses

$E_o$ (eV)
- CeY$_5$ : 3.45
- CeY$_{10}$ : 3.42
- CeY$_{15}$ : 3.38
Fig. 4.5 Photoluminescence spectra of Ce\(_2\)O\(_3\) (dotted lines) and Ce\(_2\)O\(_3\)/Yb\(_2\)O\(_3\) co-doped (solid lines) Li\(_2\)O–Y\(_2\)O\(_3–\)SiO\(_2\) glasses mixed with different concentrations of Y\(_2\)O\(_3\) recorded at room temperature (\(\lambda_{\text{exc}} = 360\) nm).
Fig. 4.6 Photoluminescence spectra of Li$_2$O–Y$_2$O$_3$–SiO$_2$ glasses doped with 1.0 mol% of Yb$_2$O$_3$ mixed with different concentrations of Y$_2$O$_3$ recorded at room temperature excited at 900 nm. Inset shows photoluminescence spectra of the same samples excited at 360 nm.
Fig. 4.7 shows the luminescence spectra of Ce$^{3+}$/Yb$^{3+}$ co-doped Li$_2$O–Y$_2$O$_3$–SiO$_2$ glasses recorded at room temperature excited at 900 nm and 360 nm. The spectra exhibited strong emission band at about 980 nm due to $^2F_{5/2} \rightarrow ^2F_{7/2}$ transition of Yb$^{3+}$ ions. With increase of Y$_2$O$_3$ content the spectral intensity of this band is enhanced and also exhibited spectrally red shift. The comparison of the spectra obtained due to excitation at two wavelengths indicated high luminescence efficiency for the samples excited at 360 nm. The energy level diagram involving observed absorption and emission transitions for Ce$^{3+}$ and Yb$^{3+}$ ions for one of the glasses (glass mixed with 15.0 mol% of Y$_2$O$_3$) is presented in the Fig.4.8.
Fig. 4.7 Photoluminescence spectra of co-doped Li$_2$O–Y$_2$O$_3$–SiO$_2$ glasses mixed with different concentrations of Y$_2$O$_3$ recorded at room temperature excited at 360 nm and 900 nm. The observed emission band is due to $^2F_{5/2} \rightarrow ^2F_{7/2}$ transition of Yb$^{3+}$ ions.
Fig. 4.8 Principal energy level diagram showing energy transfer from Ce$^{3+}$ to Yb$^{3+}$ ions in co-doped Li$_2$O–Y$_2$O$_3$–SiO$_2$ glasses.

4.5. Discussion

Among various constituents of Li$_2$O–Y$_2$O$_3$–SiO$_2$ glass composition, SiO$_2$ is a well known glass former and is expected to participate in the glass network formation with tetrahedral [SiO$_4$]$^4$ units and all the four oxygens in SiO$_4$ tetrahedra are shared. Li$_2$O is a strong modifier, enters the glass network by breaking Si–O–Si, Si–O–Y bonds (normally the oxygens of Li$_2$O break the local symmetry while Li$^+$ ions occupy interstitial positions).
Due to this depolymerization, there will be predominant formation of meta, and also small concentration of pyro and ortho-silicate structural units viz., $[\text{SiO}_{4/2}]^0$, $[\text{SiO}_{3/2}\text{O}]^-$, $[\text{SiO}_{2/2}\text{O}_2]^{2-}$, $[\text{SiO}_{1/2}\text{O}_3]^{3-}$ and $[\text{SiO}_4]^{4-}$ as per the following chemical equilibria [45]:

(i) $2[\text{SiO}_{4/2}]^0 + \text{Li}_2\text{O} \rightarrow 2 [\text{SiO}_{3/2}\text{O}]^- + 2 \text{Li}^+$

(ii) $2[\text{SiO}_{2/2}\text{O}_2]^{2-} + \text{Li}_2\text{O} \rightarrow 2 [\text{SiO}_{1/2}\text{O}_3]^{3-} + 2 \text{Li}^+$

(iii) $2\text{Y}_2\text{O}_3 \rightarrow [\text{Y}^{3+}]_o + 3[\text{YO}_{4/2}]_t$

$\text{Y}_2\text{O}_3$ is an incipient glass former, as such does not form the glass by itself; however in the presence of modifiers like Li$_2$O it participates in the glass network with tetrahedral (YO$_4$) and octahedral (YO$_6$) occupancy:
The $\text{YO}_4$ tetrahedra alternate with $\text{SiO}_4$ groups as shown in chemical equation (iii), whereas octahedral yttrium ions occupy interstitial positions [48] and induce bonding defects in the glass network.

The observed increase in the intensity of bands due to $\text{Si–O–Si}$ asymmetric vibrations, $\text{Si–O–Si}$ rocking motions and vibrations of $\text{Y–O}$ bonds for $\text{YO}_6$ octahedra at the extension of the band due to $\text{Si–O–Si}$ symmetrical groups with increase in the concentration of $\text{Y}_2\text{O}_3$ in the IR spectra suggests the increase of octahedral occupancy of yttrium ions that act as modifiers. The same conclusion can also be obtained from the data on optical energy gap. The octahedrally coordinated $\text{Y}^{3+}$ ions act as modifiers similar to $\text{Li}^+$ ions and induce non-bridging oxygens (NBO’s) in the glass network. Higher is the concentration of the modifier (octahedral ions) ions, larger is the concentration of NBO’s in the glass matrix. Due to this reason, an increase in the degree of localization for electrons there by an increase in the donor centers in the glass network is anticipated. The presence of higher concentration of these donor centers suppresses the optical band gap and show red shift with increase in the concentration of $\text{Y}_2\text{O}_3$.

The broad absorption band observed at about 445 nm in the spectra of $\text{Ce}^{3+}$ doped glasses is attributed to the $4f(2^2F_{5/2}) \rightarrow 5d(2^2A_{1g})$ transition of $\text{Ce}^{3+}$ ions based on the works of Vorsthove and U. Kynast [46]. Due to spin–orbit interaction, $2^2F$ ground splits into two $J$ states energetically separated by ~2200
The \((2J+1)\)-fold degeneracy of these states is reduced by the surrounding ligand field. Because the 4f electron is shielded from the ligand field by the closed 5s and 5p electron shells, the overall splitting of the \(^2\text{F}_J\) states is relatively small, typically only a few hundred cm\(^{-1}\). When the 4f electron is excited to the outer excited 5d state, depending on the site symmetry the degeneracy of the 5d state (typically \(\sim 5000–10000\) cm\(^{-1}\)) is partially or completely removed due to the effect of the ligand fields. Electric–dipole transitions between the 4f ground state and the 5d excited state of Ce\(^{3+}\) are parity allowed and possess a large oscillator strength contrary to long lived excited states of several lanthanides in glasses and crystals whose oscillatory strength is equal to about \(10^{-6}\). In fact, Ce\(^{3+}\) is the only trivalent lanthanide ion that has got high oscillator strength (~ 0.01–0.1) [21]. As the concentration of Y\(_2\)O\(_3\) is increased an increase in the absorption intensity of this band is observed. This may be observed due to higher probability of the \(4f(^2\text{F}_{5/2}) \rightarrow 5d(^2\text{A}_{1g})\) transition due caused by enhanced crystal field distortions in the vicinity of Ce\(^{3+}\) ions in the glass network. However, we admit here that this absorption band is also caused by complex grouping of Ce\(^{4+}\)–Ce\(^{3+}\) and Ce\(^{4+}\)–O–Fe\(^{3+}\) with exchange interaction between their metal ions if even a small concentration iron ions are present in the glass matrix as suggested by Malahskevich et.al.[49].
As mentioned earlier Li₂O–Y₂O₃–SiO₂ glass network is expected to be composed of three-dimensional yttria–silicate structural units. The lithium ions insert in the cavities and act as charge balancers compensating for the negative charge due to the substitution of Si by Y. The ytterbium ion is expected to be coordinated by three such SiO₄/YO₄ tetrahedral ligands as shown in Fig. 4.9.

![Fig. 4.9 An illustration of Yb³⁺ octahedra interlocked with SiO₄ and YO₄ tetrahedrons](image)

The evidence for six-fold co-ordination of Yb³⁺ in different glasses was derived from an application of crystal field theory on the basis of optical absorption and emission spectra by Robinson et. al.[16]. The network of Li₂O–Y₂O₃–SiO₂:Yb₂O₃ glass containing different YbO₆ spheres can be
assumed to be surrounded by yttrium of different cationic field strengths and polarizabilities. Following these reasons the characteristics of Yb-O bond in the octahedral sphere are different for the glasses containing different concentrations of $\text{Y}_2\text{O}_3$. In fact, we may expect strong distortion of the local structures in the vicinity of Yb$^{3+}$ ions in the glass containing higher concentration of Y$_2$O$_3$, since the concentration of YO$_6$ structural units is more in these glasses. Hence, the larger Stark splitting of $^2\text{F}_{5/2}$ and $^2\text{F}_{7/2}$ levels is expected in the absorption spectrum of these glasses.

The excited electronic configuration of Ce$^{3+}$ is 5d$^1$. The 5d electron of Ce$^{3+}$ is not shielded from the surroundings and thus interacts strongly with the neighboring anion (Y$^{3+}$) ligands in the compounds. Such interaction leads to the structural modifications in the vicinity of this ion in the host materials in a way that facilitates the increase of absorption and causes broadening of emission band of Ce$^{3+}$ ions with the increasing Y$_2$O$_3$ content.

As mentioned earlier, the luminescence spectra of Yb$^{3+}$ singly doped glass excited at 360 nm did not exhibit any significant emission band in the spectral range 900-1000 nm. Moreover, it exhibits prominent emission band centered at about 980 nm due to the $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ transition during excitation at 900 nm. However, the spectra of the co-doped glasses excited at wavelengths 360 nm and 900 nm exhibited bright emission band due to intra-center $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ transition of Yb$^{3+}$ ions at about 980 nm. The comparison of the spectra
corresponding to these excited wavelengths indicated remarkable spectral intensity for $\lambda_{\text{exc}} = 360$ nm. Such high spectral intensity indicates a co-operative energy transfer between the two ions as depicted in Fig. 4.8.

To be more specific as shown in the energy level diagram (Fig. 4.8), the observed result indicates that the emission of two NIR photons per one absorbed UV photon is possible with $\text{Ce}^{3+} \rightarrow \text{Yb}^{3+}$ dual ions via a co-operative energy transfer (CET) process from $\text{Ce}^{3+}$ ion to two $\text{Yb}^{3+}$ ions. Further, doping of the glass with $\text{Ce}_2\text{O}_3$ may lead to reducing of some share of $\text{Yb}^{3+}$ ions to $\text{Yb}^{2+}$. These, latter may act as sensitizers of $\text{Yb}^{3+}$ ions luminescence too.

Additionally, all glasses regardless of high purity of the chemicals used may contain iron impurity to small extent. It has been established that the $\text{Fe}^{3+}$ is very effective sensitizer of $\text{Yb}^{3+}$ ions luminescence in glasses. The sensitizer may transfer the excitations absorbed in their charge transfer band to $\text{Yb}^{3+}$ or to be an intermediate member in the transfer from $\text{Ce}^{3+}$ to $\text{Yb}^{3+}$ as reported by Malashkevich and his co-workers [50]. All these factors may account for the observed increase of luminescence associated with $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ transition of $\text{Yb}^{3+}$ ions.

It is also necessary to emphasize that with increasing $\text{Y}_2\text{O}_3$ content in the glass matrix, the spectral position of absorption band (due to $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ transition) is slightly red shifted and the absorption oscillator strength under the given peak is found to be increasingly correlating to the $\text{Y}^{3+}$ ion.
concentration. Such red spectral shift confirms weak the interaction between
the ytterbium ions and the surrounding ligand which causes a lower crystal-
field splitting for $^{2}\text{F}_{7/2}$ and $^{2}\text{F}_{5/2}$ levels in these samples. Emission cross section
for the NIR emission band of Yb$^{3+}$ ions is evaluated from the absorption
spectra using the relation [51, 52]:

$$\sigma_{em}(\lambda) = \sigma_{abs}(\lambda) \frac{Z_1}{Z_2} \exp\left(\frac{\varepsilon - \frac{hc\lambda}{kT}}{kT}\right)$$  \hspace{1cm} (4.2)

where $\sigma_{abs}(\lambda)$ is the absorption cross section at wavelength $\lambda$, which is
evaluated using:

$$\sigma_{abs}(\lambda) = 2.303 \frac{\log(I_0/I)}{N_i L}.$$  \hspace{1cm} (4.3)

In Eq. (4.2), $h$ is the Planck’s constant, $c$ is the speed of light, $k$ is Boltzmann’s
constant $\varepsilon$ is the zero line energy (energy separation between the lowest crystal
field levels of the upper and lower manifolds determined from the most intense
absorption peak of Yb$^{3+}$), $Z_1$ and $Z_2$ represent the partition functions of the
lower and upper spectral levels, respectively. For Yb$^{3+}$ ion in the glasses, $Z_1/Z_2$
is equal to about 1.33 [54]. In Eq. (4.3), $L$ is the thickness of the sample $N_i$ is
the concentration of Yb$^{3+}$ expressed as ion/cm$^3$, log $(I_0/I)$ is the optical density.
The values of $\sigma_{em}$ obtained for singly doped Yb$^{3+}$ and co-doped glasses are
given in Tables 4.3 (a and b). The emission cross section is found to increase
with the increase of the Y$_2$O$_3$ content.
The spectral shape of the measured fluorescence spectrum for Yb$^{3+}$ ions is strongly affected by radiation trapping [53, 54]. Hence, a large discrepancy between measured life time from fluorescence spectra and the intrinsic radiative lifetime may be expected. The calculated lifetime may therefore be considered as a reference in determining the true value of measured lifetime [54]. The error originated from the radiation trapping can be suppressed by evaluating radiative lifetime using [6]:

$$
\tau_R = \frac{\Lambda^4}{8 \pi c n^2 \int \sigma_{em}(\lambda) d\lambda},
$$

(4.4)

where $\Lambda^4 = \int \lambda^4 g(\lambda) d\lambda$.

The calculated lifetimes for the studied glasses indicated gradual enhancement with increasing Y$_2$O$_3$ content (Tables 4.3 (a and b)). The increasing spectral Stokes shift observed with the increasing Y$_2$O$_3$ content confirms that there exists a decreasing radiative trapping. Such increase leads to an increase of radiative lifetime as observed.

The close coexistence of the absorption and emission bands for Yb$^{3+}$ ions indicates the occurrence of possible re-absorption. The effect of the resonant absorption loss is determined by the parameter $\beta_{\text{min}} (= \sigma_{\text{abs}}/ (\sigma_{\text{abs}} + \sigma_{\text{em}}))$ which corresponds to the minimum fraction of Yb$^{3+}$ ions that must be excited to compensate the gain exactly with the ground-state absorption. The value of $\beta_{\text{min}}$ obtained for the studied glasses exhibited an increasing trend
(Tables 4.3 (a and b)) with the increasing Y$_2$O$_3$ content. Such trend indicates a gradual decrease of absorption loss with the increase of Y$_2$O$_3$.

Table 4.3 (a) Spectroscopic parameters of Yb$_2$O$_3$ doped Li$_2$O–Y$_2$O$_3$–SiO$_2$ glasses

<table>
<thead>
<tr>
<th>Glass</th>
<th>$\lambda_p$ (nm)</th>
<th>$\lambda_{em}$ (nm)</th>
<th>$\sigma_{abs}(\lambda_p)$ ($10^{-18}$ cm$^2$)</th>
<th>$\sigma_{em}(\lambda_{p})$ ($10^{-18}$ cm$^2$)</th>
<th>$\beta_{min}$</th>
<th>$\tau_R$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YbY$_5$</td>
<td>976</td>
<td>982</td>
<td>1.77</td>
<td>3.19</td>
<td>0.34</td>
<td>0.91</td>
</tr>
<tr>
<td>YbY$_{10}$</td>
<td>978</td>
<td>987</td>
<td>2.61</td>
<td>4.69</td>
<td>0.35</td>
<td>1.15</td>
</tr>
<tr>
<td>YbY$_{15}$</td>
<td>981</td>
<td>992</td>
<td>3.18</td>
<td>5.16</td>
<td>0.38</td>
<td>1.28</td>
</tr>
</tbody>
</table>

Table 4.3 (b) Spectroscopic parameters of co-doped Li$_2$O–Y$_2$O$_3$–SiO$_2$ glasses

<table>
<thead>
<tr>
<th>Glass</th>
<th>$\lambda_p$ (nm)</th>
<th>$\lambda_{em}$ (nm)</th>
<th>$\sigma_{abs}(\lambda_p)$ ($10^{-18}$ cm$^2$)</th>
<th>$\sigma_{em}(\lambda_{p})$ ($10^{-18}$ cm$^2$)</th>
<th>$\beta_{min}$</th>
<th>$\tau_R$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeYbY$_5$</td>
<td>977</td>
<td>983</td>
<td>1.97</td>
<td>3.55</td>
<td>0.36</td>
<td>0.97</td>
</tr>
<tr>
<td>CeYbY$_{10}$</td>
<td>981</td>
<td>991</td>
<td>3.09</td>
<td>5.01</td>
<td>0.38</td>
<td>1.31</td>
</tr>
<tr>
<td>CeYbY$_{15}$</td>
<td>984</td>
<td>997</td>
<td>4.58</td>
<td>6.72</td>
<td>0.41</td>
<td>1.44</td>
</tr>
</tbody>
</table>

To explain the CET process and to clarify origin of the down conversion phenomenon for NIR emission as depicted in Fig. 4.8, we have adopted the rate equation model in terms of emission probabilities as described below:

For the Yb$^{3+}$ ions doped glasses, the rate equation can be written as:
\[ \frac{dn_1}{dt} = \phi V_{01} n_0 + \phi V_{1i} n_i - (Q_i + \tau_i^{-1}) n_i \] (4.5)

Similarly for the Ce\(^{3+}\) doped glasses,

\[ \frac{dn_i}{dt} = \phi V_{0i} n_0 - \phi V_{ii} n_i - (Q_i + \tau_i^{-1}) n_i \] (4.6)

In the Eqs. (4.5) and (4.6) \(n_0\) and \(n_i\) represent the occupations of the ground state and the excited level \(i\), respectively. \(\tau_i\) indicates the life time of level \(i\) for rare earth ion and \(Q_i\) represents the energy quenching rates. The absorption cross-section for each transition is denoted by \(V_{ij}\), whereas the incident pumping flux is indicated by \(\phi\).

For the obtained fluorescence intensities of emission for Yb\(^{3+}\) ions from the level \(^2\)F\(_{7/2}\), the equations are solved under the steady state conditions. The principal results obtained are as follows:

The population in the excited state of Yb\(^{3+}\) ions is

\[ n_i = \frac{\phi V_{0i} n_0 + \phi V_{1i} n_i}{(Q_i + \tau_i^{-1})} \] (4.7)

The population of the excited state of Ce\(^{3+}\) ions is

\[ n_i' = \frac{\phi V_{0i}' n_0 - \phi V_{1i}' n_i}{(Q_i' + \tau_i'^{-1})} \] (4.8)

Substituting the value of \(n_i\) in Eq. 4.7 and solving for the population \(n_i\) of the excited state of Yb\(^{3+}\) ion, one can get:
Using Eq. (4.9), the expression for fluorescence spectral intensity (evaluated using $I_i = \hbar \omega_{io} V_{io} n_i$) can be written as:

$$I = \hbar \omega_{io} \left( \frac{\phi V_{o1} n_0}{(Q_i + \tau_i^{-1})} + \frac{\phi^2 V_{r1} V_{o1} n_0}{(Q_i + \tau_i^{-1})(Q_r + \tau_r^{-1})} \right) \left( 1 + \frac{\phi^2 V_{r1} V_{f1}}{(Q_i + \tau_i^{-1})} \right)^{-1} \quad (4.10)$$

As can be seen from Eq. (4.10), the intensity of the emission line exhibits quadratic dependence versus the pumping power, indicating that the process of down conversion produces two photons, as expected. In a number of earlier cases this type of equations are found to be valid for low pumping powers.

Furthermore, Eq. (4.10) clearly suggests that the spectral intensity of NIR emission band is proportional to the radiative life time of the upper level. The calculated values of the life time $\tau$ are found to be the largest for the co-doped glasses (Table 4.3(b)); hence the intensity $^2F_{5/2} \rightarrow ^2F_{7/2}$ emission lines is expected to be larger for the co-doped glasses as observed.

### 4.6. Conclusions

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 emission spectra of Yb$^{3+}$ doped glasses exhibited a broad spectral emission band at wavelength about 980 nm due to $^2F_{5/2} \rightarrow ^2F_{7/2}$ transition for Yb$^{3+}$ ions. A substantial enhancement in the
intensity of this NIR band is observed due to co-doping with Ce$^{3+}$ ions. With the increasing Y$_2$O$_3$, an increase in the rate of energy transfer from Ce$^{3+}$ to Yb$^{3+}$ with low phonon losses could be visualized. The reasons for such enhancement have been discussed within a framework of structural modifications taking place in the vicinity of Yb$^{3+}$ ions in the glass network due to varying concentrations of Y$_2$O$_3$. 
References


