Chapter IV

In this chapter, we have discussed the photoluminescence characteristics of trivalent dysprosium doped Sr\textsubscript{0.5}Ca\textsubscript{0.5}TiO\textsubscript{3} phosphors synthesized via solid state reaction for white light generation. The structure, composition and morphology of the prepared phosphor samples are analyzed by XRD, FTIR, SEM and EDS measurements. The band gap energy and Judd-Ofelt intensity parameters were calculated from the absorption data. The photoluminescence spectrum of Dy\textsuperscript{3+} doped Sr\textsubscript{0.5}Ca\textsubscript{0.5}TiO\textsubscript{3} shows three emission peaks at 481, 574 and 638 nm corresponding to \(^4\text{F}_{9/2} \rightarrow ^{6}\text{H}_{15/2}\), \(^4\text{F}_{9/2} \rightarrow ^{6}\text{H}_{13/2}\) and \(^4\text{F}_{9/2} \rightarrow ^{6}\text{H}_{11/2}\) transitions respectively. The effect of excitation wavelength on the emission spectra shows a tuning effect towards the pure white light regions. The radiative properties of Sr\textsubscript{0.5}Ca\textsubscript{0.5}TiO\textsubscript{3}: 2 wt\% Dy\textsuperscript{3+} phosphor are predicted by combining the Judd-Ofelt intensity parameters with luminescence spectra. The decay profiles of \(^4\text{F}_{9/2}\) excited level of Dy\textsuperscript{3+} ions show bi-exponential behaviour and also a decrease in the average lifetime with an increase in Dy\textsuperscript{3+} concentration. Yellow to blue luminescence intensity ratio, CIE chromaticity coordinates, correlated color temperature and color purity were also calculated for different concentrations of Dy\textsuperscript{3+} doped Sr\textsubscript{0.5}Ca\textsubscript{0.5}TiO\textsubscript{3} phosphor at different excitation wavelengths.
4.1 Introduction

An efficient phosphor which offers all components necessary for white light generation is emerging as an indispensable solid state light source for the next generation of the lighting industry. They are also important in many photonic applications due to their unique properties like energy saving, environmental friendliness, cost effectiveness, long persistence and small size [1-4]. The major challenges in white light emitting phosphor has been to achieve high optical stability, high luminous efficacy, good color rendering properties and cost effectiveness against conventional lighting devices, which relay on the phosphor properties. In recent times, phosphor-converted white LEDs have been highlighted because of their excellent properties such as high brightness, low power consumption, high stability of color parameters with temperature, long lifetime and high color rendering index [3-5]. The first commercially available phosphor-converted white LED is the blue LED-excited YAG: Ce³⁺ yellow phosphor. The lack of red component reduces its efficiency and also the color temperature changes with varying input power [6]. But by using UV or near-UV excited red/green/blue tricolor phosphor material, we get white light with excellent color rendering index. Because of the quantum deficit between UV pump and the tricolor phosphors, especially the low energy red phosphor,
dissipates significant energy and makes them less efficient [5, 7]. Also, due to the re-absorption of emission light makes them less efficient [8, 9]. Hence, a single component phosphor is required for UV-excited white LED to enhance the luminescence efficiency and white light reproducibility. So the search for efficient single phase phosphor material with UV excitation is very necessary to develop new luminescent materials suitable for display and lighting devices.

Phosphors have played a key role in emerging solid state white lighting technologies. Almost all widely used phosphors comprise a crystalline host doped with rare earth ion [10]. Among rare earth ions, Dy\(^{3+}\) has an electronic configuration of 4f\(^9\) and has two luminescence bands in the emission spectrum, the yellow band corresponding to \(^{4}F_{9/2} \rightarrow ^{6}H_{13/2}\) and the blue band corresponding to \(^{4}F_{9/2} \rightarrow ^{6}H_{15/2}\) [11]. The \(^{4}F_{9/2} \rightarrow ^{6}H_{13/2}\) hypersensitive transition strongly depends on the host matrix and its intensity varies with the local environment, but \(^{4}F_{9/2} \rightarrow ^{6}H_{15/2}\) transition is independent of the host matrix. So we can change the yellow to blue intensity ratio by adjusting the host composition or the concentration and we can tune the CIE color coordinates to the white light region which can found application in WLEDs. The white light emission was also observed in Dy\(^{3+}\) doped silicates [12], molybdates [13], vanadates [14], phosphates [15], germanates [16], borates [17] etc.

In search of new materials producing efficient white light emission under proper excitation, we have studied the photoluminescence characteristics of Dy\(^{3+}\) doped strontium calcium titanate. In the previous chapters we have discussed the luminescence characteristics of Pr\(^{3+}\) and Sm\(^{3+}\) in Sr\(_{0.5}\)Ca\(_{0.5}\)TiO\(_3\) and we got UV excited reddish-orange and blue
excited yellowish orange emissions respectively. In this chapter, we have discussed the emission property of Dy\textsuperscript{3+} doped Sr\textsubscript{0.8}Ca\textsubscript{0.2}TiO\textsubscript{3}, which itself can produce blue and yellow components that result in white light emission, as a contribution to the pc- white LED with the single phase phosphor material. The tuning of the emission wavelengths with Dy\textsuperscript{3+} concentration and excitation wavelengths are also discussed.

4.2 Experimental

Sr\textsubscript{0.8}Ca\textsubscript{0.2}TiO\textsubscript{3}: x Dy\textsuperscript{3+} phosphor (where x = 0.5, 1, 2 and 3 wt\%) were synthesized using conventional solid state reaction technique. Commercially purchased SrCO\textsubscript{3} A.R (CDH, 99.99%), CaCO\textsubscript{3} A.R (CDH, 99.99%), Titanium Dioxide (Sigma- Aldrich, 99.99%) and Dy (NO\textsubscript{3})\textsubscript{3}. 6H\textsubscript{2}O (CDH, 99.99%) were used as the starting materials. The stoichiometric mixture of the raw materials was weighed and sufficiently ground in an agate pestle and mortar for an hour to get a homogenous mixture. These mixtures were taken in a platinum crucible and were calcined at temperature 1200 °C for 2 hours in air at the rate of 10 °C/minutes in KSL-1700X-S High Temperature Muffle Furnace. The fine grinding of the product material after natural cooling to the room temperature gives the final phosphor samples. All the measurements carried out in this work are similar to the previous chapter, discussed in section 2.2.

4.3 Results and Discussion

4.3.1 XRD, EDS & SEM Analysis

Fig.4.1 (a), (b) and (c) shows the XRD patterns, EDS spectrum and SEM images of the prepared phosphor samples respectively. The XRD result shows the peaks identified are in good agreement with the orthorhombic perovskite strontium calcium titanate structure in the space
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group Pbnm with cell parameters, a = 5.4677 Å, b = 5.4713 Å, c = 7.7390 Å and cell volume, V = 231.52 Å³ (ICDD No. 01-070-8505). The average crystallite size of Dy3+ doped Sr0.5Ca0.5TiO3 phosphors was calculated from the most intense XRD peak using the Debye-Scherrer formula and is calculated as 34.47, 17.21, 34.45 and 34.52 nm for x= 0.5, 1, 2 and 3 respectively [18]. Doping of Dy3+ ions does not cause any significant changes in the XRD patterns of Sr0.5Ca0.5TiO3 owing to their similar ionic radii (Dy3+ = 105 pm and Ca2+ = 99 pm) and the small amount of dopant concentration [19].

![XRD pattern of Sr0.5Ca0.5TiO3: x Dy3+ phosphors.](image)

The EDS spectrum confirms the presence of Sr, Ca, Ti, O and Dy elements in the prepared samples. The absence of impurity atoms confirms the purity of the prepared samples also. The microstructures atoms of Sr0.5Ca0.5TiO3 and Dy3+ doped Sr0.5Ca0.5TiO3 are observed in the SEM images with an average particle size in the 0.1 – 2 μm range. The particles are agglomerated and irregularly shaped. As the doping concentration of Dy3+
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Fig. 4.1(b) EDS spectrum of Sr$_{0.5}$Ca$_{0.5}$TiO$_3$: 2 Dy$^{3+}$ phosphor sample.

Fig. 4.1(c) SEM images of Sr$_{0.9}$Ca$_{0.1}$TiO$_3$: x Dy$^{3+}$ phosphor samples (a) x = 0, (b) x = 0.5, (c) x = 2 and (d) x = 3.
ions increases the particles became more spherical and more uniform distribution. Generally, more uniform distribution and more homogeneous particle size will enhance the luminescence of the phosphor materials, by reducing the possibility of formation defects [20].

4.3.2 Fourier Transform Infrared Spectroscopy

Fig. 4.2 FTIR spectra of Sr_{0.5}Ca_{0.5}TiO_{3} and Sr_{0.5}Ca_{0.5}TiO_{3}: 2 wt% Dy^{3+} phosphors.

Fig. 4.2 shows the FTIR spectra of Sr_{0.5}Ca_{0.5}TiO_{3} and Sr_{0.5}Ca_{0.5}TiO_{3}: 2 wt% Dy^{3+} phosphor samples. The undoped Sr_{0.5}Ca_{0.5}TiO_{3} shows only two absorption bands at 550 cm\(^{-1}\) and 1713 cm\(^{-1}\). The band at 550 cm\(^{-1}\) corresponds to the Ti-O stretching vibration of TiO\(_6\) group [21]. The bands observed in between 700- 400 cm\(^{-1}\) can also correspond to the metal oxygen stretching vibrations [22]. The absorption band at 1713 cm\(^{-1}\) corresponds to the H-O-H bending vibration of water due to the naturally absorbed surface water and lattice hydroxyls [18]. The doping of Dy\(^{3+}\) ions does not make any change in the FTIR spectrum except the transmittance intensity and a small shift to the Ti-O stretching vibration (553 cm\(^{-1}\)) only. This
intensity variation confirms the presence of doped Dy\(^{3+}\) ions in the host matrix [23].

### 4.3.3 Absorption Spectrum

![Absorption Spectrum](image)

Fig.4.3 Absorption spectrum of 2 wt% Dy\(^{3+}\) doped Sr\(_{0.5}\)Ca\(_{0.5}\)TiO\(_3\) phosphor.

Fig.4.3 represents the NIR absorption spectrum of 2 wt% Dy\(^{3+}\) doped Sr\(_{0.5}\)Ca\(_{0.5}\)TiO\(_3\) phosphor. All the absorption transitions were originated from the ground level \(^6\)H\(_{15/2}\). We got six absorption peaks in the NIR region at 5865, 7735, 9047, 11051, 12396 and 13182 cm\(^{-1}\) corresponding to the transitions \(^6\)H\(_{15/2}\)→\(^6\)H\(_{11/2}\), \(^6\)F\(_{11/2}\), \(^6\)F\(_{9/2}\), \(^6\)F\(_{7/2}\), \(^6\)F\(_{5/2}\) and \(^6\)F\(_{3/2}\) respectively [24]. In some rare earth ions, the position and intensity of several transitions are very sensitive to the local environment of the ion. Such kind of transitions is termed as a hypersensitive transition which obeys the transition rules, \(|\Delta S| = 0\), \(|\Delta L| \leq 2\) and \(|\Delta J| \leq 2\). In the case of Dy\(^{3+}\) doped Sr\(_{0.5}\)Ca\(_{0.5}\)TiO\(_3\) the hypersensitive transition \(^6\)H\(_{15/2}\)→\(^6\)F\(_{11/2}\) is found to be more intense than the other transitions. The direct band gap energy of Sr\(_{0.5}\)Ca\(_{0.5}\)TiO\(_3\): 2 wt% Dy\(^{3+}\)
phosphor was calculated from the absorption spectrum and is found to be 3.25 eV.

Table 4.1 Energies for 2 wt% Dy$^{3+}$ in Sr$_{0.5}$Ca$_{0.5}$TiO$_3$ ($v_e$) and aquo-ion ($v_a$) along with nephelauxetic ratio ($\beta$) and bonding parameter ($\delta$).

<table>
<thead>
<tr>
<th>SI No.</th>
<th>$S'L'J'$</th>
<th>$v_e$ (cm$^{-1}$)</th>
<th>$v_a$ (cm$^{-1}$)</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$^4$H$_{15/2}$</td>
<td>5865</td>
<td>5833</td>
<td>1.0054</td>
</tr>
<tr>
<td>2</td>
<td>$^4$F$_{11/2}$</td>
<td>7735</td>
<td>7730</td>
<td>1.0006</td>
</tr>
<tr>
<td>3</td>
<td>$^4$F$_{9/2}$</td>
<td>9047</td>
<td>9087</td>
<td>0.9955</td>
</tr>
<tr>
<td>4</td>
<td>$^6$H$_{15/2}$</td>
<td>11051</td>
<td>11025</td>
<td>1.0023</td>
</tr>
<tr>
<td>5</td>
<td>$^6$F$_{9/2}$</td>
<td>12396</td>
<td>12434</td>
<td>0.9971</td>
</tr>
<tr>
<td>6</td>
<td>$^6$F$_{7/2}$</td>
<td>13182</td>
<td>13212</td>
<td>0.9977</td>
</tr>
</tbody>
</table>

$\beta = 0.9998$
$\delta = 0.0179$ (covalent bonding)

By evaluating the nephelauxetic ratio ($\beta$) and bonding parameter ($\delta$) the nature of Dy$^{3+}$ ligand bond in the Sr$_{0.5}$Ca$_{0.5}$TiO$_3$ can be understood [25]. Table 4.1 represents the values of nephelauxetic ratios ($\beta$) and bonding parameter ($\delta$) for the 2 wt% Dy$^{3+}$ doped Sr$_{0.5}$Ca$_{0.5}$TiO$_3$ phosphor. The nature of the Dy$^{3+}$ ligand bond in Sr$_{0.5}$Ca$_{0.5}$TiO$_3$ host is found to be covalent in nature since the bonding parameter is positive.

4.3.3.1 Judd-Ofelt intensity parameters

The Judd-Ofelt theory has been applied to the NIR absorption bands for 2 wt% Dy$^{3+}$ doped Sr$_{0.5}$Ca$_{0.5}$TiO$_3$ in the spectral region 800-2000 nm. Table 4.2 shows the values for the intensity parameters ($\Omega_2$, $\Omega_4$, $\Omega_6$), experimental ($f_{exp}$) and calculated ($f_{cal}$) oscillator strength of the Dy$^{3+}$ doped Sr$_{0.5}$Ca$_{0.5}$TiO$_3$ phosphor. From the table it is observed that $\Omega_2 > \Omega_4 > \Omega_6$ indicating the covalent nature of the bonding between the Dy$^{3+}$ ions and the host matrix, as $\Omega_2$ is a covalency dependent parameter whereas $\Omega_4$ and
\( \Omega_6 \) are structure dependent parameters. This similar trend has been observed for different host matrices also [26-28]. The quantity of

\[ \sigma = 0.032 \times 10^{-6} \]

<table>
<thead>
<tr>
<th>S'L'J'</th>
<th>( E_{exp} ) (cm(^{-1}))</th>
<th>( E_{cal} ) (cm(^{-1}))</th>
<th>( \Delta E ) (cm(^{-1}))</th>
<th>matrix elements</th>
<th>( f_{exp} ) (( \times 10^{2} ))</th>
<th>( f_{cal} ) (( \times 10^{3} ))</th>
<th>( \Delta f ) (( \times 10^{4} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^{6}H_{15/2} )</td>
<td>5865</td>
<td>5833</td>
<td>32</td>
<td>0.0023</td>
<td>0.0366</td>
<td>0.6410</td>
<td>0.21</td>
</tr>
<tr>
<td>( ^{6}F_{11/2} )</td>
<td>7735</td>
<td>7730</td>
<td>5</td>
<td>0.9387</td>
<td>0.8292</td>
<td>0.2048</td>
<td>0.93</td>
</tr>
<tr>
<td>( ^{6}F_{9/2} )</td>
<td>9047</td>
<td>9087</td>
<td>-50</td>
<td>0.0000</td>
<td>0.5736</td>
<td>0.7213</td>
<td>0.55</td>
</tr>
<tr>
<td>( ^{6}F_{7/2} )</td>
<td>11051</td>
<td>11025</td>
<td>26</td>
<td>0.0000</td>
<td>0.1360</td>
<td>0.7146</td>
<td>0.31</td>
</tr>
<tr>
<td>( ^{6}F_{5/2} )</td>
<td>12396</td>
<td>12434</td>
<td>-36</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.3452</td>
<td>0.18</td>
</tr>
<tr>
<td>( ^{6}F_{3/2} )</td>
<td>13182</td>
<td>13212</td>
<td>-30</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0610</td>
<td>0.02</td>
</tr>
</tbody>
</table>

\( \lim_{n} = 0.6309 \times 10^{-20} \text{cm}^2 \)

\( \lim_{n} = 0.5013 \times 10^{-20} \text{cm}^2 \)

\( \lim_{n} = 0.3291 \times 10^{-20} \text{cm}^2 \)

\( \chi = 1.5232 \)

the best fit between experimental and calculated oscillator strengths was observed from the low value of \( \sigma \). For the present host matrix the spectroscopic quality factor (\( \chi \)) is determined to be 1.5232 and is larger than other host matrices like yttrium scandium gallium garnet [29] and alkali lead tellurofluoroborate [27]. This high value of the quality factor suggests that Dy\(^{3+}\) doped Sr\(_{0.5}\)Ca\(_{0.5}\)TiO\(_{3}\) phosphor appears to be good optical material for various device applications.

4.3.4 Spectral analysis and color tuning properties

The excitation spectrum of different concentrations of Dy\(^{3+}\) doped Sr\(_{0.5}\)Ca\(_{0.5}\)TiO\(_{3}\) phosphors under an emission wavelength of 574 nm is shown in Fig.4.4. The spectrum shows six excitation bands centred at 351, 365, 386, 425, 450 and 472 nm corresponding to the transitions \( ^{6}H_{15/2} \rightarrow ^{6}P_{7/2} \), \( ^{6}P_{5/2} \), \( ^{4}I_{13/2} \), \( ^{4}G_{11/2} \), \( ^{4}I_{5/2} \) and \( ^{4}F_{9/2} \) respectively [30]. The near-UV peaks at 351, 365 and 386 nm are used as the excitation wavelengths for the efficient emission from Dy\(^{3+}\) doped Sr\(_{0.5}\)Ca\(_{0.5}\)TiO\(_{3}\) phosphor. In order to study the
effect of excitation wavelengths on the photoluminescence intensity of Dy$^{3+}$ doped Sr$_{0.5}$Ca$_{0.5}$TiO$_3$ phosphor, the PL spectra were recorded with different excitation wavelengths (351, 365 and 386 nm) are shown in Fig.4.5(a), 4.5(b) & 4.5(c). The emission spectra show two luminescence peaks at 481 and 574 nm corresponding to the transitions $^4F_9/2 \rightarrow ^6H_{15/2}$ and $^4F_9/2 \rightarrow ^6H_{13/2}$ respectively under 351 and 365 nm excitation. But in the case of 386 nm excitation, in addition to the characteristic blue and yellow emissions we observed a weak red emission peak at 638 nm corresponding to the transition $^4F_9/2 \rightarrow ^6H_{11/2}$ [31]. We can also observe that there is a variation in the emission intensity with Dy$^{3+}$ concentration and the excitation wavelength. We got maximum emission intensity under 386 nm excitation wavelength. Thus, we can tune the emission from Dy$^{3+}$ doped Sr$_{0.5}$Ca$_{0.5}$TiO$_3$ phosphors by changing the excitation wavelength and Dy$^{3+}$ doping concentration.

![Fig.4.4](image_url) Excitation spectra of Sr$_{0.5}$Ca$_{0.5}$TiO$_3$: x Dy$^{3+}$ phosphor samples with $\lambda_{em} = 574$ nm.
Chapter IV

The blue emission at 481 nm corresponding to the transition \(^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}\) belongs to the magnetic dipole (MD) transition (\(\Delta J = 0, \pm 1\) but \(0 \rightarrow 0\) is forbidden) and is less sensitive to the host, whereas the yellow emission corresponding to the transition \(^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}\) belongs to the electric dipole (ED) transition (\(\Delta J = \pm 2\)) and is more hypersensitive to the host matrix [32]. The asymmetry ratio of \(\text{Dy}^{3+}\) can be found by calculating the ratio of yellow to blue emission (ED to MD), which varies in different host lattices. From the emission spectra, it is clear that the yellow emission is more intense than the blue emission representing the asymmetric nature of the \(\text{Sr}_{0.5}\text{Ca}_{0.5}\text{TiO}_3\) host. The Y/B ratios of different concentrations of \(\text{Dy}^{3+}\) doped \(\text{Sr}_{0.5}\text{Ca}_{0.5}\text{TiO}_3\) at different excitation wavelength are also calculated and are shown in Table 4.4. The higher values of Y/B indicate the higher degree of covalency between the dysprosium and oxygen ions in the host matrix [32].

![Emission Spectra](image)

**Fig.4.5(a)** Emission spectra of different concentration of \(\text{Dy}^{3+}\) doped \(\text{Sr}_{0.5}\text{Ca}_{0.5}\text{TiO}_3\) phosphors with \(\lambda_{ex} = 351\) nm.


Fig. 4.5(b) Emission spectra of different concentration of Dy$^{3+}$ doped Sr$_{0.5}$Ca$_{0.5}$TiO$_3$ phosphors with $\lambda_{ex} = 365$ nm.

Fig. 4.5(c) Emission spectra of different concentration of Dy$^{3+}$ doped Sr$_{0.5}$Ca$_{0.5}$TiO$_3$ phosphors with $\lambda_{ex} = 386$ nm.
Fig. 4.6 Variation of $^4F_{9/2} \rightarrow ^6H_{13/2}$ and $^4F_{9/2} \rightarrow ^6H_{15/2}$ emission transition intensity with Dy$^{3+}$ concentration.

Fig. 4.6 shows the variation of intensity of $^4F_{9/2} \rightarrow ^6H_{13/2}$ (574 nm) and $^4F_{9/2} \rightarrow ^6H_{15/2}$ (484 nm) transitions with Dy$^{3+}$ concentration. It is found that the emission intensity increases with the increase of Dy$^{3+}$ concentration, reaching a maximum at 2 wt% of Dy$^{3+}$ and then decreases with increase in concentration. This is owed to the concentration quenching effect in rare earth doped systems due to the increased mutual Dy$^{3+}$ - Dy$^{3+}$ interactions at higher concentrations [33].

4.3.5 Radiative properties

By combining the JO intensity parameters obtained from the absorption data with the experimental photoluminescence spectra the radiative parameters of the $^4F_{9/2}$ level of 2 wt% Dy$^{3+}$ doped Sr$_{0.5}$Ca$_{0.5}$TiO$_3$ phosphors were calculated. The radiative transition probability ($A_R$), radiative lifetime ($\tau_R$), radiative branching ratio ($\beta_R$) and stimulated
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emission cross section ($\sigma_e$) for 2 wt% Dy3+ doped Sr0.5Ca0.5TiO3 phosphor sample were calculated using equations Eqn.1.13- 1.19 and are tabulated in Table.4.3. The transition, $^4F_{9/2}$$\rightarrow$$^6H_{13/2}$ at 574 nm has got maximum radiative transition probability and from the total radiative probability we have calculated the radiative lifetime. The value of $\tau_R$ is found to be 3.216 ms. From the table it is clear that the yellow emission transition has shown maximum radiative branching ratio. Using the relative area of the observed emission bands we have also calculated the experimental branching ratio ($\beta_{exp}$). For $^4F_{9/2}$$\rightarrow$$^4H_{13/2}$ transition, the value of $\beta_{exp}$ is found to be 0.5421. The non-radiative contributions from $^4F_{9/2}$ level of Dy3+ ions in the Sr0.5Ca0.5TiO3 host matrix attributes the variations in the calculated and experimental branching ratios [34].

To identify the potential emission transitions of rare earth ions in a host matrix we have to calculate the value of stimulated emission cross-section ($\sigma_e$). For a good optical transition large value of $\sigma_e$ is required. In the present host matrix, the value of $\sigma_e$ is found to be 4.620x10^{-22} \text{cm}^2 for the $^4F_{9/2}$$\rightarrow$$^4H_{13/2}$ transition. The values of gain bandwidth ($\sigma_e \times \Delta \lambda_{eff}$) and optical gain ($\sigma_e \times \tau_R$) are very important to predict the amplification of the medium in which the rare earth ions were incorporated. The higher values of gain bandwidth and optical gain parameter indicate the Dy3+ doped Sr0.5Ca0.5TiO3 phosphor may be used as a good optical candidate. The values of gain bandwidth and optical gain for the three emission transitions of Dy3+ ions were presented in Table.4.3. For $^4F_{9/2}$$\rightarrow$$^4H_{13/2}$ transition, the values of gain bandwidth and optical gain was found to be 5.544x10^{-28} \text{cm}^3 and 14.857x10^{-25} \text{cm}^2s respectively which is greater than that of lead.
tungsten tellurite [26], lead telluroborate [34] and barium fluoroborate glasses [35].

Table 4.3 Radiative properties of dominant emission transitions of 2 wt% Dy<sup>3+</sup> doped Sr<sub>0.5</sub>Ca<sub>0.5</sub>TiO<sub>3</sub>.

<table>
<thead>
<tr>
<th>Radiative properties</th>
<th>&lt;sup&gt;4&lt;/sup&gt;F&lt;sub&gt;9/2&lt;/sub&gt; → &lt;sup&gt;4&lt;/sup&gt;H&lt;sub&gt;15/2&lt;/sub&gt;</th>
<th>&lt;sup&gt;4&lt;/sup&gt;F&lt;sub&gt;9/2&lt;/sub&gt; → &lt;sup&gt;4&lt;/sup&gt;H&lt;sub&gt;13/2&lt;/sub&gt;</th>
<th>&lt;sup&gt;4&lt;/sup&gt;F&lt;sub&gt;9/2&lt;/sub&gt; → &lt;sup&gt;4&lt;/sup&gt;H&lt;sub&gt;11/2&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak Wavelength λ (nm)</td>
<td>481</td>
<td>574</td>
<td>638</td>
</tr>
<tr>
<td>Effective Bandwidth Δλ&lt;sub&gt;eff&lt;/sub&gt; (nm)</td>
<td>12</td>
<td>12</td>
<td>5</td>
</tr>
<tr>
<td>Spontaneous Probability A&lt;sub&gt;R&lt;/sub&gt; (s&lt;sup&gt;−1&lt;/sup&gt;)</td>
<td>44.90</td>
<td>121.81</td>
<td>27.63</td>
</tr>
<tr>
<td>Radiative Branching Ratio β&lt;sub&gt;R&lt;/sub&gt;</td>
<td>0.04</td>
<td>0.39</td>
<td>0.08</td>
</tr>
<tr>
<td>Experimental Branching ratio β&lt;sub&gt;exp&lt;/sub&gt;</td>
<td>0.4228</td>
<td>0.5421</td>
<td>0.0157</td>
</tr>
<tr>
<td>Stimulated Emission Cross-section σ&lt;sub&gt;e&lt;/sub&gt; (×10&lt;sup&gt;−22&lt;/sup&gt; cm&lt;sup&gt;2&lt;/sup&gt;)</td>
<td>0.839</td>
<td>4.620</td>
<td>3.869</td>
</tr>
<tr>
<td>Gain Bandwidth (σ&lt;sub&gt;e&lt;/sub&gt; × Δλ&lt;sub&gt;eff&lt;/sub&gt;) (×10&lt;sup&gt;−28&lt;/sup&gt; cm&lt;sup&gt;2&lt;/sup&gt;)</td>
<td>1.0068</td>
<td>5.5440</td>
<td>1.9345</td>
</tr>
<tr>
<td>Optical Gain (σ&lt;sub&gt;e&lt;/sub&gt;τ&lt;sub&gt;R&lt;/sub&gt;) (×10&lt;sup&gt;−25&lt;/sup&gt; cm&lt;sup&gt;2&lt;/sup&gt; s)</td>
<td>2.698</td>
<td>14.857</td>
<td>12.442</td>
</tr>
</tbody>
</table>

4.3.6 CIE coordinates, Correlated Color Temperature and Color Purity

The Commission internationale de l’Eclairage (CIE) chromaticity coordinates (x, y) and correlated color temperature (CCT) for different concentrations of Dy<sup>3+</sup> doped Sr<sub>0.5</sub>Ca<sub>0.5</sub>TiO<sub>3</sub> phosphor samples at different excitation wavelengths, namely 351, 365 and 386 nm are listed in Table 4.4 and Table 4.5. The chromaticity coordinates of 2 wt% Dy<sup>3+</sup> doped Sr<sub>0.5</sub>Ca<sub>0.5</sub>TiO<sub>3</sub> phosphor material at an excitation wavelengths of 351, 365 and 386 nm are found to be (0.3246, 0.3692), (0.3275, 0.3721) and (0.3293, 0.3727) respectively and are represented in Fig 4.7. The CIE coordinates obtained for the present phosphor samples are comparable with the CIE coordinates obtained for other host matrices like oxyfluoride [36] and oxyfluoroborate [37] and are presented in Table 4.4. All the CIE coordinates lie in the white light region of the chromaticity diagram which can found application in the fabrication of white light emitting diodes. On adding different concentrations of Dy<sup>3+</sup> ions we got yellow and blue emissions with different intensities which could possibly lead to white light emission by a
single rare earth. By adjusting the Dy\textsuperscript{3+} concentration and excitation wavelength we can tune the CIE coordinates of the present phosphor samples to pure white light.

![CIE chromaticity diagram](image)

**Fig.4.7** CIE chromaticity diagram of Sr\textsubscript{0.5}Ca\textsubscript{0.5}TiO\textsubscript{3}: x Dy\textsuperscript{3+} phosphors at different excitation wavelengths.

The correlated color temperature (CCT) values for the prepared phosphor samples at different excitation wavelengths was calculated using McCamy’s approximate formula and are presented in Table.4.5. It suggests that the correlated color temperature of Sr\textsubscript{0.5}Ca\textsubscript{0.5}TiO\textsubscript{3}: x Dy\textsuperscript{3+} phosphors can be controlled by changing the excitation wavelength. The CCT values of Sr\textsubscript{0.5}Ca\textsubscript{0.5}TiO\textsubscript{3}: x Dy\textsuperscript{3+} phosphors are found to be higher than the fluorescent tube (3935K) and daylight (5500K) [38], and lower than the commercial white light LED (6400K) [39].
Table 4.4 Yellow to blue ratio (Y/B) and chromaticity coordinates (x, y) of different concentrations of Dy³⁺ doped Sr₀.₅Ca₀.₅TiO₃ phosphor at different excitation wavelengths.

<table>
<thead>
<tr>
<th>Sample (wt%)</th>
<th>λₑₓ = 351 nm</th>
<th>λₑₓ = 365 nm</th>
<th>λₑₓ = 386 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x</td>
<td>y</td>
<td>Y/B</td>
</tr>
<tr>
<td>0.5</td>
<td>0.3197</td>
<td>0.3644</td>
<td>1.11</td>
</tr>
<tr>
<td>1</td>
<td>0.3271</td>
<td>0.3712</td>
<td>1.09</td>
</tr>
<tr>
<td>2</td>
<td>0.3246</td>
<td>0.3692</td>
<td>1.06</td>
</tr>
<tr>
<td>3</td>
<td>0.3177</td>
<td>0.3625</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Table 4.5 Color purity and correlated color temperature (CCT) of different concentrations of Dy³⁺ doped Sr₀.₅Ca₀.₅TiO₃ phosphor at different excitation wavelengths.

<table>
<thead>
<tr>
<th>Sample (wt%)</th>
<th>λₑₓ = 351 nm</th>
<th>λₑₓ = 365 nm</th>
<th>λₑₓ = 386 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Color Purity</td>
<td>CCT (K)</td>
<td>Color Purity</td>
</tr>
<tr>
<td>0.5</td>
<td>0.0710</td>
<td>6007</td>
<td>0.0737</td>
</tr>
<tr>
<td>1</td>
<td>0.0817</td>
<td>5702</td>
<td>0.0860</td>
</tr>
<tr>
<td>2</td>
<td>0.0783</td>
<td>5801</td>
<td>0.0834</td>
</tr>
<tr>
<td>3</td>
<td>0.0687</td>
<td>6095</td>
<td>0.0728</td>
</tr>
</tbody>
</table>

The color purity of the emission wavelength is necessary to understand whether a light source is suitable for LED applications. On comparing the CIE coordinates of the sample with coordinates corresponding to standard white light (0.33, 0.33) and dominant wavelength (0.4778, 0.5221) gives the value of color purity. The color purity of Sr₀.₅Ca₀.₅TiO₃: x Dy³⁺ phosphors excited at a different wavelength is presented in Table 4.5. The color purity of standard white light is 0% [40]. So the materials with low color purity value can produce white light emissions. The low color purity values of the present samples indicate that the white light emission from the prepared phosphor samples is close to
the standard white light source. The color purity values obtained for the present phosphor samples are comparable with Dy\(^{3+}\) doped zinc fluorophosphates (0.070), lead tellurofluoroborate (0.073) and bismuth oxychloride (0.075) host matrices [41-43]. The observed luminescence spectra with excellent color purity indicate that the Dy\(^{3+}\) doped Sr\(_{0.5}\)Ca\(_{0.5}\)TiO\(_3\) is a potential candidate for white light generation.

### 4.3.7 Luminescence decay analysis

The decay profiles of \(^{4}F_{9/2}\)→\(^{6}H_{13/2}\) emission level in Sr\(_{0.5}\)Ca\(_{0.5}\)TiO\(_3\) phosphor with different concentrations of Dy\(^{3+}\) ions under 386 nm excitation are shown in Fig.4.8 (a), (b), (c) & (d). All the decay curves were well fitted by biexponential function Eqn.1.22 and the average lifetime was found to be 0.3320, 0.2979, 0.2807 and 0.2650 ms for 0.5, 1, 2 and 3 wt\% Dy\(^{3+}\) doped Sr\(_{0.5}\)Ca\(_{0.5}\)TiO\(_3\) respectively. The decrease of \(\bar{\tau}\) with increasing Dy\(^{3+}\) concentration is mainly due to the increased interaction among Dy\(^{3+}\) ions at higher concentrations. The predicted radiative lifetime for 2 wt\% Dy\(^{3+}\) doped sample obtained from the JO theory is higher than the experimental lifetime. This indicates that the emission from \(^{4}F_{9/2}\) level is not completely radiative but there should be non-radiative contributions too. The energy transfer among Dy\(^{3+}\) ions or multiphonon relaxation or both causes the non-radiative contributions [34]. Using the value of experimental lifetime and radiative lifetime we can express the non-radiative energy transfer (\(W_{NR}\)) between Dy\(^{3+}\) ions as in Eqn.1.24. Using Eqn.1.24 the non-radiative energy transfer for Dy\(^{3+}\) ions in Sr\(_{0.5}\)Ca\(_{0.5}\)TiO\(_3\) phosphor was calculated as 3.251×10\(^{3}\) s\(^{-1}\), which is greater than that of Sm\(^{3+}\) doped Sr\(_{0.5}\)Ca\(_{0.5}\)TiO\(_3\) and less than that of Pr\(^{3+}\) doped Sr\(_{0.5}\)Ca\(_{0.5}\)TiO\(_3\) phosphor samples. The value of \(W_{NR}\) obtained for Dy\(^{3+}\) in Sr\(_{0.5}\)Ca\(_{0.5}\)TiO\(_3\) matrix is comparable with other host matrices [27].
4.4 Conclusions

Sr$_{0.5}$Ca$_{0.5}$TiO$_3$: $x$ Dy$^{3+}$ phosphors were synthesized via solid state reaction method. XRD profile confirmed the orthorhombic perovskite structure of the prepared phosphor samples. The chemical bonding and composition of the prepared phosphors were confirmed by FTIR and EDS spectra respectively. The microstructure of the phosphor samples was analyzed using SEM images. Using absorption spectra, the band gap energy of the prepared phosphor samples were estimated. The positive value of the bonding parameter confirmed covalent nature of the Dy$^{3+}$ ligand bond in the present host. The JO intensity parameters of 2 wt% Dy$^{3+}$ in Sr$_{0.5}$Ca$_{0.5}$TiO$_3$ under an excitation wavelength of 386 nm.
Sr0.5Ca0.5TiO3 were derived using the NIR absorption peaks and are found to be \( \Omega_2 = 0.6309 \times 10^{-20} \text{ cm}^2 \), \( \Omega_4 = 0.5013 \times 10^{-20} \text{ cm}^2 \) and \( \Omega_6 = 0.3291 \times 10^{-20} \text{ cm}^2 \). The higher values of \( \Omega_2 \) indicates higher degree of covalency between Dy\(^{3+}\) ions and surrounding ligands. The prepared phosphor samples give strong blue and yellow emissions corresponding to \( ^4F_{9/2} \rightarrow ^6H_{15/2} \) and \( ^4F_{9/2} \rightarrow ^6H_{13/2} \) transitions respectively, whereas under 386 nm excitation weak red emission corresponding to \( ^4F_{9/2} \rightarrow ^4H_{11/2} \) transition were also observed. The Y/B ratio depends to the Dy\(^{3+}\) concentration as well as excitation wavelength. The higher value of Y/B ratio indicates higher degree of covalence between Dy\(^{3+}\) and O\(^2-\) ions. The high value of stimulated emission cross-section, branching ratio and gain parameters of \( ^4F_{9/2} \rightarrow ^6H_{13/2} \) transition suggests the application of the prepared phosphor as a promising material for optical amplification in addition to the application in the field of white light generation. The CIE color coordinates of the prepared phosphor samples lie in the near white light region. Changes in correlated color temperature were obtained for Sr0.5Ca0.5TiO3: Dy\(^{3+}\) phosphor samples with varying Dy\(^{3+}\) concentration and different excitation wavelength. The experimental lifetime of Dy\(^{3+}\) ions doped Sr0.5Ca0.5TiO3 shows a non-exponential decrease with increasing Dy\(^{3+}\) concentration due to the concentration quenching effect. The observed luminescence spectra with excellent color purity indicate that the Dy\(^{3+}\) doped Sr0.5Ca0.5TiO3 is an ultimate candidate for white light generation.
Chapter IV

References


Spectroscopic $\ldots$ $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{TiO}_3$: $x \text{Dy}^{3+}$ for white LED applications


