PHOTOLUMINESCENCE STUDIES

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4.2.1 PL of vacuum grown CsBr\textsubscript{1-x}Cl\textsubscript{x}:Eu\textsuperscript{2+}\textsubscript{y} 
(x=0.05, 0.1, 0.2, 0.3 & y=100 ppm, 200 ppm) 
crystal and powder samples

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4.1 Introduction

The process of fluorescence in condensed matter has found wide applications in different branches of science and technology [1,2]. Spectroscopists have used fluorescence measurements to obtain energy level information on molecules, study bonding and structure, and probe energy flow processes in molecules.

In a typical fluorescence experiment, molecules are first excited from their ground state to an excited higher energy state. The excitation can be achieved by using number of processes such as an electric discharge, chemical reactions and light. The excited molecule can then return to the ground state by the emission of photon.

The various photo processes that occur due to excitation of a molecule are normally explained with the aid of Jablonski diagram (figure 4.1). It can be observed from the Jablonski diagram that the fluorescence emission usually occurs at longer wavelengths compared with the excitation wavelength, which is referred to a “Stokes shift”. The emission observed in the condensed phase due to the excitation of the impurity ion is termed as ‘photoluminescence’ [3] where the emission strictly follows ‘Stokes shift’.

The PL emission spectra of europium doped alkali halides have been investigated systematically by Hernandez et.al., [4]. They have also calculated the Stokes shift positions for different emission bands. Nasu and coworkers [5] have investigated the PL emission spectra of KCl, KBr and NaCl doped with Eu$^{2+}$ at
Figure 4.1: Jablonski Diagram

- **Absorption**
- **Internal conversion**
- **Intersystem crossing**
- **Fluorescence**
- **Phosphorescence**
4.2K arising from $d \rightarrow f$ transitions. Baldini and Guzzi[6] have measured the PL emission spectra of Eu$^{2+}$ in alkali chloride series in 15-175K temperature range and observed zero phonon transitions. Clark and coworkers [7] in their work on mixed alkali chloride system of $Na_{1-x}K_xCl$ doped with Eu$^{2+}$ observed PL emission band at 418 nm. Europium doped cesium chloride gives out PL emission at 440 nm as observed by Radhakrishnan and Selvasekarapandian [8]. Till date there has been no PL studies carried out on europium doped mixed halide system of cesium.

Results of the photoluminescence studies carried out on vacuum grown and open air atmosphere grown $CsBr_{1-x}Cl_x:Eu^{2+}_y$ ($x=0.05, 0.1, 0.2, 0.3$ & $y=100$ ppm, 200 ppm) crystal and powder samples are presented and discussed in this chapter.

4.2 Results

4.2.1 PL of Vacuum grown $CsBr_{1-x}Cl_x:Eu^{2+}_y$ ($x=0.05, 0.1, 0.2, 0.3$ & $y=100$ ppm, 200 ppm) crystal and powder samples

The photoluminescence emission spectra of vacuum grown $CsBr_{0.95}Cl_{0.05}:Eu^{2+}$ (100 ppm) (200 ppm), $CsBr_{0.9}Cl_{0.1}:Eu^{2+}$ (100ppm) (200 ppm) (300 ppm), and $CsBr_{0.7}Cl_{0.3}:Eu^{2+}$ (100 ppm) (200 ppm) samples are shown in figures 4.2a&b, 4.4a&b, 4.5a&b, 4.6a&b, 4.7a&b, 4.8a&b and 4.9a&b respectively.

Above mentioned samples are excited with 270 nm and 345 nm light source except for $CsBr_{0.95}Cl_{0.05}:Eu^{2+}$ (100 ppm, 200 ppm) samples which are excited at 260 nm and 345 nm light. The excitation wavelengths 260 nm, 270 nm...
Figure 4.2a. PL emission spectrum of vacuum grown CsBr\textsubscript{x}CsCl\textsubscript{1-x}:Eu\textsuperscript{2+} (100 ppm) for 345 nm excitation.

Figure 4.2b. PL emission spectrum of vacuum grown CsBr\textsubscript{x}CsCl\textsubscript{1-x}:Eu\textsuperscript{2+} (100 ppm) for 260 nm excitation.
Figure 4.4a. PL emission spectrum of vacuum grown CsBr$_x$Cl$_{1-x}$Eu$^{3+}$ (200 ppm) for 345 nm excitation.

Figure 4.4b. PL emission spectrum of vacuum grown CsBr$_x$Cl$_{1-x}$Eu$^{3+}$ (200 ppm) for 260 nm excitation.
Figure 4.5a. PL emission spectrum of vacuum grown CsBr:Cl:Eu (100 ppm) for 345 nm excitation.

Figure 4.5b. PL emission spectrum of vacuum grown CsBr:Cl:Eu (100 ppm) for 270 nm excitation.
Figure 4.6a. PL emission spectrum of vacuum grown CsBr₃CsI₂Eu²⁺ (200 ppm) for 345 nm excitation.

Figure 4.6b. PL emission spectrum of vacuum grown CsBr₃CsI₂Eu²⁺ (200 ppm) for 270 nm excitation.
Figure 4.7a. PL emission spectrum of vacuum grown CsBr_{0.7}Cl_{1.3}Eu^{2+} (300 ppm) for 345 nm excitation.

Figure 4.7b. PL emission spectrum of vacuum grown CsBr_{0.7}Cl_{1.3}Eu^{2+} (300 ppm) for 270 nm excitation.
Figure 4.8a. PL emission spectrum of vacuum grown CsBr$_2$Cl$_3$:Eu$^{3+}$ (100 ppm) for 345 nm excitation.

Figure 4.8b. PL emission spectrum of vacuum grown CsBr$_2$Cl$_3$:Eu$^{3+}$ (100 ppm) for 270 nm excitation.
Figure 4.9a. PL emission spectrum of vacuum grown CsBr$_2$Cl$_3$:Eu$^{2+}$ (200 ppm) for 345 nm excitation.

Figure 4.9b. PL emission spectrum of vacuum grown CsBr$_2$Cl$_3$:Eu$^{2+}$ (200 ppm) for 270 nm excitation.
and 345 nm are the optical absorption band positions observed for the above mentioned samples ascribed to Eu²⁺ ions.

Exciting vacuum grown CsBr₀.₉₅Cl₀.₀₅:Eu²⁺ (100 ppm, 200 ppm) samples at 260 nm and 345 nm, CsBr₀.₉Cl₀.₁:Eu²⁺ (100 ppm, 200 ppm, 300 ppm), CsBr₀.₈Cl₀.₂:Eu²⁺ (100 ppm, 200 ppm) and CsBr₀.₇Cl₀.₃:Eu²⁺ (100 ppm, 200 ppm) samples at 270 nm and 345 nm, PL emission band is observed at 442 nm which is sharp and intense.

In addition to 442 nm PL emission band,

- For 345 nm excitation, PL emission band at 390 nm is observed for CsBr₀.₉₅Cl₀.₀₅:Eu²⁺ (100 ppm) samples; 395 nm PL emission band is observed for CsBr₀.₉₅Cl₀.₅:Eu²⁺ (200 ppm), CsBr₀.₈Cl₀.₂:Eu²⁺ (200 ppm) & CaBr₀.₇Cl₀.₃:Eu²⁺ (100 ppm) samples; 412 nm PL emission band is observed for CsBr₀.₉Cl₀.₁:Eu²⁺ (100 ppm) & CsBr₀.₈Cl₀.₂:Eu²⁺ (100 ppm) and 480 nm PL emission band is observed for CsBr₀.₉Cl₀.₁:Eu²⁺ (200 ppm) & CsBr₀.₇Cl₀.₃:Eu²⁺ (200 ppm) samples.

- For 260 nm excitation, 480 nm and 485 nm PL emission bands are observed for CsBr₀.₉₅Cl₀.₀₅:Eu²⁺ (100 ppm) and CsBr₀.₉₅Cl₀.₀₅:Eu²⁺ (200 ppm) samples respectively.

- For 270 nm excitation, PL emission band at 395 nm is observed for CsBr₀.₇Cl₀.₃:Eu²⁺ (100 ppm) sample; 480 nm & 490 nm PL emission bands are observed for CsBr₀.₉Cl₀.₁:Eu²⁺ (200 ppm) & CsBr₀.₇Cl₀.₃:Eu²⁺ (200 ppm) samples respectively and 485 nm PL emission band is observed for
CsBr_{0.9}Cl_{0.1}:Eu^{2+} (100 ppm, 300 ppm) samples & CsBr_{0.8}Cl_{0.2}:Eu^{2+} (100 ppm, 200 ppm) samples.

PL emission intensity is higher for 200 ppm europium doped samples than that of 100 ppm europium doped samples in all the compositions of CsBr_{1-x}Cl_{x}:Eu^{2+y} (x=0.05, 0.1, 0.2, 0.3 & y=100 ppm, 200 ppm) for both 270 nm and 345 nm excitations. In the case of CsBr_{0.9}Cl_{0.1}:Eu^{2+} (300 ppm) samples the intensity of PL emission decreases when compared to CsBr_{0.9}Cl_{0.1}:Eu^{2+} (200 ppm) samples. For all the compositions of CsBr_{1-x}Cl_{x}:Eu^{2+y} (x=0.05, 0.1, 0.2, 0.3 & y=100 ppm, 200 ppm), PL emission intensity is higher for 260 nm & 270 nm excitation than 345 nm excitation.

Powder samples for all compositions of CsBr_{1-x}Cl_{x}:Eu^{2+y} (x=0.05, 0.1, 0.2, 0.3 & y=100 ppm, 200 ppm) show similar trend in PL emission as that of its crystal samples, except for additional emission bands at 315 nm and 320 nm for 100 ppm and 200 ppm doped CsBr_{0.95}Cl_{0.05}:Eu^{2+} samples respectively; 315 nm for 100 ppm and 200 ppm doped CsBr_{0.9}Cl_{0.1}:Eu^{2+} and 310 nm for 300 ppm doped CsBr_{0.8}Cl_{0.2}:Eu^{2+} samples; 330 nm for 100 ppm and 200 ppm doped CsBr_{0.7}Cl_{0.3}:Eu^{2+} samples.

By exciting the crystal and powder samples, CsBr_{0.95}Cl_{0.05}:Eu^{2+} (100 ppm, 200 ppm), CsBr_{0.9}Cl_{0.1}:Eu^{2+}(100 ppm, 200 ppm, 300 ppm), CsBr_{0.7}Cl_{0.3}:Eu^{2+}(100 ppm, 200 ppm) using 442 nm light, a clear emission band at 345 nm with well resolved “Staircase” structure (figure 4.3) is observed.
Figure 4.3. PL emission spectrum of vacuum grown CsBr$_{0.95}$Cl$_{0.05}$:Eu$^{2+}$ (100 ppm) for 442 nm excitation.
4.2.2 PL of Open-air atmosphere grown CsBr$_{1-x}$Cl$_x$:Eu$^{2+}$ (x=0.05, 0.1, 0.2, 0.3 & y=100 ppm, 200 ppm) crystal and powder samples

The photoluminescence emission spectra of open air atmosphere grown CsBr$_{0.95}$Cl$_{0.05}$:Eu$^{2+}$ (100 ppm, 200 ppm), CsBr$_{0.9}$Cl$_{0.1}$:Eu$^{2+}$ (100 ppm, 200 ppm, 300 ppm), and CsBr$_{0.7}$Cl$_{0.3}$:Eu$^{2+}$ (100 ppm, 200 ppm) samples are shown in figures 4.10a&b, 4.11a&b, 4.12a&b, 4.13a&b, 4.14a&b, 4.15a&b and 4.16a&b respectively.

Above mentioned samples are excited with 270 nm and 345 nm light except CsBr$_{0.95}$Cl$_{0.05}$:Eu$^{2+}$ (100 ppm, 200 ppm) which is excited at 260 nm and 345 nm light. The excitation wavelengths 260 nm, 270 nm and 345 nm are the optical absorption band positions observed for the above-mentioned samples ascribed to Eu$^{2+}$ ions.

Exciting open air atmosphere grown CsBr$_{0.95}$Cl$_{0.05}$:Eu$^{2+}$ (100 ppm, 200 ppm) samples at 260 nm and 345 nm, CsBr$_{0.9}$Cl$_{0.1}$:Eu$^{2+}$ (100 ppm, 200 ppm, 300 ppm), CsBr$_{0.8}$Cl$_{0.2}$:Eu$^{2+}$ (100 ppm, 200 ppm) & CsBr$_{0.7}$Cl$_{0.3}$:Eu$^{2+}$ (100 ppm, 200 ppm) samples at 270 nm and 345 nm, PL emission band is observed at 442 nm, as observed in vacuum grown samples.

In addition to 442 nm PL emission band,

- For 260 nm excitation PL emission bands at 475 nm and 485 nm are observed for CsBr$_{0.95}$Cl$_{0.1}$:Eu$^{2+}$ (100 ppm, 200 ppm) samples.
- For 270 nm excitation, PL emission bands at 365 nm are observed in CsBr$_{0.9}$Cl$_{0.1}$:Eu$^{2+}$ (200 ppm, 300 ppm) & CaBr$_{0.7}$Cl$_{0.3}$:Eu$^{2+}$ (200 ppm) samples and PL emission bands at 470 nm & 485 nm are observed in CsBr$_{0.9}$Cl$_{0.1}$
Figure 4.10a. PL emission spectrum of open air atmosphere grown CsBr$_{0.95}$Cl$_{0.05}$Eu$^{2+}$ (100 ppm) for 345 nm excitation.

Figure 4.10b. PL emission spectrum of open air atmosphere grown CsBr$_{0.95}$Cl$_{0.05}$Eu$^{2+}$ (200 ppm) for 260 nm excitation.
Figure 4.11a. PL emission spectrum of open air atmosphere grown CaBr₂:Cl₆:Eu²⁺ (200 ppm) for 345 nm excitation.

Figure 4.11b. PL emission spectrum of open air atmosphere grown CaBr₂:Cl₆:Eu²⁺ (200 ppm) for 260 nm excitation.
Figure 4.12a. PL emission spectrum of open air atmosphere grown CsBr$_2$Cl$_2$:Eu$^{3+}$ (100 ppm) for 345 nm excitation.

Figure 4.12b. PL emission spectrum of open air atmosphere grown CsBr$_2$Cl$_2$:Eu$^{3+}$ (100 ppm) for 270 nm excitation.
Figure 4.13a. PL emission spectrum of open air atmosphere grown CsBr_xCl_y:Eu^{2+} (200 ppm) for 345 nm excitation.

Figure 4.13b. PL emission spectrum of open air atmosphere grown CsBr_xCl_y:Hu^{2+} (200 ppm) for 270 nm excitation.
Figure 4.14a. PL emission spectrum of open air atmosphere grown CsBr+CdCl₂:Eu³⁺ (300 ppm)
for 345 nm excitation.

Figure 4.14b. PL emission spectrum of open air atmosphere grown CsBr+CdCl₂:Eu³⁺ (300 ppm)
for 270 nm excitation.
Figure 4.15a. PL emission spectrum of open air atmosphere grown CsBr₂ClₓEu⁺(100 ppm) for 345 nm excitation.

Figure 4.15b. PL emission spectrum of open air atmosphere grown CsBr₂ClₓEu⁺(100 ppm) for 270 nm excitation.
Figure 4.16a. PL emission spectrum of open air atmosphere grown CaB$_2$Cl$_2$:Eu$^{2+}$(200 ppm) for 345 nm excitation.

Figure 4.16b. PL emission spectrum of open air atmosphere grown CaB$_2$Cl$_2$:Eu$^{2+}$(200 ppm) for 270 nm excitation.
(200 ppm, 300 ppm) samples & CsBr$_{0.7}$Cl$_{0.3}$:Eu$^{2+}$ (100 ppm, 200 ppm) samples.

For 345 nm excitation, PL emission bands at 390 nm, 470 nm & 485 nm are observed in CsBr$_{0.95}$Cl$_{0.05}$:Eu$^{2+}$ (100 ppm, 200 ppm), CsBr$_{0.9}$Cl$_{0.1}$:Eu$^{2+}$ (100 ppm, 300 ppm) and CsBr$_{0.7}$Cl$_{0.3}$:Eu$^{2+}$ (200 ppm) samples. For CsBr$_{0.7}$Cl$_{0.3}$:Eu$^{2+}$ (100 ppm) sample PL emission band is observed at 470 nm and for CsBr$_{0.9}$Cl$_{0.1}$:Eu$^{2+}$ (200 ppm) sample PL emission band is observed at 470 nm & 485 nm for excitation at 345 nm.

By exciting the sample CsBr$_{0.95}$Cl$_{0.05}$:Eu$^{2+}$ with 442 nm light, emission bands are observed at 345 nm and 260 nm with well resolved ‘staircase structure’ in 345 nm band. In all the other samples grown in open air atmosphere similar results are got by excitation at 442 nm except for disappearance of 260 nm band.

Figures 4.17 and 4.18 show the plot of bromide ion concentration versus PL intensity of the emission band at 442 nm, for different excitations (260 nm/270 nm and 345 nm), in all the compositions of CsBr$_{1-x}$Cl$_x$:Eu$^{2+y}$ (x=0.05, 0.1, 0.2, 0.3 & y=100 ppm, 200 ppm) for vacuum grown and open air atmosphere grown samples respectively. It is observed from the figure 4.17 for vacuum grown CsBr$_{1-x}$Cl$_x$:Eu$^{2+y}$ (x=0.05, 0.1, 0.2, 0.3 & y=100 ppm, 200 ppm) samples that the PL emission intensity of the emission band at 442 nm increases with decrease in bromide ion concentration. In the case of open air atmosphere grown CsBr$_{1-x}$Cl$_x$:Eu$^{2+y}$ (x=0.05, 0.1, 0.2, 0.3 & y=100 ppm, 200 ppm) samples, an initial decrease in PL intensity is observed for 95% bromide concentration. With further
Figure 4.17. Plot of bromide ion concentration versus PL intensity in vacuum grown CsBr$_{1-x}$Cl$_x$:Eu$^{2+}$ (x=0.05, 0.1, 0.2, 0.3 & y=100 ppm, 200 ppm)
Figure 4.18. Plot of bromide ion concentration versus PL intensity in open air atmosphere grown CsBr$_{1-x}$Cl$_x$:Eu$^{2+}$ (x=0.05, 0.1, 0.2, 0.3 & y=100ppm, 200ppm)
decrease in bromide ion concentration upto 80%, the PL emission intensity is found to be unchanged. When the bromide ion concentration is decreased further to 70%, the PL emission intensity increases drastically.

4.3 Discussion

Hernandez [9] and Lopez et.al., [10] have carried out studies on the PL emission spectra of the alkali halides such as RbCl, NaCl, KCl and NaBr doped with europium. Hernandez [9] has observed photoluminescence emission for NaCl doped europium around 427 nm at 300K. These workers have also observed the emission for KCl and RbCl at 419 nm and 417 nm respectively. They have been able to deduce that the peak position of the PL emission band shifts to shorter wavelength side as the lattice parameter increases within a given series. In the present study the sharp emission band at 442 nm for CsBr$_{0.95}$Cl$_{0.05}$:Eu$^{2+}$ grown both in vacuum and open air atmosphere is due to the emission of Eu$^{2+}$ in the sample. This is attributed to the transition from $T_{2g}$ component of the 4f$^6$5d configuration to the ground state $^8S$. The 260 nm excitation also gives emission bands at 442 nm and 480 nm for the sample CsBr$_{0.95}$Cl$_{0.05}$:Eu$^{2+}$. It is observed that the intensity of higher energy excited PL emission at 442 nm is double that of the low energy ones. The structure of both the emission bands due to 260 nm and 345 nm excitations are similar but for a small shoulder in the higher energy excitation.
In open air grown CsBr$_{0.95}$Cl$_{0.05}$:Eu$^{2+}$, CsBr$_{0.9}$Cl$_{0.1}$:Eu$^{2+}$, CsBr$_{0.8}$Cl$_{0.2}$:Eu$^{2+}$ and CsBr$_{0.7}$Cl$_{0.3}$:Eu$^{2+}$ samples it is observed that the intensity of PL emission due to 270 nm excitation is more than that due to 345 nm excitation. By exciting the 270 nm, by default the OH$^-$ impurity is getting excited along with the Eu$^{2+}$ dopant. As a result there is enhanced emission at 442 nm due to 270 nm excitation. The intensity of PL emission in open air atmosphere grown CsBr$_{1-x}$Cl$_x$:Eu$^{2+}$y (x=0.05, 0.1, 0.2, 0.3 & y=100 ppm, 200 ppm) samples is greater than the crystals grown in vacuum, as OH$^-$ present in open air grown samples increases the emission. The emission bands at 365 nm and 368 nm are due to OH$^-$ emission. There is a possibility of energy transfer mechanism between OH$^-$ and Eu$^{2+}$. Overlap of emission band of OH$^-$ on the lower energy absorption band of Eu$^{2+}$ may facilitate the radiative energy transfer. This mechanism was studied by Radhakrishnan and Selvasekarapandian [8]. The energy transfer of non-radiative type is also a possibility due to the proximity of OH$^-$ and Eu$^{2+}$ higher energy absorption bands. There is an increase in intensity of 442 nm emission when the dopant concentration is increased from 100 ppm to 200 ppm. When the dopant concentration is further increased to 300 ppm, there is a drastic decrease in intensity of the emission peak. PL emission bands for CsBr$_{1-x}$Cl$_x$:Eu$^{2+}$y (x=0.05, 0.1, 0.2, 0.3 & y=100 ppm, 200 ppm) samples, the associated peaks and their intensities are given in tables 4.1 and 4.2 for vacuum grown and open air atmosphere grown samples respectively. Hernandez et.al., [11] have noticed that with increase in concentration of europium above a certain level no free

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europium ions that can produce luminescence are present in the crystals which can give characteristic emission. In the present CsBr$_{1-x}$Cl$_x$:Eu$^{2+}$ (x=0.05, 0.1, 0.2, 0.3 & y=100 ppm, 200 ppm) samples, it is observed that as the concentration of the dopant is increased above 200 ppm the intensity of emission is quenched and probably an increase in concentration above 300 ppm would have given the results observed by Hernandez et al.,[11]. Rubio [12] speculated that the additional PL emission bands at 410 nm, 439 nm, and 485 nm for NaCl samples doped with europium might be due to the crystal field acting at aggregate site of europium impurity. Later Electron Microscopy experiments performed by Yacaman and Bassett [13] on the same samples employed by Rubio proved that the 410 nm, 439 nm and 485 nm emission bands to be associated with the metastable precipitated EuCl$_2$ like plate zones parallel to the host (NaCl) matrix. This was later confirmed by Cordero Borboa and co-workers [14] through their X-ray diffraction studies. The emission bands observed at 390 nm, 480 nm and 485 nm for CsBr$_{0.95}$Cl$_{0.05}$:Eu$^{2+}$ samples (grown in vacuum and open air atmosphere) and at 390 nm, 393 nm, 395 nm, 396 nm, 412 nm, 480 nm, 482 nm 485 nm and 490 nm for CsBr$_{0.75}$Cl$_{0.25}$:Eu$^{2+}$ (100 ppm, 200 ppm, 300 ppm), CsBr$_{0.5}$Cl$_{0.5}$:Eu$^{2+}$ (100 ppm, 200 ppm) and CsBr$_{0.3}$Cl$_{0.7}$:Eu$^{2+}$ (100 ppm, 200 ppm) samples grown in vacuum and open air atmosphere are attributed to the metastable precipitation of EuCl$_2$ like plate zones parallel to the planes of CsBrCl matrix. The thermal treatment of any material in open air always introduces much of oxygen impurity in the host lattice. Also the O$^{2-}$ impurity is known to have emission
between 450 nm and 550 nm [15]. The PL emission bands at 463 nm, 465 nm, 468 nm, and 470 nm observed in the emission spectra for open air grown samples are attributed to the $O^{2-}$ emission.

It is observed that in the powder samples there are extra bands that are not observed in crystal samples. These bands are neither associated with Eu$^{2+}$, nor with EuCl$_2$ plate zone precipitation nor with $O^{2-}$ emission. The excitation of the 440 nm and 442 nm band in the samples mentioned above gives two distinct emission bands at 270 nm and 345 nm. The "staircase" structure of 345 nm band is well resolved in this spectra. In the case of CsBr$_{0.95}$Cl$_{0.05}$:Eu$^{2+}$ samples the excitation of the emission band at 442 nm gives rise to two emissions at 345 nm and 260 nm. The photoluminescence spectra resolves the "Stair case" structure of the low energy characteristic absorption band of europium. The deexcitation spectrum for all the samples correlate quite well with their absorption spectrum. The presence of $E_g$ band in the excitation spectrum indicates a decay from $E_g$ level to $T_{2g}$ level from which fluorescence (345 nm and 270 nm) originates. The transition from $E_g$ and $T_{2g}$ has been studied in detail by Merckle and Powell [16]. They have speculated that there may be two decay paths for $E_g$, one of them the radiation less relaxation to the ground state through the excited state $6p_{7/2}$ of the 4f$^7$ configuration, second being the multiphonon transition to the $T_{2g}$ level producing fluorescence [17]. Thus PL emission at 345 nm and 270 nm is observed by exciting the emission band at 440 nm. From tables 4.1 and 4.2 for vacuum and open air atmosphere grown CsBr$_{1-x}$Cl$_x$:Eu$^{2+}$ (x=0.05, 0.1, 0.2, 0.3 & y=100 ppm,
Table 4.1. PL Emission band positions and intensities for vacuum grown CsBr$_{1-x}$Cl$_{x}$:Eu$^{2+}$ (x=0.05, 0.1, 0.2, 0.3 & y=100ppm, 200ppm) samples

<table>
<thead>
<tr>
<th>Material</th>
<th>Excitation Wavelength(nm)</th>
<th>Emission bands(nm)</th>
<th>Emission Intensity (442nm) (a.u)</th>
</tr>
</thead>
</table>
| CsBr$_{0.95}$Cl$_{0.05}$:Eu$^{2+}$  
(100ppm) | 345 | 442,390 | 67.3 |
|                           | 260 | 442,480 | 124 |
| CsBr$_{0.95}$Cl$_{0.05}$:Eu$^{2+}$  
(200ppm) | 345 | 442,395 | 124.6 |
|                           | 260 | 442,485 | 160.5 |
| CsBr$_{0.9}$Cl$_{0.1}$:Eu$^{2+}$  
(100ppm) | 345 | 442,412 | 112.4 |
|                           | 270 | 442,485 | 184 |
| CsBr$_{0.9}$Cl$_{0.1}$:Eu$^{2+}$  
(200ppm) | 345 | 442,480 | 168.4 |
|                           | 270 | 442,480 | 219 |
| CsBr$_{0.9}$Cl$_{0.1}$:Eu$^{2+}$  
(300ppm) | 345 | 442,485 | 88 |
|                           | 270 | 442,485 | 102 |
| CsBr$_{0.8}$Cl$_{0.2}$:Eu$^{2+}$  
(100ppm) | 345 | 442,412 | 112.4 |
|                           | 270 | 442,485 | 184 |
| CsBr$_{0.8}$Cl$_{0.2}$:Eu$^{2+}$  
(200ppm) | 345 | 442,395 | 168.4 |
|                           | 270 | 442,485 | 219 |
| CsBr$_{0.7}$Cl$_{0.3}$:Eu$^{2+}$  
(100ppm) | 345 | 442,395 | 220 |
|                           | 270 | 442,395 | 315 |
| CsBr$_{0.7}$Cl$_{0.3}$:Eu$^{2+}$  
(200ppm) | 345 | 442,480 | 285 |
|                           | 270 | 442,490 | 360 |
Table 4.2. PL Emission band positions and intensities for open air atmosphere grown CsBr_{1-x}Cl_{x}:Eu^{2+} (x=0.05, 0.1, 0.2, 0.3 & y=100ppm, 200ppm) samples

<table>
<thead>
<tr>
<th>Material</th>
<th>Excitation Wavelength (nm)</th>
<th>Emission Bands (nm)</th>
<th>Emission Intensity (a.u)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsBr_{0.95}Cl_{0.05}:Eu^{2+} (100ppm)</td>
<td>345</td>
<td>442,390,470,485</td>
<td>120.5(470nm)</td>
</tr>
<tr>
<td></td>
<td>260</td>
<td>442,310,475,485</td>
<td>172.5(475nm)</td>
</tr>
<tr>
<td>CsBr_{0.95}Cl_{0.05}:Eu^{2+} (200ppm)</td>
<td>345</td>
<td>442,390,470,485</td>
<td>190.7(470nm)</td>
</tr>
<tr>
<td></td>
<td>260</td>
<td>442,310,475,485</td>
<td>273.5(475nm)</td>
</tr>
<tr>
<td>CsBr_{0.9}Cl_{0.1}:Eu^{2+} (100ppm)</td>
<td>345</td>
<td>442,396,412,465,482</td>
<td>95(442nm)</td>
</tr>
<tr>
<td></td>
<td>260</td>
<td>442,468,320,485</td>
<td>113.7(468nm)</td>
</tr>
<tr>
<td>CsBr_{0.9}Cl_{0.1}:Eu^{2+} (200ppm)</td>
<td>345</td>
<td>442,368,470,485</td>
<td>150.7(470nm)</td>
</tr>
<tr>
<td></td>
<td>270</td>
<td>442,368,470,485</td>
<td>226.8(470nm)</td>
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<td>CsBr_{0.9}Cl_{0.1}:Eu^{2+} (300ppm)</td>
<td>345</td>
<td>442,393,463,485</td>
<td>55.1(442nm)</td>
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<td></td>
<td>270</td>
<td>442,365,470,485</td>
<td>97.2(470nm)</td>
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<td>CsBr_{0.7}Cl_{0.3}:Eu^{2+} (100ppm)</td>
<td>345</td>
<td>442,485,470</td>
<td>183.5(470nm)</td>
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<td></td>
<td>270</td>
<td>442,315,470,485</td>
<td>210.2(470nm)</td>
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<td>CsBr_{0.7}Cl_{0.3}:Eu^{2+} (200ppm)</td>
<td>345</td>
<td>442,395,465,485</td>
<td>270(465nm)</td>
</tr>
<tr>
<td></td>
<td>270</td>
<td>442,470,368,485</td>
<td>389(470nm)</td>
</tr>
</tbody>
</table>
200 ppm) samples respectively, it is clear that the difference in intensity of the emission bands for lower and higher energy excitation bands decrease with the variations in composition of the first and second halide ions. This supports the view that there is change in emission behavior with change in lattice parameters.

From figures 4.17 & 4.18 it clear that in vacuum grown CsBr$_{1-x}$Cl$_x$:Eu$^{2+}$ (x=0.05, 0.1, 0.2, 0.3 & y=100 ppm, 200 ppm) samples the PL emission intensity increases with decrease in bromide ion concentration. Due to the presence of higher concentration and bigger size (0.197 nm) of bromide ion compared to chloride ion (0.181 nm), some of Eu$^{2+}$ ions might have not been able to participate in PL emission.
References


