CHAPTER 5B
EFFECT OF Bi$^{3+}$ CODOPING ON LUMINESCENT PROPERTIES OF Ca(La/Gd)$_{1-x}$NbWO$_6$ : xEu$^{3+}$ PHOSPHORS

5B.1 Introduction

Metal tungstates and molybdates are two important families of inorganic materials that have potential applications in various fields such as phosphors, optical fibers, scintillators, magnets and catalysts (Wang H et al 1992; Geng J et al 2005; Moszyn’ski M et al 2005; Kato A et al 2005; Nazarov M. V et al 2004; Zhang G. X et al 2006). Tungstates doped with rare earth ions have shown incredible optical characteristics and hence considered as important optical materials. As mentioned in the previous chapters, red phosphors based on Eu$^{3+}$ activated scheelite type tungstates are appropriate for pc-WLED applications because of the presence of broad - intense CT band arising from WO$_4$ tetrahedron unit, chemical stability and high average refractive index (Gundiah G et al 2008; Minami T et al 2003; Dai Q et al 2007). These red phosphors are utilizing the peculiarities of energy levels of both host lattice and activator ions for the efficient energy transfer process and luminescence performance. The red emission from Eu$^{3+}$ activated phosphors under near UV or blue excitations are primarily due to forced electric dipole transition ($^5$D$_0$ - $^7$F$_2$) of Eu$^{3+}$ and these transitions are hypersensitive to the site symmetry of the activator ion and its crystalline environment. Materials research in this regard has got more technological importance nowadays.

It would be much beneficial to improve the luminescence intensity of phosphor materials for practical applications. Specifically for the current red phosphors, the brightness is still a limitation ( ~8 times less than that of the green and blue phosphors). Thus various ways to achieve enhanced luminescence behavior and good color purity of the current red phosphors is to be understood. The codopant incorporation in various host lattices can improve their luminescence performance. The codopants can enhance luminescence intensity by acting as a flux or sensitizer and sometimes create oxygen vacancies in the host lattices or alter the crystal field surrounding the activator ions (Liu X et al 2007). In this regard, codoping of rare earth ions to tungstate based phosphor materials are studied by various research groups. Powell and co-workers studied the luminescent properties and energy transfer of CaWO$_4$: Eu$^{3+}$ phosphors (Treadaway M. J et al 1974; Tyminski J. K et al 1982). However, these materials need a high doping concentration of activator (24 mol% Eu$^{3+}$) for the strong red emission (Yan S et al 2007) and the substitution of Eu$^{3+}$ for Ca$^{2+}$ site is non equivalent. To overcome some of these problems, many authors adopted charge compensation approach using Li$^+$, Na$^+$ or K$^+$ as a charge compensator (Shi S et al 2008). Co substitution of Sm$^{3+}$, Bi$^{3+}$ has also been considered for improving the emission intensity of
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Eu\(^{3+}\) (Wang Z et al 2006). The enhanced luminescence property of CaWO\(_4\): Eu\(^{3+}\), Bi\(^{3+}\) under UV excitation (277 nm) is studied by Pode et al and the energy transfer mechanism is also reported (Pode R. B et al 1997).

In Chapter 4 we had seen the optimum luminescence behavior of tungstate based scheelite type red phosphors, CL/GNW with respect to activator (Eu\(^{3+}\)) concentration. It is observed that the CT band position of these phosphors is located at a higher energy position (~290/303 nm) compared to that of the corresponding molybdate red phosphors (~313 nm). Moreover, the CT band of tungstates is relatively shallower than the molybdates, due to the higher sixth ionization potential of Mo\(^{6+}\). Thus there is an easy charge transfer transition in MoO\(_4\) group than WO\(_4\) group. In line with this, an attempt has been made to strengthen and shift the CT band of the aforementioned tungstate phosphors to a lower energy position. For this purpose, suitable codopant (Bi\(^{3+}\)) is introduced into the lattice and its effect on the structural, microstructural and luminescent properties is investigated in detail. The present part of this chapter elucidates the results regarding Bi\(^{3+}\) codoping in the CL/GNW phosphors. Role of Bi\(^{3+}\) in the luminescence mechanism is also incorporated.

5B.2 Experimental

Selected compositions of CaLa\(_{0.80}\)\(\gamma\)-NbWO\(_8\): 0.20Eu\(^{3+}\), \(\gamma\)Bi\(^{3+}\) \((\gamma = 0.10, 0.15, 0.20)\) (CLNW) and CaGd\(_{0.75}\)\(\gamma\)-NbWO\(_8\): 0.25Eu\(^{3+}\), \(\gamma\)Bi\(^{3+}\) \((\gamma = 0.10, 0.15, 0.20, 0.25)\) (CGNW) were synthesized by solid state reaction route. Stoichiometric amount of starting materials such as CaCO\(_3\), La\(_2\)O\(_3\)/Gd\(_2\)O\(_3\), Bi\(_2\)O\(_3\), Nb\(_2\)O\(_5\), WO\(_3\), and Eu\(_2\)O\(_3\) (Chemicals are from Acros Organics and Sigma Aldrich with 99.99% purity) were weighed and thoroughly wet mixed in an agate mortar with acetone as the wetting medium. The mixing was followed by drying in an air oven. The mixing and drying were repeated thrice to obtain a homogenous mixture and was calcined at 1200°C for 6 h in a platinum crucible in an air atmosphere furnace.

The crystal structure as well as the phase purity of the calcined samples were examined by recording the powder X ray diffraction patterns using a PANalytical X’pert Pro diffractometer with Ni filtered CuK\(_\alpha\) radiation \((\lambda = 1.54056\) Å\). The morphological analysis of the powder samples was done by a scanning electron microscope (JEOL, JSM- 5600LV). The UV Visible absorption spectra of the samples were recorded by UV–Vis Spectrophotometer (Shimadzu UV-2401). Photoluminescence excitation spectra and emission spectra were recorded using a Horiba Yvon Fluorolog® 3 Spectrofluorimeter with a 450W xenon flash lamp as the exciting source. To record the emission spectra, the excitation wavelength is fixed at 394/395 and 465 nm respectively and the emitted light intensity is measured at the wavelength range of 500 - 750 nm. For recording excitation spectra, the emission
monochromator is fixed at 613 nm emission wavelength and the excitation wavelength is scanned in 200 - 500 nm spectral range. Both the excitation and emission spectra were recorded by fixing the excitation and emission monochromator slit width at 0.5 and 1 nm respectively. The CIE chromaticity coordinates of the phosphors were also calculated. Luminescence lifetime of the phosphors was recorded by the phosphorimeter attached to Fluorolog® 3 Spectrofluorimeter.

5B3 Results and Discussion

5B3.1 Powder X ray diffraction analysis

The X ray diffraction patterns of CaLa$_{0.80-y}$NbWO$_8$: 0.20Eu$^{3+}$, yBi$^{3+}$ ($y = 0.10, 0.15, 0.20$) (CLNWB) and CaGd$_{0.75-y}$NbWO$_8$: 0.25Eu$^{3+}$, yBi$^{3+}$ ($y = 0.10, 0.15, 0.20, 0.25$) (CGNWB) are shown in Fig. 5B.1 and Fig. 5B.2 respectively. All the peaks in the XRD patterns are very sharp, which indicate the crystalline nature of the samples. The phase purity of the prepared samples were confirmed by comparing the observed powder XRD pattern with the reported CaWO$_4$ (JCPDS file no.41-1431) tetragonal scheelite structure with the
space group $I4_1/a$ (88) and $Z=4$ (Achary S. N et al 2006). The prominent peaks in the XRD patterns correspond to (101), (112), (004), (200), (204), (220), (116), (312) and (316) lattice planes. No traces of additional peaks from other phases are observed in Eu$^{3+}$, Bi$^{3+}$ coactivated systems.

Thus all the samples are single phase, forming solid solutions of CaLa$_{0.80-y}$NbWO$_8$: 0.20Eu$^{3+}$, yBi$^{3+}$ and CaGd$_{0.75-y}$NbWO$_8$: 0.25Eu$^{3+}$, yBi$^{3+}$. Looking closer to the crystal structure, the host cations such as Ca$^{2+}$, La$^{3+}$/Gd$^{3+}$, and activator/coactivator ions such as Eu$^{3+}$/Bi$^{3+}$ occupy eight coordinated sites, Nb$^{5+}$ and W$^{6+}$ share four coordinated sites. Since the ionic radii of Eu$^{3+}$ [$r = 1.07$ Å when coordination number (CN) = 8] and Bi$^{3+}$ ($r = 1.17$ Å when CN = 8) are close to that of La$^{3+}$ ($r = 1.16$ Å when CN = 8) and Gd$^{3+}$($r = 1.05$ Å when CN = 8), both Eu$^{3+}$ and Bi$^{3+}$ ions prefer the La$^{3+}$ sites to occupy. It should be mentioned here that the phosphors were synthesized without any charge compensation approach as required in the case of CaWO$_4$: Eu$^{3+}$.
5B.3.2 Microstructural characterization

Fig. 5B.3 Scanning electron micrographs of CaLa\textsubscript{0.80-}\textsubscript{y}NbWO\textsubscript{8}: 0.20Eu\textsuperscript{3+}, yBi\textsuperscript{3+} with varying Bi\textsuperscript{3+} concentrations: (a) $y = 0.10$, (b) $y = 0.15$, (c) $y = 0.20$ (x5, 000 magnification).

Fig. 5B.4 Scanning electron micrographs of CaGd\textsubscript{0.75-}\textsubscript{y}NbWO\textsubscript{8}: 0.25Eu\textsuperscript{3+}, yBi\textsuperscript{3+} with (a) $y = 0.10$, (b) $y = 0.15$, (c) $y = 0.20$, (d) $y = 0.25$ (x 5, 000 magnification).
The scanning electron micrographs of CLNWB and CGNMB with varying Bi$^{3+}$ concentration are presented in Fig. 5B.3 and Fig. 5B.4 (x5,000 magnification). The micrographs of the Bi$^{3+}$ coactivated phosphors reveal their crystalline nature. The CLNWB samples are more agglomerated compared to that of CGNWB samples and they are characterized by sharp edges also. The morphology of CGNWB is improved to a great extent by Bi$^{3+}$ codoping. Notable observations with respect to Bi$^{3+}$ codoping are the reduction of particle agglomeration, relatively spherical nature of the particles, uniform shape and size distributions. Moreover on a closer look into the micrographs of CGNWB phosphors, it is seen that the particle size is increasing with Bi$^{3+}$ concentration and becoming more homogenous. The smooth edges of the particles reduce the scattering loss. The morphological improvement of the tungstate based red phosphors is achieved with Bi$^{3+}$ codoping and hence Bi$^{3+}$ is acting as a flux in the present case. The average particle size of CL/GNW is ~5µm. This notable improvement in the morphology of present samples can contribute strongly to their luminescence performance and is discussed in the succeeding sections.

5B.3.3 UV Visible absorption

![UV-Vis absorption spectra of CaLa$_{0.80-y}$NbWO$_8$: 0.20Eu$^{3+}$,yBi$^{3+}$](image)

*Fig. 5B.5* UV-Vis absorption spectra of CaLa$_{0.80-y}$NbWO$_8$: 0.20Eu$^{3+}$,yBi$^{3+}$ ($y = 0, 0.10, 0.15, 0.20$).
UV Visible absorption spectra of CL/GNWB with different Bi$^{3+}$ codopant concentrations are shown in Fig. 5B.5 and Fig. 5B.6. The spectra of Bi$^{3+}$ uncodoped ($y = 0$) sample are also included. It is observed that Bi$^{3+}$ codoped samples also have almost same absorption spectral profile with a band of absorption in the UV region and sharp lines of absorption in the visible region.

The notable variation observed for the Bi$^{3+}$ codoped samples from uncodoped sample is the presence of an additional absorption band in the UV region. The first band of absorption centering at ~258 nm (CLNWB) and 269 nm (CGNWB) corresponds to the CT transitions arising from WO$_4$/NbO$_4$ and O$^2$- - Eu$^{3+}$ groups (Ahmad G et al 2006; Liu X et al 2007; Su Y et al 2008). The second band in the UV region is owing to the Bi$^{3+}$ absorption via the electronic transition from ground state ($^0$S$_1$) to its excited states ($^1$P$_1$) (Xie A et al 2009). The absorption band for the Bi$^{3+}$ codoped samples is extended to lower energy position compared to that of the Bi$^{3+}$ uncodoped samples. The absorption lines due to intra configurational f-f transitions (394 and 465 nm) of Eu$^{3+}$ are clearly observable in the present case unlike the Bi$^{3+}$ codoped molybdate (CL/GNMB) samples. Also the intensity of these two absorption peaks is
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Increasing with Bi$^{3+}$ concentration. The increase in the absorption strengths of the peaks at 394 and 465 nm positions lead to an increase in their excitation intensity and the corresponding emission. Thus Bi$^{3+}$ codoping in the tungstate based samples broadened their absorption band in the UV region and consequently a red shift of the absorption edge, which is a prior requisite for a phosphor for pc-WLED application.

SB.3.4 Photoluminescence properties

SB.3.4.1 Excitation spectra

The photoluminescence excitation spectra of CL/GNWB phosphors for an emission at 613 nm with different Bi$^{3+}$ concentration are shown in Fig. 5B.7 and Fig. 5B.8. The spectra of Bi$^{3+}$ uncoded samples ($\gamma = 0$) are also shown. The spectra of both Bi$^{3+}$ codoped and uncoded samples show broad band of excitation at UV region and sharp peaks from near UV to visible region. The broad band of excitation is due to the CT transitions of O - W/O - Nb in the WO$_4$/NbO$_4$ group, and that of Eu$^{3+}$ - O$^{2-}$ (Pode R. B et al 1997; Hsiao Y. J et al 2007). The CT band of Bi$^{3+}$ uncoded samples is in the range of 240 - 350 nm, and is

![Excitation spectra of CaLa$_{0.80-y}$NbWO$_8$: 0.20Eu$^{3+}$, yBi$^{3+}$ ($\gamma = 0, 0.15, 0.20$) for an emission at 613 nm.](attachment:excitation_spectra.png)

Fig. 5B.7 Excitation spectra of CaLa$_{0.80-y}$NbWO$_8$: 0.20Eu$^{3+}$, yBi$^{3+}$ ($\gamma = 0, 0.15, 0.20$) for an emission at 613 nm.
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centered at $\sim$290 nm (CLNW) and $\sim$303 nm (CGNW). With the introduction of Bi$^{3+}$ in CLNW and CGNW lattices, the CT band is extended to a longer wavelength of $\sim$360 nm. Consequently, the CT band is red shifted from 290 to 324 nm (CLNWB) and 303 to 327 nm (CGNWB). A remarkable increase in the relative intensity of CT band is also observed with Bi$^{3+}$ codoping. Thus, with Bi$^{3+}$ codoping in the tungstate based samples, the CT band becomes broader and stronger. The sharp peaks of both CL/GNWB samples are observed at 362, 383, 394/395, 416, 465 nm and are corresponding to the $^7$F$_0$-$^5$D$_4$, $^7$F$_0$-$^5$G$_{2,4}$, $^7$F$_0$-$^5$L$_6$, $^7$F$_0$-$^5$D$_3$, $^7$F$_0$-$^5$D$_2$ transitions respectively (Blasse G 1979), which have no significant variation in the energy position.

![Excitation spectra of CaGd$_{0.75-y}$NbWO$_8$: 0.25Eu$^{3+}$, yBi$^{3+}$](image)

**Fig. 5B.8** Excitation spectra of CaGd$_{0.75-y}$NbWO$_8$: 0.25Eu$^{3+}$, yBi$^{3+}$ ($y = 0, 0.10, 0.15, 0.20, 0.25$) for an emission at 613 nm.
The red shift of CT band observed in the case of Bi$^{3+}$ codoped tungstates, CL/GNWB is mainly due to Bi$^{3+}$ absorption. Bi$^{3+}$ ion has an outer 6s$^2$ configuration with a ground state of $^1S_0$. The excited states have a 6s6p configuration and are splitting into $^3P_0$, $^3P_1$, $^3P_2$ and $^1P_1$ levels in the sequence of energy increase. If no other configurations are taken into account, the transitions from $^1S_0$ to $^3P_0$ and $^3P_2$ are completely spin forbidden. The other two excited levels $^3P_1$ and $^1P_1$ are mixed by spin-orbit coupling. Thus, the broad absorption from 300 to 360 nm is an overlap of the transition from $^1S_0$ to $^3P_1$ and $^1P_1$ levels (Shin S. H et al 2001).

In the first part of this chapter we had seen that, Bi$^{3+}$ codoping in molybdate based red phosphors red shifted the CT band position with no significant improvement in its intensity. But in the present case of tungstate based samples, it is clearly observed that both red shift and intensification of CT band happened with Bi$^{3+}$ codoping. As mentioned in the earlier chapters, (MoO$_4$) groups in molybdates are in general having strong CT band while tungstates are characterized by shallow CT band positioned at comparatively higher energy region. The enhanced CT band in the solid solution phosphors (CL/GNM) containing MoO$_4$ can be explained by the fact that Mo has a higher sixth ionization potential (70 eV) than W (61eV) (Lee G. H et al 2011). That is, Mo has a greater tendency to receive an electron from an oxygen ligand and MoO$_4$ requires a lower energy for ligand - metal charge transfer (LMCT). By the introduction of Bi$^{3+}$ in the current tungstate based red phosphors, the absorption process between Bi$^{3+}$ energy levels (from $^1S_0$ to $^3P_1$ and $^1P_1$) prominently contributed to the intensification of the CT band. In other words, Bi$^{3+}$ codoping in tungstate based samples enhanced the probability of CT from WO$_4$ group. In line with the Bi$^{3+}$ absorption process the red shift of the CT band is also observed.

The dependence of excitation intensity of intra configurational transitions such as $^7F_0$–$^5L_6$ (394 nm) and $^7F_0$–$^5D_2$ (465 nm) of CL/GNWB phosphors with respect to Bi$^{3+}$ concentrations is presented in Fig. 5B.9(a) and Fig. 5B.9(b) respectively. It is observed that all the Bi$^{3+}$ codoped samples have more excitation intensity compared to that of uncodoped analogues. For CLNWB samples, the excitation intensity is linearly increasing up to 20 mol% of Bi$^{3+}$ but for CGNWB samples, the intensity of excitation is reducing beyond 20 mol% of Bi$^{3+}$. This may be due to the formation of aggregates in the samples at higher concentrations of codopant ions which are acting as killers or quenchers of luminescence performance of the phosphor.
Fig. 5B.9 Dependence of excitation intensity ($\lambda_{em}: 613$ nm) of $^{7}F_{0}^{-5}L_{6}$ and $^{7}F_{0}^{-5}D$ transitions of (a) $\text{CaLa}_{0.80-y}\text{NbWO}_{6}: 0.20\text{Eu}^{3+}, y\text{Bi}^{3+}$ ($y = 0, 0.10, 0.15, 0.20$) and (b) $\text{CaGd}_{0.75-y}\text{NbWO}_{6}: 0.25\text{Eu}^{3+}, y\text{Bi}^{3+}$ ($y = 0, 0.10, 0.15, 0.20, 0.25$).

The improvement in these excitation intensity or absorption strength of the samples directly increases the luminescence emission intensity under the same excitation. Major
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The motive for the enhancement in the intra configurational excitation intensity with Bi$^{3+}$ codoping is the red shift of CT band, better morphology and crystallinity of the samples. This red shift in the CT band can contribute indirectly to the enhancement of excitation intensity of parity forbidden intra configurational $f$-$f$ transitions of Eu$^{3+}$. The detailed discussion on these aspects is included in the coming section.

In the earlier chapter, we have seen a marginal improvement in the luminescence emission intensity for CL/GNMB phosphors compared to the uncodoped samples (CL/GNM). However, it is expected that the enhancement in the CT band intensity and intra configurational $f$-$f$ transition intensity and red shift of CT band by Bi$^{3+}$ codoping will enhance the luminescence emission intensity of CL/GNWB samples to a great extent.

### 5B.3.4.2 Emission spectra

![Emission spectra of CaLa$_{0.80-y}$NbWO$_8$: 0.20Eu$^{3+}$,yBi$^{3+}$](image)

Fig. 5B.10 Emission spectra of CaLa$_{0.80-y}$NbWO$_8$: 0.20Eu$^{3+}$,yBi$^{3+}$ ($y = 0.10, 0.15, 0.20$) under 394 nm excitation.
The emission spectra of CLNWB ($y = 0, 0.10, 0.15, 0.20, 0.25$) and CLNWB ($y = 0, 0.10, 0.15, 0.20, 0.25$) samples under near UV excitation are shown in Fig. 5B.10 and Fig. 5B.11 respectively. The spectral profile of Bi$^{3+}$ codoped samples are same as that of the uncoded samples. The spectra include emission peaks corresponding to intra configurational $f$-$f$ transitions ($^5D_0 - ^7F_j$, $J = 0, 1, 2$) of Eu$^{3+}$ (Liu et al. 2007). Similar emission spectra are observed under blue (465 nm) excitation also. The dominant red emission peak observed at 613 nm is due to parity forbidden $^5D_0 - ^7F_2$ electric dipole transition which hints that Eu$^{3+}$ is also occupying in a non centrosymmetric site in the Bi$^{3+}$ codoped samples (Xie et al. 2009).

Fig. 5B.11 Emission spectra of CaGd$_{0.75-y}$NbWO$_8$: 0.25Eu$^{3+}$, yBi$^{3+}$ ($y = 0, 0.10, 0.15, 0.20, 0.25$) under 395 nm excitation.

In the present samples, Eu$^{3+}$ is occupying the non centrosymmetric A site shared by Ca$^{2+}$, La$^{3+}$/Gd$^{3+}$ and Bi$^{3+}$ ions. It is observed that the emission intensity of the CLNWB is increasing with respect to Bi$^{3+}$ concentration and for CGNMB phosphors; it is observed that
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The red emission intensity is increasing with Bi$^{3+}$ concentration up to 20 mol% and it starts decreasing beyond that. This observation is in line with that of the excitation spectra. When compared with Bi$^{3+}$ uncodoped samples ($y = 0$, CLNW20 & CGNW25) the red emission intensity of CLNWB and CGNWB samples is doubled.

Considering the factors such as lifetimes and absorption strengths of CL/GNWB phosphors, their luminescence mechanism can be well understood. For this, a closer look into the decay curves and absorption or excitation spectra of CL/GNWB with different codopant (Bi$^{3+}$) concentration is essential.

![Figure 5A.12 Decay curves of CaLa$_{0.80-y}$NbWO$_8$: 0.20Eu$^{3+}$, yBi$^{3+}$ (y = 0, 0.10, 0.15, 0.20) under near UV excitation.](image)

**Fig. 5A.12** Decay curves of CaLa$_{0.80-y}$NbWO$_8$: 0.20Eu$^{3+}$, yBi$^{3+}$ (y = 0, 0.10, 0.15, 0.20) under near UV excitation.

**Table 5B.1** Lifetimes of CaLa$_{0.80-y}$NbWO$_8$: 0.20Eu$^{3+}$, yBi$^{3+}$ and CaGd$_{0.75-y}$NbWO$_8$: 0.25Eu$^{3+}$, yBi$^{3+}$ phosphors under near UV excitation

<table>
<thead>
<tr>
<th>Sample</th>
<th>CaLa$_{0.80-y}$NbWO$_8$: 0.20Eu$^{3+}$, yBi$^{3+}$</th>
<th>CaGd$_{0.75-y}$NbWO$_8$: 0.25Eu$^{3+}$, yBi$^{3+}$</th>
</tr>
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<tbody>
<tr>
<td>$y$</td>
<td>0.01  0.15  0.20</td>
<td>0.01  0.15  0.20  0.25</td>
</tr>
<tr>
<td>Lifetime (ms)</td>
<td>0.6593  0.6512  0.6629</td>
<td>0.7118  0.7202  0.6765  0.6277</td>
</tr>
</tbody>
</table>
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![Graph showing decay curves of CaGd$_{0.75-y}$NbWO$_6$: 0.25Eu$^{3+}$, yBi$^{3+}$ (y = 0, 0.10, 0.15, 0.20, 0.25) under near UV excitation.]

Fig. 5A.13 Decay curves of CaGd$_{0.75-y}$NbWO$_6$: 0.25Eu$^{3+}$, yBi$^{3+}$ (y = 0, 0.10, 0.15, 0.20, 0.25) under near UV excitation.

The decay curves of the samples under near UV excitation with different Bi$^{3+}$ concentrations are shown in Fig. 5B.12 and Fig. 5B.13. The decay curves for $^5D_0$ excited state (emission level in CL/GNWB) of Eu$^{3+}$ for both samples show single exponential behavior and is well fitted with the function $I = A \exp(-t/\tau)$ where $I$, $\tau$ and $A$ are intensity, decay time and fitting parameter respectively and the corresponding lifetimes of phosphors are enlisted in Table 5B.1. It is observed that the lifetime of tungstate based phosphors are not showing any notable regular variation with Bi$^{3+}$ codoping. Consequently, quantum efficiency of the phosphors is hardly affected by Bi$^{3+}$ codoping similar to that of CL/GNMB.

The absorption strength of the samples is the other factor to be considered with the Bi$^{3+}$ codopant incorporation in tungstate based phosphors. From the excitation spectra and absorption spectra of the samples, it is clearly observed that the absorption strength of both CL/GNWB phosphors is increased compared to that of their uncodoped samples. Specifically, the intensity of $^7F_0$-$^5L_6$ (394/395 nm) and $^7F_0$-$^5D_2$ (465 nm) transitions (excitation wavelengths of phosphors) are increasing linearly upto 20 mol% of Bi$^{3+}$ in CL/GNWB phosphors (Fig. 5B.9). The observation of increase of absorption strength of phosphors with Bi$^{3+}$ is similar to that of corresponding molybdates discussed in the earlier part of this chapter.
The different factors that might contribute to the increase of absorption strength of phosphors such as symmetry distortions, morphology, crystallinity, CT band position and intensity are to be checked in the present case of tungstate based red phosphors also (Blasse G 1979; Su Q et al 1995). In CL/GNWB phosphors, the Bi$^{3+}$ and Eu$^{3+}$ are respectively sharing the site occupied by La$^{3+}$ and Gd$^{3+}$ and all are having the same oxidation state and matching ionic radii. In other words, no significant symmetry distortion to the Eu$^{3+}$ crystalline environment is expected in the CL/GNWB lattice similar to that of CL/GNMB. The asymmetry ratio ($I_{590}/I_{613}$) of CL/GNWB is in the range of $\sim$ 9 - 8 with Bi$^{3+}$ concentration. Thus in the present case also there is only a minor contribution of symmetry variations to the improvement of parity forbidden $f-f$ transition. From XRD and SEM analysis, it is observed that Bi$^{3+}$ has improved the crystallinity as well as morphology of the phosphors. The presence of relatively spherical particles lead to efficient absorption of light irradiated on the phosphor surface and thereby better excitation process. The scattering loss is also reduced to some extent.

Looking closer into the aspect of the position and intensity of CT band of CL/GNWB phosphors with Bi$^{3+}$ codoping, we had seen a red shift of $\sim$34 nm (CLNWB) and $\sim$24 nm (CGNWB) with respect to Bi$^{3+}$ codoping in comparison with the uncodoped samples. The amount of red shift of tungstate based phosphors is more than that of the corresponding molybdates, CL/GNMB ($\sim$17 nm). This makes an easier CT process in the tungstates with Bi$^{3+}$ codoping. In addition to the red shift in the CT band position, a remarkable increase in the intensity of CT band is observed in both CL/GNWB phosphors and is in contrast to that of CL/GNMB phosphors. The red shift in the CT band position and increase of its intensity act as a channel for enhancing the probability of intra configurational transitions in CL/GNWB phosphors and their luminescence performance. i.e., the parity forbidden will achieve intensity via non radiative energy transfer from the lowest strong absorption band which is the CT band (Su Q et al 1995).

Another aspect responsible for the enhancement of luminescence is the energy transfer from Bi$^{3+}$ to Eu$^{3+}$ and it can be of radiative or non radiative nature. The excitation spectra ($\lambda_{em}$: 490 nm) of CaLa$_{0.8}$NbWO$_8$: 0.2Bi$^{3+}$ sample exhibits a band centered around 313 nm (shown in the inset of Fig. 5B.14) and is consistent with the excitation spectrum of CaLa$_{0.6}$NbWO$_8$: 0.2Bi$^{3+}$, 0.2Eu$^{3+}$. It is also clear from Fig. 5B.13 that there is a considerable spectral overlap between the Eu$^{3+}$ excitation transitions and the emission band of Bi$^{3+}$, $^3P_1 - ^1S_0$ centered at 490 nm, suggesting the occurrence of resonance radiative energy transfer from Bi$^{3+}$ to Eu$^{3+}$ (similar for CGNWB also).

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Fig. 5B.14 Spectral overlap between the excitation spectrum of (a) CaLa$_{0.80}$NbWO$_8$: 0.20Eu$^{3+}$ ($\lambda_{\text{em}}$: 613 nm) and emission spectrum of (b) CaLa$_{0.80}$NbWO$_8$: 0.20Bi$^{3+}$ ($\lambda_{\text{ex}}$: 313 nm).

Fig. 5B.15 Schematic configurational coordinate diagram for $\text{Bi}^{3+}$ and $\text{Eu}^{3+}$ and the possible energy transfer process from $\text{Bi}^{3+}$ to $\text{Eu}^{3+}$ under the excitation of 313 nm.
However, this effectively occurs in the UV region (under an excitation of 313 nm). i.e., when the phosphor is excited by wavelength corresponding to the Bi$^{3+}$ excitation wavelength of 313 nm, the excited energy state of Bi$^{3+}$ ($^3P_1$) relaxes to its ground state ($^1S_0$) and the corresponding energy is transferred to the $4f$ levels of Eu$^{3+}$ resulting in a red emission through the $^5D_0$-$^7F_j$ transition of Eu$^{3+}$.

Schematic representation of this process is shown in Fig. 5B.15. However this type of resonance radiative energy transfer process is not utilized in the current phosphors, since they are excited by near UV (395 nm) and blue irradiations (465 nm) corresponding to Eu$^{3+}$ intra configurational transition wavelengths. The same ET process happens when the samples are excited to CT states (under an excitation of 324 or 327 nm), where the CT states will transfer energy to Eu$^{3+}$ excited state instead of Bi$^{3+}$ energy levels.

Another ET process is the non radiative process and it occurs from the CT states of the CL/GNW phosphors to excited levels of Eu$^{3+}$ and is schematically illustrated in Fig. 5B.16.

Fig. 5B.16 Configurational co-ordinate diagram of the possible non radiative energy transfer process from CT states to Eu$^{3+}$ level under near UV or blue excitations.
We had already seen that the CT states of Bi$^{3+}$ uncoded phosphors (CL/GNW) are positioned at a higher energy region (290 and 303 nm) and is shifted to a lower energy position (324 and 327 nm) via Bi$^{3+}$ codoping. Thus there is more possibility for the overlap between the CT states and $f-f$ levels of Eu$^{3+}$; leading to a non radiative ET from the CT states to excited levels ($^5$L$_{6}$ and $^5$D$_{2}$) of Eu$^{3+}$ and attaining more intensity for $f-f$ transitions (Blasse G 1979; Struck et al 1970) Lifetime variation of the phosphors (both tungstates and molybdates) can also be related to this. This process happens in molybdate based phosphors (CL/GNMB) also and is more effective in the current tungstate based red phosphors (CL/GNWB).

These phosphors are also characterized by good color purity and its CIE chromaticity co ordinates are (0.64, 0.35), which are comparable to that of NTSC standards. Thus in the Bi$^{3+}$ codoped phosphates also, the increase of absorption strength via CT band red shift, morphological improvement and crystallinity played key role in luminescence enhancement.

5B.4 Conclusions

In conclusion, scheelite type tungstate based red emitting phosphors, CaLa$_{0.80-y}$NbWO$_6$: 0.20Eu$^{3+}$, $y$Bi$^{3+}$ and CaGd$_{0.75-y}$NbWO$_6$: 0.25Eu$^{3+}$, $y$Bi$^{3+}$ have been synthesized by solid state reaction route and its structural, microstructural and photoluminescent properties are investigated in detail. It is observed that Bi$^{3+}$ codoping improved the crystallinity as well as morphology of the samples. Notable observations in the luminescence properties with Bi$^{3+}$ coping are the red shift and intensification of CT band of excitation (unlike to the corresponding molybdates) leading to an increment in the absorption strength of the phosphors. The photoluminescent properties of CaLa$_{0.80-y}$NbWO$_6$: 0.20Eu$^{3+}$, $y$Bi$^{3+}$ points out that the samples exhibit enhanced (~2 times) red emission of Eu$^{3+}$ (615 nm) under the excitation of near UV and blue light that correspond to the emission lines from near UV and blue LED. The possible mechanism behind luminescence enhancement is explored. With the incorporation of Eu$^{3+}$ and Bi$^{3+}$ in the host lattice, host sensitized non radiative energy transfer is effectively occurred in the current phosphor samples. The phosphors also exhibit sharp red emission peaks with good color purity having matching color co ordinates of standard red phosphors.