Chapter 6

Synthesis, characterization and photoluminescence properties of Bi$^{3+}$ codoped CaSiO$_3$:Eu$^{3+}$ nanoporphosphor
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6.1 Introduction

In both rare earth physics and chemistry the study of luminescence of rare earth doped solid state materials is an interesting area for research, among the lanthanide group europium is a special element and exhibits the property of valence fluctuation besides the common properties of rare earth elements, the different valences is attributed by different luminescence characteristics. The use of Eu$^{3+}$ ion has been immense in color television, panel display, cathode ray tube and fluorescent powders of three primary colors due to its property of red light emission [232–234]. Hence for the fabrication of white LEDs it is vital to develop more efficient red emitting phosphors that is suitable. Due to the high quantum efficiency, water resistance, low cost, excellent chemical and thermal stability there has been an extensive investigation about silicate-based phosphors. Materials including Eu$^{3+}$, are the most interesting topic for red phosphors which is widely used as a red-emitting activator through the $^{5}$D$\text{0}$$\rightarrow$$^{7}$F$\text{2}$ transition at about 614 nm. The transition metal ions usually are co-doped as sensitizers to enhance the red emission intensity of Eu$^{3+}$ [235, 236]. In addition, Calcium silicate (CaSiO$_3$) also known as wollastonite, is a good matrix of luminescent material. CaSiO$_3$ possesses a higher luminous efficiency after it is doped with activated ions. Over the past two decades, researchers had gradually started investigating the luminescent material with matrix CaSiO$_3$,
thereby leading to an enhancement of the research and application fields of CaSiO$_3$ [237-240].

Although several studies have been performed on the luminescence of Eu$^{3+}$ ions, only a few articles have reported the luminescent phenomenon of Eu$^{3+}$ ions in CaSiO$_3$. The samples were normally synthesized by the solid state reaction method, which had some disadvantages such as high sintering temperature, nonuniform mixing, more impurities [241, 242]. Hence, it is necessary to find an alternative synthetic method to prepare pure luminescent material. Therefore we have prepared the materials using solution combustion synthesis methods because it is simple, fast and economic. To show the effect of Bi$^{3+}$ on Eu$^{3+}$ luminescence in CaSiO$_3$ the role of sensitizer is played by Bi$^{3+}$. This chapter also explains the energy transfer between Bi$^{3+}$ and Eu$^{3+}$ and the luminescence characteristics from the investigated samples.

6.2 Synthesis Ca$_{0.96-x}$Eu$_{0.04}$Bi$_x$SiO$_3$ ($X = 0.01 - 0.05$) phosphor

The starting chemicals used for the preparation Ca$_{0.96-x}$Eu$_{0.04}$Bi$_x$SiO$_3$ ($X = 0.01 - 0.05$) were analar grade calcium nitrate [Ca(NO$_3$)$_2$], fumed silica [SiO$_2$, surface area 200 m$^2$/g], europium oxide [Eu$_2$O$_3$] and bismuth nitrate [Bi(NO$_3$)$_3$]. The diformylhydrazine [DFH: C$_2$H$_4$N$_2$O$_2$] is used as a fuel. In a typical synthesis, europium oxide was converted into europium nitrate the detailed procedure was described in the chapter 3 (3.2), then
an aqueous solution containing stoichiometric amounts of calcium nitrate, bismuth nitrate, silica fumes and DFH have been taken in a cylindrical Petri dish of approximately ~300 ml capacity. Then the Petri dish was introduced into a muffle furnace maintained at 500 ± 10 °C. Then similar procedure is followed as described in the chapter 5. The 0-5 mol% Bi$^{3+}$ doped CaSiO$_3$:Eu$^{3+}$ (4 mol %) nanophosphors are prepared to study the luminescence properties.

6.3 Results and discussion

6.3.1 Powder X-ray diffraction

The PXRD patterns of the samples Ca$_{0.96-x}$Eu$_{0.04}$Bi$_x$SiO$_3$ ($X = 0.01 - 0.05$) are shown in Fig. 6.1. The XRD patterns are well agreed with the Joint Committee on Powder Diffraction Standards (JCPDS) 87-2172. In addition, it can be visualized that the limited doped Eu$^{3+}$ ions and Bi$^{3+}$ do not cause any significant changes in the host structure.
Fig 6.1. PXRD patterns of (a) Ca_{0.95}Eu_{0.04}Bi_{0.01}SiO_{3} (b) Ca_{0.94}Eu_{0.04}Bi_{0.02}SiO_{3} (c) Ca_{0.93}Eu_{0.04}Bi_{0.03}SiO_{3} (d) Ca_{0.92}Eu_{0.04}Bi_{0.04}SiO_{3} (e) Ca_{0.91}Eu_{0.04}Bi_{0.05}SiO_{3}

Fig 6.2. W-H Plots of (a) Ca_{0.95}Eu_{0.04}Bi_{0.01}SiO_{3} (b) Ca_{0.94}Eu_{0.04}Bi_{0.02}SiO_{3} (c) Ca_{0.93}Eu_{0.04}Bi_{0.03}SiO_{3} (d) Ca_{0.92}Eu_{0.04}Bi_{0.04}SiO_{3} (e) Ca_{0.91}Eu_{0.04}Bi_{0.05}SiO_{3}
Table 6.1 shows the details of crystallite size and strain values of Ca$_{0.96-x}$Eu$_x$Bi$_x$SiO$_3$ (X = 0.01 - 0.05) nanophosphor powders.

The results of the analysis show that CaSiO$_3$: Eu$^{3+}$, Bi$^{3+}$ sample has a perovskite structure belonging to a monoclinic system, and its space group is P2$_1$/a [243]. In the unit cell of perovskite CaSiO$_3$, Si$^{4+}$ ions are positioned at the center of a cube, O$^{2-}$ ions are positioned at six-face centers of the cube and Ca$^{2+}$ ions are positioned at the eight apex angles of the cube. Octahedrons were made up of Si$^{4+}$ ions and the nearest neighbor O$^{2-}$ ions and the coordination number are six. Icosahedrons were made up of Ca$^{2+}$ ions and the nearest neighbor O$^{2-}$ ions and the coordination number are twelve. The coordination numbers of both Si$^{4+}$ ions and Ca$^{2+}$ ions are eight [244]. The structure of the crystal remains unaltered even after doping the Eu$^{3+}$ ions and Bi$^{3+}$ ions as the doping content was small.
6.3.2 Scanning electron microscopy

Fig. 6.3(a), (b) and (c) shows the SEM micrographs used to study the micro-structures of the CaSiO$_3$:Eu$^{3+}$, Bi$^{3+}$ powders.

Fig 6.3. SEM micrographs of (a) Ca$_{0.95}$Eu$_{0.04}$Bi$_{0.01}$SiO$_3$ (b) Ca$_{0.93}$Eu$_{0.04}$Bi$_{0.03}$SiO$_3$ (c) Ca$_{0.91}$Eu$_{0.04}$Bi$_{0.05}$SiO$_3$ nano phosphor powder.

The morphological characteristics of the prepared powders are strongly dependent on the heat and complex decomposition in combustion method. While the heat gases generated during the released is an important factor for crystal growth the preparation of tiny particles is
done through the large amount of gases. An inspection of the morphology of the synthesized powder samples Calcined 950° C 3h, reveals that the phosphor powders are characterized by flakes up to 5 μm. During the combustion process the surface of the powder samples shows voids and pores formed by the escaping gases. The wide particle-size distribution as well as irregular shapes of the particles is probably due to the non-uniform distribution of temperature and mass flow in the combustion wave.

6.3.3 Transmission electron microscopy

TEM observation was carried out to study the crystalline characteristics of the nanoparticles. Fig.6.4 depicts the TEM images of CaSiO₃:Eu₀.₀₄Bi₀.₀₃ particles. Which are spherical in shape having average size in the range of 30 – 40 nm. This was also confirmed by the Debye–Scherrer’s equation and W-H plots.
6.3.4 Fourier transform infrared spectroscopy

The FT-IR spectra of CaSiO$_3$: Eu$^{3+}$, Bi$^{3+}$ phosphors Calcined 950 °C, 3h are shown in Fig.6.5 (a), (b) and (c). The spectroscopic analysis confirmed that the IR peaks at 465, 680 and 964 cm$^{-1}$ are due to CaSiO$_3$ [245, 246]. It is observed that the broad band from 840–1240 cm$^{-1}$ is due to asymmetric stretching vibration of Si–O–Si bond and stretching vibrations of terminal Si–O bonds. The peaks at 434–564 cm$^{-1}$, 680 cm$^{-1}$ are the characteristic stretching vibrations of Si–O–Si bridges. The sharp peak corresponding to 680 cm$^{-1}$ can be ascribed to Si–O bond, which exists in the form of SiO$_3^{2-}$. The peak at 1480 cm$^{-1}$ is due to the existence of CaO in the structure. It can be noticed that there is no change in the
position or intensity of absorption bands for the Ca$_{0.96-x}$Eu$_{0.04}$Bi$_x$SiO$_3$ ($X = 0.01, 0.03$ and $0.05$). Which confirms that the dew-point has not altered its phase and crystallinity. These results are consistent with those of PXRD results [Fig.6.1].

![FTIR spectra of Ca$_{0.95}$Eu$_{0.04}$Bi$_{0.01}$SiO$_3$, Ca$_{0.93}$Eu$_{0.04}$Bi$_{0.03}$SiO$_3$, Ca$_{0.91}$Eu$_{0.04}$Bi$_{0.05}$SiO$_3$](image)

Fig 6.5.FTIR spectra of (a) Ca$_{0.95}$Eu$_{0.04}$Bi$_{0.01}$SiO$_3$ (b) Ca$_{0.93}$Eu$_{0.04}$Bi$_{0.03}$SiO$_3$ (c) Ca$_{0.91}$Eu$_{0.04}$Bi$_{0.05}$SiO$_3$ nano phosphor powder.

**6.3.5 UV-Visible absorption**

UV-Visible absorption spectrum of Ca$_{0.96-x}$Eu$_{0.04}$Bi$_x$SiO$_3$ ($X = 0.01, 0.03$ and $0.05$) nanophosphors is shown in Fig. 6.6 (a), (b) and (c). The samples of Bi$^{3+}$ co-doped CaSiO$_3$:Eu$^{3+}$ shows a strong absorption band in the region $300$-$550$ nm which is attributed to the excitation absorption of Bi$^{3+}$ and Eu$^{3+}$ respectively [247]. The strong absorption peak at $280$ nm is corresponding to oxygen to silicon (O-Si) ligand-to-metal charge-transfer
(LMCT) in the SiO$_3^{2-}$ group. The broadband is due to 4f – 4f transition. The absorption intensity from 320-380 nm is decreased by the incorporation of Bi$^{3+}$ ion. The absorption band around 260, 340 nm is assigned to the excitation absorption of Bi$^{3+}$ [248, 249]. The absorption band is found to be shifted towards higher wavelength side with increasing concentration of Bi$^{3+}$. This is due to the transition between the conduction band and the impurity level generated due to Bi$^{3+}$ doping.

![Absorbance spectra](image)

**Fig 6.6.** UV-Visible spectra of (a) Ca$_{0.95}$Eu$_{0.04}$Bi$_{0.01}$SiO$_3$ (b) Ca$_{0.93}$Eu$_{0.04}$Bi$_{0.03}$SiO$_3$ (c) Ca$_{0.91}$Eu$_{0.04}$Bi$_{0.05}$SiO$_3$ nano phosphor powder.

The optical band gap energy ($E_g$) relates to the absorption co-efficient $\alpha$ by the Tauc relation (Ref. Eq. 2.5, Chapter 2). Fig. 6.7(a), (b) shows the plots of $(\alpha h\nu)^2$ versus $h\nu$ for the Ca$_{0.96-x}$Eu$_{0.04}$Bi$_x$SiO$_3$ ($X = 0.03$ and $0.05$)
nanophosphor while the phosphors calcined from 950 °C for 3h, more
ordered/crystalline materials are shown by the absorption spectra. On
the basis of this information, if the structure becomes more ordered with
the calcined samples i.e. when the concentration of structural defects
(oxygen vacancies, distortions and/or strains in the lattice) is reduced.
The presence of intermediary energy levels (deep and shallow holes) is
minimized within the optical band gap and consequently, the $E_g$ values
increase. It can be observed from Fig 6.7(a), (b) that the gap in energy
values mainly depend on the added dopants and experimental conditions
such as calcination, processing time etc. These key factors in particular
can inhibit or favour the formation of structural defects that help
controlling in material the degree of structural order and disorder and the
amount of energy levels within the band gap.

![Graph](image)

Fig.6.7. Optical band gap of (a) $\text{Ca}_{0.93}\text{Eu}_{0.04}\text{Bi}_{0.03}\text{SiO}_3$

(b) $\text{Ca}_{0.91}\text{Eu}_{0.04}\text{Bi}_{0.05}\text{SiO}_3$
6.3.6 Photoluminescence

The emission spectra excited at 280 nm contain main emission lines peaking at 530, 590, 613, 649 nm, in which the peak at 530 nm is due to Bi$^{3+}$ ions, the remaining peaks are characteristic emission of Eu$^{3+}$, and they correspond to the $^5D_0 \rightarrow ^7F_j$ ($j = 1, 2, 3, 4$) transitions of Eu$^{3+}$. The emission bands of Eu$^{3+}$ are generally due to the transitions of $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$. The transition of the magnetic dipole located at 590 nm corresponds to $^5D_0 \rightarrow ^7F_1$ ions of Eu$^{3+}$ and transition of the electronic dipole that is located at about 613 nm corresponds to $^5D_0 \rightarrow ^7F_2$ of Eu$^{3+}$ ions. The magnetic dipole transition is displayed by Eu$^{3+}$ ions if they are located in the inversion center lattices and they possess the same rule as that of free ions. In case the Eu$^{3+}$ ions are located in non-inversion center lattices the transition that is forbidden is unchained and mainly depicts the transition of electronic dipole and the electric dipolar $^5D_0 \rightarrow ^7F_2$ transition (hypersensitive) is relatively sensitive to ligand field [243, 244]. It can be seen from the emission spectrum that the hypersensitive $^5D_0 \rightarrow ^7F_2$ red emission at 613 nm is the most prominent, indicating that Eu$^{3+}$ ions are located in more non-inversion center lattices. In the CaSiO$_3$ crystal, the symmetry property is low, and the unequivalent substitution of Eu$^{3+}$ for Ca$^{2+}$ can cause the crystal lattice distortion, the parity-forbidden is unchained. Therefore, the $^5D_0 \rightarrow ^7F_2$ emission is the most prominent in CaSiO$_3$ crystal. For the enhancement of the red emission
intensity of Eu\(^{3+}\), Bi\(^{3+}\) was codoped into CaSiO\(_3\) as sensitizer [250]. The emission spectra of Ca\(_{0.96}\)Eu\(_{0.04}\)SiO\(_3\) and Ca\(_{0.96-x}\)Eu\(_{0.04}\)Bi\(_x\)SiO\(_3\) (X = 0.01-0.05) phosphors under 280 nm excitation were shown in Fig 6.8. Compared with Ca\(_{0.96}\)Eu\(_{0.04}\)SiO\(_3\) phosphor, the luminescence intensity of Ca\(_{0.93}\)Eu\(_{0.04}\)Bi\(_{0.03}\)SiO\(_3\) phosphor has increased by 2.5 times. However, with increasing Bi\(^{3+}\) concentration beyond 0.03, the emission intensity starts decreasing due to the sensitization effect of the Bi\(^{3+}\) ion on the Eu\(^{3+}\) emission varies with the Bi\(^{3+}\) concentration.

Fig 6.8 PL emission spectra of (a) Ca\(_{0.96}\)Eu\(_{0.04}\)Bi\(_{0.0}\)SiO\(_3\)
(b) Ca\(_{0.95}\)Eu\(_{0.04}\)Bi\(_{0.01}\)SiO\(_3\)
(c) Ca\(_{0.94}\)Eu\(_{0.04}\)Bi\(_{0.02}\)SiO\(_3\)
(d) Ca\(_{0.93}\)Eu\(_{0.04}\)Bi\(_{0.03}\)SiO\(_3\)
(e) Ca\(_{0.92}\)Eu\(_{0.04}\)Bi\(_{0.04}\)SiO\(_3\)
(f) Ca\(_{0.91}\)Eu\(_{0.04}\)Bi\(_{0.05}\)SiO\(_3\) calcined at 950°C for 3h.

For larger the concentration of Bi\(^{3+}\) ions, shorter the distance between Bi\(^{3+}\) ions, farther the distraction of energy transfer along the Bi\(^{3+}\) ions will be resulting in greater probability of transferring energy from Bi\(^{3+}\) ions to
the quenching centres [251]. Bi\(^{3+}\) ions aggregates may be formed that acts as the trapping centre and dissipate the absorbed energy nonradiatively rather than it being transferred to the Eu\(^{3+}\) activator ions [252].

### 6.4 Conclusions

In order to study the transfer of energy from Bi\(^{3+}\) to Eu\(^{3+}\) ions, the Bi\(^{3+}\) (1- 5 mol %) co-doped CaSiO\(_3\):Eu\(^{3+}\) (4 mol %) nanophosphors with monoclinic and space group P\(_{21}/a\) were successfully synthesized by solution combustion method. The particle size from Scherer’s and W-H method was estimated and found to be in the range [30-42] nm. As the Bi\(^{3+}\) concentration increases, the shift in excitation band to the longer wavelength side was observed. There is a efficient energy transformation from Bi\(^{3+}\) to Eu\(^{3+}\) ions due to the spectral overlap between emission bands of Bi\(^{3+}\) ions and excitation band of Eu\(^{3+}\) ions. The energy transfer probability is strongly dependent upon the Bi\(^{3+}\) doping concentration. It was found that the optimum doping concentration is 3 mol % of Bi\(^{3+}\) from fluorescence measurements. For higher concentrations of Bi\(^{3+}\) (> 4mol %) the absorbed energy was non-radiatively dissipated due to the formation of Bi\(^{3+}\) aggregates, which reduced the effectiveness of Bi\(^{3+}\) ions on sensitizing Eu\(^{3+}\) ions. The results of fluorescence intensity from Eu\(^{3+}\) and from Bi\(^{3+}\) due to the transfer of energy) makes CaSiO\(_3\):Eu\(^{3+}\), Bi\(^{3+}\) nanophosphor is an attractive candidate for solid-state lighting.