CHAPTER 5

STRUCTURAL, OPTICAL AND PHOTOLUMINESCENCE PROPERTIES OF Eu$^{3+}$ DOPED K$_3$La(PO$_4$)$_2$ AND K$_3$Gd(PO$_4$)$_2$ NANOPHOSPHORS

5.1. INTRODUCTION

Intended for various applications, a lot of research has been carried out on rare-earth (RE) doped different inorganic/organic phosphors. Eu$^{3+}$ ion is an interesting activator among the rare earth and transition metal ions, because of their unique optical properties, such as, a narrow band light emission, long lifetime and higher luminescence efficiency, etc., in contrast to other dopant materials (Zhang et al., 2002; Park et al., 2003; Wu et al., 2003; Liu et al., 2004; Shinde et al., 2009). Accordingly, Eu$^{3+}$/Eu$^{2+}$ doped phosphors have been studied widely for their potential applications in light emitting devices, displays, solid state lasers, optical amplifiers, sensors and optoelectronics devices etc. (Simon et al., 2007; Sivakumar and Jeon, 2009; Hao et al., 2003; Schweizer et al., 2003; Tsuboi, 2004; Deshmukh et al., 2009; Pal et al., 2014).

Owing to a strong luminescence center, the Eu$^{3+}$ ion reveals a clear red fluorescence due to its $^5D_0 \rightarrow ^7F_J$ ($J = 1, 2, 3, 4$) transitions and gives good contribution to raise the color rendering index in W-LEDs (Wang et al., 2006). Rare earth elements have unique 4f electronic configurations, which are not influenced by the 5s and 5p electrons. The luminescent properties are due to the transitions of 4f electrons between different energy levels. Rare earths doped luminescent materials produce different colors because of the large number of 4f energy levels of rare-earth ions and they are usually used in color television sets and picture tubes (Zhou et al., 2007; Wang et al., 2005). A number of studies have been carried out particularly on rare earth doped phosphors for white LEDs (Wang et al., 2007; Ye et al., 2010).

The rare earth doped phosphate is an important family of luminescent materials for solid state lighting applications as they possess excellent properties, such as large band gap, moderate phonon energy, high thermal and chemical stability, exceptional optical damage threshold, and high absorption of PO$_4^{3-}$ in the VUV region (Lammers et
al., 1987; Poort et al., 1997; Silva et al., 2006). Among the phosphate family, orthophosphates are the promising host materials because of their easy synthesis, low-cost and can accommodate large amount of dopants due to its large band gap. Reports on potassium K\textsubscript{3}RE(PO\textsubscript{4})\textsubscript{2} orthophosphates demonstrates that approximately all rare earth ions crystallizes in the monoclinic phase of the P\textsubscript{2}1\textsubscript{m} and P\textsubscript{2}1\textsubscript{n} symmetry (Jungowska and Znamierowska, 1991). Currently, there are several techniques used to synthesize these materials, such as colloidal (Buissette et al., 2004; Riwotzki et al., 2000), sonochemical (Brown et al., 2005), spray pyrolysis (Lenggoro et al., 2001), and high temperature solid-state reactions (Tuan et al., 2005; Serra and Campos, 1991).

This chapter presents the structural, optical and photoluminescence (PL) properties of the Eu\textsuperscript{3+} activated K\textsubscript{3}La(PO\textsubscript{4})\textsubscript{2} (Gupta et al., 2014) nanophosphors which are synthesized by the combustion technique for their possible application in near-UV light emitting diodes. In addition, also the structural, optical and PL properties of Eu\textsuperscript{3+} doped K\textsubscript{3}Gd(PO\textsubscript{4})\textsubscript{2} are included.

5.2. EXPERIMENTAL DETAILS

Potassium nitrate (KNO\textsubscript{3}·4H\textsubscript{2}O/KNO\textsubscript{3}), lanthanum (III) nitrate hexahydrate (La(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O), gadolinium oxide (Gd\textsubscript{2}O\textsubscript{3}), ammonium dihydrogen tetraoxophosphate (V) (NH\textsubscript{4}H\textsubscript{2}(PO\textsubscript{4}), urea (NH\textsubscript{2}CONH\textsubscript{2}) and europium nitrate (Eu(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O) are used as the starting materials for the synthesis of Eu\textsuperscript{3+} doped K\textsubscript{3}La(PO\textsubscript{4})\textsubscript{2} and K\textsubscript{3}Gd(PO\textsubscript{4})\textsubscript{2} phosphors.

5.2.1. SYNTHESIS OF NANOPHOSPHORS

Using urea as a fuel the phosphors K\textsubscript{3}La(PO\textsubscript{4})\textsubscript{2}: Eu\textsuperscript{3+} (2 mol\%) and K\textsubscript{3}Gd(PO\textsubscript{4})\textsubscript{2}: Eu\textsuperscript{3+} (2 mol\%) are synthesized by combustion method. All the chemicals used in the preparation are of analytical grade and used without further purification. The reagents are weighed according to the balanced chemical reaction (equation 5.1 & 5.2) given below:

\[ 3KNO_3 \cdot 4H_2O + (1 - x)La(NO_3)_3 \cdot 6H_2O + 2NH_4H_2PO_4 + 4NH_2CONH_2 \]
\[ + xEu(NO_3)_3 \cdot 6H_2O = K_3La_{1-x}Eu_x(PO_4)_2 + \text{gaseous products} \]

\[ 5.1 \]

\[ 3KNO_3 + 0.5(1 - x)Gd_2O_3 + 2NH_4H_2PO_4 + 1.5NH_2CONH_2 + xEu(NO_3)_3 \cdot 6H_2O \]
\[ = K_3Gd_{1-x}Eu_x(PO_4)_2 + \text{gaseous products} \]

\[ 5.2 \]
The ratio of the metal nitrates (oxidizers) and urea (fuel) is calculated using the total oxidizing and reducing valences of the components to get an equivalent ratio of unity to enable complete combustion. The ratio of an oxidizer and fuel is expressed as follows:

$$\phi_c = \frac{\sum \text{coefficient of oxidizing element} \times \text{Valency}}{-1 \sum \text{coefficient of reducing element} \times \text{Valency}}$$  \hfill (5.3)

In the reaction (5.1), KNO$_3$, 4H$_2$O (-5) and La(NO$_3$)$_3$6H$_2$O (-15) are oxidizing elements, whereas NH$_4$H$_2$PO$_4$ (+3) and NH$_2$CONH$_2$ (+6) are reducing elements and in reaction (5.2), KNO$_3$(-5) and Gd$_2$O$_3$ (0) are oxidizing elements, whereas NH$_4$H$_2$PO$_4$ (+3) and NH$_2$CONH$_2$ (+6) are reducing elements. By using the oxidizing and reducing values in (5.3), we have

$$\phi_c = \frac{3 \times (-5) + 1 \times (-15)}{(-1)[2 \times (+3) + 4 \times (+6)]} = 1$$  \hfill (5.4)

&

$$\phi_c = \frac{3 \times (-5) + 0.5 \times (0)}{(-1)[2 \times (+3) + 1.5 \times (+6)]} = 1$$  \hfill (5.5)

The weighed reactants are dissolved in few drops of distilled water and thoroughly mixed in agate mortar to obtain thick paste. The paste is transferred to alumina crucible and placed in a furnace, preheated to a temperature of 550°C. The paste underwent volumetric combustion with the evolution of large amounts of gasses. The reaction took 3–5 minutes to be completed. The final white foamy product is cooled to room temperature and ground to obtain a fine powder. The final powders are annealed at 800°C for 2 hours to improve the crystallinity and also to remove reactants which could not be decomposed at lower temperature.

### 5.2.2. CHARACTERIZATION

The structure of the product is examined by using a Bruker Advance D8 X-ray diffractometer with CuKα irradiation ($\lambda = 1.5406$ Å). Transmission electron microscopy (TEM) is used to examine the particle size and morphology of the Eu$^{3+}$ doped K$_3$La(PO$_4$)$_2$ phosphor. The TEM images are taken with a JEM-2100 at an accelerating voltage of 200 kV. The diffuse reflectance (DR) spectra are recorded using a Shimadzu UV-VIS-2600 double beam spectrophotometer coupled with an ISR (integrating sphere.
assembly) in the wavelength range 190-1400 nm. The emission and excitation spectra (PL) of the phosphors are recorded by using a Cary-Eclipse Spectrofluorometer equipped with a 150W Xenon lamp as an excitation source with slit width 5 nm. The entire measurements are done at room temperature.

5.3. RESULTS AND DISCUSSIONS

5.3.1. STUDIES ON Eu$^{3+}$ DOPED K$_3$La(PO$_4$)$_2$

5.3.1.1. STRUCTURAL STUDIES

The formation of the sample is confirmed from the XRD pattern. Figure 5.1 shows the X-ray diffraction (XRD) pattern of the annealed K$_3$La(PO$_4$)$_2$:Eu$^{3+}$ nanophosphor. The characteristic reflections confirm the monoclinic phase of the K$_3$La(PO$_4$)$_2$ orthophosphates. The crystal structure of the host matrix is not affected by the addition of small amount of the Eu$^{3+}$ dopant ions. Since the ionic radii of Eu$^{3+}$ (0.947 Å) and La$^{3+}$ (1.03 Å) are approximately the same, the Eu$^{3+}$ ions can therefore easily incorporate in La$^{3+}$ sites in host lattice. The XRD pattern is compared with those of the standard JCPDS data (47-0468) and the peaks are indexed accordingly. The diffraction peaks at 23.7°, 28.5°, and 25.5° (in terms of 2θ) indicate that some impurity phases are present in the host. The average crystallite size calculated by the Debye-Scherrer equation (Cullity, 1956) is found to be 30nm.

Figure 5.2 displays the TEM image of the K$_3$La(PO$_4$)$_2$:Eu$^{3+}$ nanophosphors. From figure 5.2, the average particle size is estimated in the range of ∼28 ± 2 nm and this result is inconsistent with the XRD data. It is generally known that the morphological characteristics of the combustion derived products are strongly dependent on heat; and gas generated during the reaction. Large amounts of gases generated during the combustion process are suitable for the preparation of fine particles, while the heat released is an important factor for crystal growth. This type of porous network is typically the characteristic of combustion synthesized powders.
The porous powders are highly friable which facilitates easy grinding to obtain finer particles. The evolution of gas with high pressure leads to the formation of pores along with the simultaneous growth of small particles near the pores (Serra and Campos, 1991).
5.3.1.2. SPECTRAL STUDIES

The diffuse reflectance spectrum of K$_3$La(PO$_4$)$_2$:Eu$^{3+}$(2 mol%) is shown in figure 5.3. The sharp absorption band from 200 nm to 300 nm peaking at 240 nm can be assigned to charge transfer (CT) from the Oxygen (O$^{2-}$) to the Europium (Eu$^{3+}$) ions. The multiple peaks from 310 nm to 410 nm correspond to the 4f-4f shell transitions of the Eu$^{3+}$ ion, which is consistent with the excitation spectrum.

Using Kubelka Munk theory as described in chapter 2, the band gap of the Eu$^{3+}$ doped K$_3$La(PO$_4$)$_2$ phosphor is approximated from the diffuse reflectance spectra, and is depicted in the inset of figure 5.3. The band gap of Eu$^{3+}$ doped K$_3$La(PO$_4$)$_2$ phosphor is found to be 4.25 eV.

![Diffuse reflectance spectrum of K$_3$La(PO$_4$)$_2$:Eu$^{3+}$ phosphor.](image)

The photoluminescence excitation spectrum (recorded at 617 nm emission) of the K$_3$La(PO$_4$)$_2$:Eu$^{3+}$ phosphor is shown in Figure 5.4. The spectrum has a broad band from 200 nm to 310 nm with a set of sharp lines protruding from the band. The broad band is ascribed to charge transfer (CT) from O$^{2-} \rightarrow$ Eu$^{3+}$, while the sharp lines at wavelengths of 318, 360, 382, and 392 nm are assigned to ($^7$F$_0 \rightarrow^5$H$_3$, $^5$D$_4$, $^5$G$_j$, $^5$L$_7$, $^5$L$_6$) intraconfigurational 4f-4f transitions of Eu$^{3+}$ ion.
The PL emission spectra at different excitation wavelengths are presented in figure 5.5 and it is clear that the peak positions and shapes of the spectra did not change for all the excitation wavelengths. The emission spectrum consists of four typical emission peaks at
591, 617, 653, and 703 nm, which results from the intra configurational 4f-4f characteristic transitions \( ^5D_0 \rightarrow ^7F_{j,i} \) of the \( \text{Eu}^{3+} \) ion, respectively. The emission line at 591nm is due to magnetic dipole transition \( ^5D_0 \rightarrow ^7F_1 \) which is insensitive to the site symmetry, whereas the emission at 617 nm is due to the electric dipole transition of \( ^5D_0 \rightarrow ^7F_2 \) and it is induced by the lack of inversion symmetry at the \( \text{Eu}^{3+} \) site. Generally, the forced electric dipole transitions arise from the lack of a centre of symmetry and it is much stronger than that of the \( ^5D_0 \rightarrow ^7F_1 \) transition. Also, the \( ^5D_0 \rightarrow ^7F_2 \) transition is dependent upon the local symmetry, while the \( ^5D_0 \rightarrow ^7F_1 \) emission is related to the local symmetry due to insensitivity to the site symmetry. Therefore, in the present case, the \( \text{Eu}^{3+} \) ion occupies a symmetric and a nonsymmetric site almost equally, as both the peak intensities of the \( \text{Eu}^{3+} \) ion due to \( ^5D_0 \rightarrow ^7F_2 \) and \( ^5D_0 \rightarrow ^7F_1 \) transitions are the same (Zhou et al., 2009; Lu and Zhang, 2007).

5.3.1.3. CIE PARAMETERS

The CIE 1931 color space chromaticity coordinates are calculated and are presented in the CIE diagram in Figure 5.6. The diagram is constructed using the Commission International de L’Eclairage (CIE) coordinate calculator. The calculated CIE coordinates of our materials are (0.63, 0.37) which correspond to the shade of orange-red emission of the \( \text{Eu}^{3+} \) ion. Bright orange-red light emitting diodes may be fabricated by the combination of the synthesized \( \text{K}_3\text{La(PO}_4)_2:\text{Eu}^{3+} \) with 392 nm emitting InGaN based chips.

![CIE diagram](image)

Figure 5.6: The 1931 CIE chromaticity diagram of \( \text{Eu}^{3+} \) doped \( \text{K}_3\text{La(PO}_4)_2 \) (2mol\%) phosphors synthesized by combustion method under excitation 392 nm.
5.3.2. STUDIES ON Eu\(^{3+}\) DOPED K\(_3\)Gd(PO\(_4\))\(_2\)

5.3.2.1. STRUCTURAL STUDIES

The phase formation of Eu\(^{3+}\) doped K\(_3\)Gd(PO\(_4\))\(_2\) is determined by XRD pattern. Figure 5.7 displays the X-ray diffraction (XRD) pattern of the Eu\(^{3+}\) doped K\(_3\)Gd(PO\(_4\))\(_2\) nanophosphor. It can be clearly seen that all of the diffraction peaks are in good agreement with that of the JCPDS cards, which indicates that the samples are single phase. The crystal structure of the host matrix is not affected by the addition of small amounts of Eu\(^{3+}\) dopant ions. Since, the ionic radii of Eu\(^{3+}\) (0.947 Å) and Gd\(^{3+}\) (0.935 Å) are approximately the same, the Eu\(^{3+}\) ions can therefore easily incorporate in La\(^{3+}\) sites in host lattice. The XRD pattern is compared with those of the standard JCPDS data (47-0468) and the peaks are indexed accordingly. The diffraction peaks at 23.7°, 28.5°, and 25.5° (in terms of 2\(\theta\)) indicate that some impurity phases are present in the host. The average crystallite size calculated by the Debye-Scherrer equation (Cullity, 1956) is found to be 30nm.

![XRD patterns](image)

Figure 5.7: XRD patterns of (a) standard data of JCPDS Card No. 049-1085 and (b) Eu\(^{3+}\) doped K\(_3\)Gd(PO\(_4\))\(_2\) phosphor synthesized by combustion method.
5.3.2.2. OPTICAL STUDY

The diffuse reflectance spectrum of Eu$^{3+}$ doped K$_3$Gd(PO$_4$)$_2$ (2 mol%) nanophosphor is recorded from 190-1400 nm. Figure 5.8 shows the diffuse reflectance and absorption spectra of the Eu$^{3+}$ doped K$_3$Gd(PO$_4$)$_2$ (2 mol%). The peak in Figure 5.8 at 274 nm appears because of the Gd$^{3+}$ ion is present in the host material. The sharp band at 200 to 268 nm corresponds to the charge transfer from O$^{2-}$ to Eu$^{3+}$ ion. The band gap of K$_3$Gd(PO$_4$)$_2$:Eu$^{3+}$ (2 mol%) is calculated by using Kubelka Munk theory as described in chapter 2. The band gap of Eu$^{3+}$ doped K$_3$GdPO$_4$$_2$ phosphor is shown in Figure 5.9 and found to be 5.06 eV.

![Figure 5.8: The diffuse reflectance and absorption spectra of Eu$^{3+}$ doped K$_3$Gd(PO$_4$)$_2$ (2 mol%) nanophosphors.](image)

![Figure 5.9: Plot of F(R) versus $h\nu$ of Eu$^+$ doped K$_3$Gd(PO$_4$)$_2$ nanophosphor.](image)
5.3.2.3. PL STUDY

Figure 5.10 shows the photoluminescence excitation(a) and photoluminescence emission(b) spectra of Eu$^{3+}$ doped K$_3$Gd(PO$_4$)$_2$ (2 mol%). As the Eu$^{3+}$ emission (614 nm) is monitored, the excitation spectrum (figure 5.10(a)) is obtained in the spectral region 200-420 nm. The excitation spectrum exhibits an intense band and various 4f-4f transitions. The excitation spectrum presents the features due to both Gd$^{3+}$ and Eu$^{3+}$ ions. The broad band from 200 nm-268 nm is assigned to the charge transfer from O$^{2-}$ to Eu$^{3+}$. The peaks at 274 nm and 310 nm arise due to the presence of Gd$^{3+}$ ion in the host material. In this spectrum, other peaks due to the 4f-4f transitions of Eu$^{3+}$ are observed at $^{7}F_0 \rightarrow ^{6}H_3(318)$, $^{7}F_0 \rightarrow ^{5}D_4(360)$, $^{7}F_0 \rightarrow ^{5}L_7(381)$, $^{7}F_0 \rightarrow ^{5}L_6(392)$, $^{7}F_0 \rightarrow ^{5}D_3(414)$. Among all the peaks, most intense peak is found at 392 nm.

![Excitation and Emission Spectra](image)

Figure 5.10: (a) The excitation spectrum under 614 nm emission wavelength and (b) the emission spectrum under 392 nm excitation wavelength of the Eu$^{3+}$ doped K$_3$Gd(PO$_4$)$_2$ nanophosphor.

To attain the emission spectrum, the light corresponding to 392 nm is used as the exciting source. The emission spectrum is shown in figure 5.10(b) which exhibits four characteristic emission bands at 592, 614, 653 and 702 nm is corresponding to allowed
transition $^5D_0 \rightarrow ^7F_1$, $^7F_2$, $^7F_3$ and $^7F_4$ of Eu$^{3+}$ ion, respectively. The prominent emission band at 614 nm corresponds to electric-dipole allowed $^5D_0 \rightarrow ^7F_2$ hypersensitive allowed transition that followed $\Delta J = 2$ selection rule (Raju and Reddy, 2012; Karunakaran et al., 2009) where as the emission band at 592 nm is due to the magnetic-dipole transition $^5D_0 \rightarrow ^7F_1$. The intensity of electric-dipole allowed $^5D_0 \rightarrow ^7F_2$ transition is enormously sensitive to the coordination environment of Eu$^{3+}$ ions, although the intensity of magnetic-dipole allowed transition is slightly differs with the environment of the Eu$^{3+}$ ions. For that reason the intensity ratio (R) of ($^5D_0 \rightarrow ^7F_2$)/($^5D_0 \rightarrow ^7F_1$) transitions, usually known as asymmetric ratio is applied as a condition for the site symmetries of Eu$^{3+}$ ions.

Figure 5.11: Decay curve of K$_3$Gd(PO$_4$)$_2$:Eu$^{3+}$ (2mol%) nanophosphor by monitoring the excitation wavelength at 392 nm and emission wavelength at 614 nm.

The PL decay curve of Eu$^{3+}$ doped K$_3$Gd(PO$_4$)$_2$ (2 mol%) phosphor is recorded by monitoring the excitation wavelength 392 nm and emission wavelength 614 nm as shown in Figure 5.11. In figure 5.11, the decay time is determined by fitting the profile with double exponential function ($y = y_0 + A_1 e^{-(x-x_0)/t_1} + A_2 e^{-(x-x_0)/t_2}$) in the Origin.
Program. The lifetime is obtained at the same time and the fitted curve is displayed in figure 5.11. The average luminescent lifetime is calculated using the following equation (5.6) (Blasse, 1969).

\[
\langle \tau_{av} \rangle = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}
\]

(5.6)

where \( \langle \tau_{av} \rangle \) is the average lifetime, \( \tau_1 \) (2.44 ms) and \( \tau_2 \) (4.00 ms) are the lifetimes, and \( A_1 \) (28.8) and \( A_2 \) (90.93) are the constants. The average lifetime of \( \text{Eu}^{3+} \) doped \( \text{K}_3\text{Gd(PO}_4\text{)}_2 \) (2 mol%) is 3.74 ms.

5.3.2.4. CIE PARAMETERS

Figure 5.12 presented the Commission Internationale de l’Eclairage (CIE) chromaticity coordinates of \( \text{Eu}^{3+} \) doped \( \text{K}_3\text{Gd(PO}_4\text{)}_2 \) (2 mol%) phosphor synthesized by combustion method. The chromaticity coordinates of \( \text{Eu}^{3+} \) doped \( \text{K}_3\text{Gd(PO}_4\text{)}_2 \) phosphor is calculated using the CIE calculator software under 392 nm excitation. The CIE coordinates of \( \text{K}_3\text{Gd(PO}_4\text{)}_2\text{:Eu}^{3+} \) are measured as x=0.64, y=0.35. From the CIE diagram, it is found that the coordinates calculated for \( \text{K}_3\text{Gd(PO}_4\text{)}_2\text{:Eu}^{3+} \) (0.64, 0.35) are similar to the commercially available \( \text{Y}_2\text{O}_2\text{S:Eu}^{3+} \) (0.622, 0.351). Therefore, the material may be a good candidate for the production of the red component in the UV chip based WLEDs.

Figure 5.12: The CIE 1931 chromaticity diagram for \( \text{K}_3\text{Gd(PO}_4\text{)}_2\text{:Eu}^{3+}(2 \text{ mol%}) \) nanophosphor under 392 nm excitation.
5.4. CONCLUSIONS

In summary, \( \text{Eu}^{3+} \) doped \( \text{K}_3\text{La(PO}_4\text{)}_2 \) and \( \text{K}_3\text{Gd(PO}_4\text{)}_2 \) nanophosphors are synthesized by the combustion method. Their structural, optical and photoluminescence properties have been discussed. The band gaps of the \( \text{Eu}^{3+} \) doped \( \text{K}_3\text{La(PO}_4\text{)}_2 \) and \( \text{K}_3\text{Gd(PO}_4\text{)}_2 \) is approximated to 4.25 eV and 5.06 eV. The phosphors are excited with UV light and with this excitation, the \( \text{Eu}^{3+} \) doped \( \text{K}_3\text{La(PO}_4\text{)}_2 \) and \( \text{K}_3\text{Gd(PO}_4\text{)}_2 \) materials showed an orange-red emission. Hence, these materials used as a potential candidate for the near-UV light emitting diode applications. The CIE chromaticity coordinates of the \( \text{Eu}^{3+} \) doped \( \text{K}_3\text{La(PO}_4\text{)}_2 \) and \( \text{K}_3\text{Gd(PO}_4\text{)}_2 \) phosphors are calculated to be \((x = 0.63, y = 0.37)\) and \((0.64, 0.35)\) which corresponds to the orange-red shade.

REFERENCES


Buissette, V., Moreau, M., Gacoin, T., Boilot, J.-P., Chane-Ching, J.-Y., Mercier, T. L. (2004). Colloidal synthesis of luminescent rhabdophane \( \text{LaPO}_4\cdot\text{Ln}^{3+}\cdot\text{xH}_2\text{O} \) (\( \text{Ln} = \text{Ce}, \text{Tb}, \text{Eu}; \text{x} \approx 0.7 \)) nanocrystals. Chemistry of Materials, 16(19), pp. 3767–3773.


Hao, J., Gao, J., Cocivera, M. (2003). Green, blue, and yellow cathodoluminescence of \( \text{Ba}_2\text{B}_3\text{O}_6\text{Cl}\text{Ba}_2\text{B}_3\text{O}_6\text{Cl} \) thin-films doped with \( \text{Tb}^{3+}, \text{Tm}^{2+} \) and \( \text{Mn}^{2+} \). Appl. Phys. Lett. 82(14), pp. 2224-2226.


