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Photoluminescence of Eu^{2+} -doped strontium cyanamide: A novel host lattice for Eu^{2+}

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Abstract

Eu^{2+} -doped SrCN_2 with different Eu^{2+} contents were prepared by a high-temperature solid-state reaction under NH_3 atmosphere. SrCN_2 has an energy gap of 4.56 eV by the reflection spectra. The photoluminescence spectra of $\text{SrCN}_2:\text{Eu}^{2+}$ at different temperatures were measured. The results show that Eu^{2+} -doped SrCN_2 shows a broad band emission with a peak at 610 nm when it is excited by 350–520 nm at 77 K. With the temperature increasing, the emission intensity decreases remarkably, indicating that Eu^{2+} -doped SrCN_2 has a low quenching temperature.

I. Introduction

The emission and absorption spectra of Eu^{2+} usually consist of broad bands due to electronic transitions between the $^8\text{S}_{7/2}$ ($4f^7$) ground state and the crystal field components of the $4f^65d$ excited state configuration. Because the involved $5d$ orbitals are external, the position of these

energy levels and consequently the wavelengths of excitation and emission bands strongly depend on the host matrix [1]. With the increasing covalency between Eu^{2+} and ligands, the emission of Eu^{2+} shifts to longer wavelength [2]. For example, the Eu^{2+} emits from near violet to blue in halide hosts due to highly electronegative halogen ions, but at longer wavelengths in nitrides due to lower electronegative N^{3-} [2].

SrCN_2 belongs to the hexagonal *Pnma* space group (no. 62) with $a = 512.41 \text{ \AA}$, $b = 53.96 \text{ \AA}$, and $c = 55.39 \text{ \AA}$. In the SrCN_2 host crystal, $[\text{CN}_2]^{2-}$ anions in two orientations built up layers parallel to the a - c plane of the unit cell. The Sr^{2+} ions also belong to these layers, forming distorted octahedra around the anions. Distorted nitrogen octahedra centered by Sr^{2+} ions are connected via sharing corners and by NCN bridges [3].

As Sr^{2+} ions connect to N^{3-} , it is reasonable to expect that SrCN_2 would be used as host lattice for divalent lanthanides. However, reported work in this respect is rare. In the present work, Eu^{2+} -doped SrCN_2 were prepared and its optical properties were investigated in detail.

II. Experiments Procedures

Powder samples with general formula $\text{Sr}_{(1-x)}\text{CN}_2:\text{Eu}_x$ ($x = 0.01, 0.02, 0.03, 0.04,$ and 0.06) were prepared by using SrCO_3 , Eu_2O_3 , and active carbon (CARBIO 12 SA—ref: C1220 G 90) as raw materials following a process inspired from the literature [4]. The mixture of europium oxide and the strontium carbonate was placed at the end of a graphite boat, while the active carbon was put in the upcoming flowing gas at the other end. The mixture was then fired at 1223 K under NH_3 atmosphere for 6 h in a tubular furnace.

The synthesized powder samples were analyzed by X-ray diffraction (XRD) (Philips PW3710, PANalytical B.V., Almelo, the Netherlands) at room temperature using $\text{CuK}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). A step size of 0.02° (2θ) was used with a scan speed of $2^\circ/\text{min}$. The nitrogen and oxygen contents were determined with an LECO TC-600 analyzer (LECO

Corporation, St. Joseph, MI) using the inert gas fusion method. The measurements of photoluminescence (PL) and PL excitation spectra between 77 and 293 K were carried out by a Fluorolog-3 spectrofluorometer (Jobin Yvon Inc./specx, HORIBA Jobin Yvon Inc., Edison, NJ) equipped with a VNF-100 liquid nitrogen cryostat controlled by a cryogenic temperature controller model 32, and the excitation light resource is a 450 W Xe lamp. Diffuse reflectance spectra in the range of 200–700 nm were collected using a Varian Cary 100 UV-Vis spectrophotometer (Varian Inc., Fontaine, Grenoble, France) equipped with an integrating sphere Labsphere (DRC-CA-30) with 70 mm diameter.

III. Results and Discussion

(1) Phase Characterization

The XRD patterns of the series of powder samples $\text{Sr}_{(1-x)}\text{CN}_2:\text{Eu}_x$ ($x = 0.01, 0.02, 0.03, 0.04,$ and 0.06) are displayed in Fig. 1. The results show that all the products are of a single phase of SrCN_2 , in good agreement with the JCPDS 82-0988 file. However, with the increasing Eu^{2+} content, the diffraction peaks shift slightly to a lower d-value. This is most likely due to the partial substitution of Sr^{2+} by Eu^{2+} , which has the lower ionic radius (0.107 nm) than Sr^{2+} (0.112 nm).

(2) The Reflection Spectra

The diffuse reflection spectra of $\text{SrCN}_2:\text{Eu}$ samples are gathered in Fig. 2. Both undoped and Eu^{2+} -doped samples show a remarkable drop in reflection in the UV range around 280 nm, corresponding to the valence-to-conduction band transitions of the SrCN_2 host lattice. The intense reflection in the visible spectral range is in agreement with the observed white daylight color for undoped SrCN_2 . In order to better localize the thresholds for host lattice absorption and the absorption by Eu^{2+} , the absorption spectra $F(R)$ were obtained (inset) from the diffuse reflection spectra by using the Kubelka–Munk function as follows [5]:

$$F(R) = (1-R)^2/2R = K/S \quad (1)$$

where R, K, and S are the reflectivity, the absorption coefficient, and the scattering coefficient, respectively. The value of the optical band gap is calculated to be about 4.56 eV. For the samples of high Eu^{2+} concentration, two broad absorption bands can also be seen in the wavelength ranges of 320–500 and 280–320 nm, respectively. Both of them can be attributed to the $4f-5d$ absorption of Eu^{2+} ions, compared with that of undoped SrCN_2 . As expected, their intensities increase with the increasing Eu^{2+} concentrations. In contrast to the undoped samples with the white daylight color, $\text{Sr}_{1-x}\text{CN}_2:\text{Eu}_x$ shows light yellow to bright yellow colors, varying with the Eu^{2+} concentration ($0 < x \leq 0.06$) due to a strong absorption in the visible range of 380–500 nm.

(3) The PL Characteristics at Low Temperature

The PL spectra of $\text{SrCN}_2:\text{Eu}_{0.02}$ at 77 K are presented in Fig. 3. With different excitation wavelengths at 396 and 491 nm, emission spectra show the similar broad orangish-red emission with a maximum at about 610 nm ($16\,393\text{ cm}^{-1}$) and full-width at half maximum about 82 nm ($\Gamma = 2163\text{ cm}^{-1}$). This broad emission band can be assigned to the $4f^65d^1-4f^7$ transition of Eu^{2+} . We do not observe the characteristic sharp emission peaks due to Eu^{3+} ions, which confirms existence of only Eu^{2+} ions in the present phosphors. Because only an exclusive transition is observed, we can deduce that all Eu^{2+} ions occupy identical sites. This is identical to the expectation because there is only one crystallographically distinct Sr^{2+} ion in SrCN_2 host. The unusual long-wavelength and broad emission bands are due to the effect of the nitrogen-rich surrounding on Eu^{2+} ions in SrCN_2 , which caused the large ligand-field splitting of the $\text{Eu}^{2+} 5d$ levels, and then a larger nephelauxetic effect.

The excitation spectrum at 77 K monitored at an emission wavelength of 610 nm is also shown in Fig. 5. It consists of a broad band with several subbands, which are due to the parity

allowed $4f^7(^8S_{7/2})-4f^65d$ transitions of Eu^{2+} ions. These subbands structures, peaked at 335, 396, 449, 456, and 491 nm, are assigned to the crystal field splitting of the $5d$ level of Eu^{2+} ions. The excited $5d$ levels are not shielded from the ligand field, giving rise to a marked splitting of the excited levels. The symmetry of the anion coordination polyhedron around the emission centers determines the number of the splitting level. Dorenbos [6] has made a clear correlation between the splitting and the coordination polyhedron, revealing that the crystal field splitting tends to be the largest for octahedral coordination followed by cubic, dodecahedral, and it is the smallest for tricapped trigonal prism (3ctp) and cuboctahedron coordination. In the $\text{SrCN}_2:\text{Eu}^{2+}$ crystal, Sr^{2+} ions coordinating with six N^{3-} with different bond lengths form an asymmetric structure. Because the doped Eu^{2+} ions occupy asymmetric Sr^{2+} sites and are exposed to a strong ligand field due to the presence of highly covalent bonding of $\text{Eu}-\text{N}$, a large ligand-field splitting occurs to Eu^{2+} ions, resulting in their excitation band extending into visible region. According to the excitation spectrum, the crystal field splitting is estimated to be about $12\,019\text{ cm}^{-1}$, assuming no $5d$ subbands to be positioned in the conduction band of the host lattice. A rough estimate of the Stokes shift determined by the maxima of the emission and excitation bands is 8859 cm^{-1} , which is fairly large and attributed to the distortion of the excited state of Eu^{2+} due to CN_2^{2-} anion groups surrounding the Eu^{2+} ions emission centers.

The broad excitation band and orangish-red emission mean that the SrCN_2 should be a good host lattice for doping Eu^{2+} , like $(\text{Ca},\text{Sr})\text{S}$ and $\text{Sr}_2\text{Si}_5\text{N}_8$, which have been used as the red components of white light-emitting diodes illumination [7,8]. However, the emission of $\text{SrCN}_2:\text{Eu}^{2+}$ is strongly quenched with increasing temperatures and not observable at room temperature. The emission intensity dependence on the temperature using the excitation wavelength of 396 and 491 nm is depicted in Fig. 4. When it is excited at 396 nm, the temperature at which the intensity is half of that at 77 K is about $T_{1/2} = 90\text{ K}$, and at 227 K the

emission is completely quenched. These temperatures are slightly lower than those excited at 491 nm ($T_{1/2} = 92$ K). Besides, the emission peaks slightly broaden and shift to the longer wavelength with the increasing temperature.

The luminescence behavior of $\text{SrCN}_2:\text{Eu}^{2+}$ is similar to those of $\text{Ba}(\text{SCN})_2:\text{Eu}^{2+}$ and $\text{Sr}(\text{SCN})_2:\text{Eu}^{2+}$. In $\text{Sr}(\text{SCN})_2:\text{Eu}^{2+}$, it can be well explained by photoionization of the excited states in the conduction band of the host lattice [9,10], that is, the lowest $5d$ state is located at the level in the band gap of the host lattice slightly lower than the conduction band. After excitation, conventional $d \rightarrow f$ emission and/or nonradiative relaxation from an excitation state located in the conduction band may occur depending on the thermal population of the excitation state. However, this model seems unable to explain the thermal quenching behavior of $\text{SrCN}_2:\text{Eu}^{2+}$ in the present case. This is because upon 491 nm excitation on $\text{SrCN}_2:\text{Eu}^{2+}$, the excited electrons of Eu^{2+} ions most likely remained in the lower $5d$ levels rather than moved to the higher levels due to large crystal splitting energy ($12\,019\text{ cm}^{-1}$). Besides, the low quenching temperature is not due to a large displacement between the ground and excited state in the configuration coordinate diagram [11]. Therefore, we present a configurational coordinate diagram as shown in Fig. 5 to explain the temperature dependence of luminescence, as well as the red shift and broadening of emission with the increasing temperature occurring to $\text{SrCN}_2:\text{Eu}^{2+}$ phosphors. The lower and higher potential curves represent the total energy of the ground state of $4f^7(^8S_{7/2})$ and the excited state of $4f^65d$, respectively. The equilibrium positions of the two states are different from each other because of the spatial distribution of the electron orbitals. Generally, $A \rightarrow B1, B2$ represents the absorption process and $C1 \rightarrow D1$ the emission [12]. However, with the increasing temperature, the excited electrons would depart to nonequilibrium positions of the excited state (e.g., C2 or O, the crossing point between the excited state and the defect level). As a result, the emission shifts to the longer wavelength and its intensity decreases [13].

In general, the low quenching temperature originates from the crystal defect or the effect of activated ions with the host crystal. The best probability is from the crystal defect. In fact, in as-prepared samples, almost 1% molar oxygen remained as measured by an LECO analyzer, and they were most likely introduced in the preparation process from the raw materials SrCO_3 and Eu_2O_3 . The oxygen could be incorporated on the N site in Eu^{2+} -doped SrCN_2 , forming the defect of $(\text{ON})^\bullet$. To realize the charge compensation of O substitution on N sites, some cation vacancies such as $(V_{\text{Sr}})''$ have to be formed. Upon UV excitation of the host lattice, these defects may serve as carrier traps by capturing electrons or holes. It is reasonable to assume that $(\text{ON})^\bullet$ will capture electrons, while $(V_{\text{Sr}})''$ will capture holes. Hence, when $\text{SrCN}_2:\text{Eu}^{2+}$ is excited by UV light, the excited electrons could be captured by $(\text{ON})^\bullet$, resulting in nonradiative transition. Therefore, it is essential to prepare oxygen-free samples, and thus the synthesis process should be investigated further.

IV. Conclusion

Singe-phase $\text{SrCN}_2:\text{Eu}^{2+}$ powder samples were prepared by a high-temperature solid-state reaction under NH_3 atmosphere. SrCN_2 has an energy gap about 4.56 eV obtained from its reflection spectrum. Eu^{2+} -doped SrCN_2 shows a broad band emission with a peak at 610 nm when it is excited by 350–520 nm at 77 K. With the temperature increasing, the emission intensity decreases remarkably. When it is excited by 396 nm, the temperature at which the intensity is half of that at 77 K is about $T_{1/2} = 90$ K, and at 227 K the emission is completely quenched; these temperatures are slightly lower than those excited by 491 nm ($T_{1/2} = 92$ K). Besides, the emission peaks experience a slight red shift and become broader with the increasing temperature. These phenomena can be explained by the configurational coordinate diagram and could be attributed to the defect levels originated from the oxygen impurity in the host.

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Figures

Figure 1 : The X-ray diffraction spectra of $\text{Sr}_{(1-x)}\text{CN}_2:\text{Eu}_x^{2+}$.

Figure 2 : The diffuse reflection and absorption spectra of $\text{Sr}_{(1-x)}\text{CN}_2:\text{Eu}_x^{2+}$.

Figure 3 : The emission and excitation spectra of $\text{Sr}_{0.98}\text{CN}_2:\text{Eu}_{0.02}$ at 77 K.

Figure 4 : (a) The emission spectra of $\text{Sr}_{0.98}\text{CN}_2:\text{Eu}_{0.02}$ excited by 396 nm at different temperatures. (b) The emission spectra of $\text{Sr}_{0.98}\text{CN}_2:\text{Eu}_{0.02}$ excited by 491 nm at different temperatures.

Figure 5 : Schematic illustration of a configurational coordinate model.

Figure 1

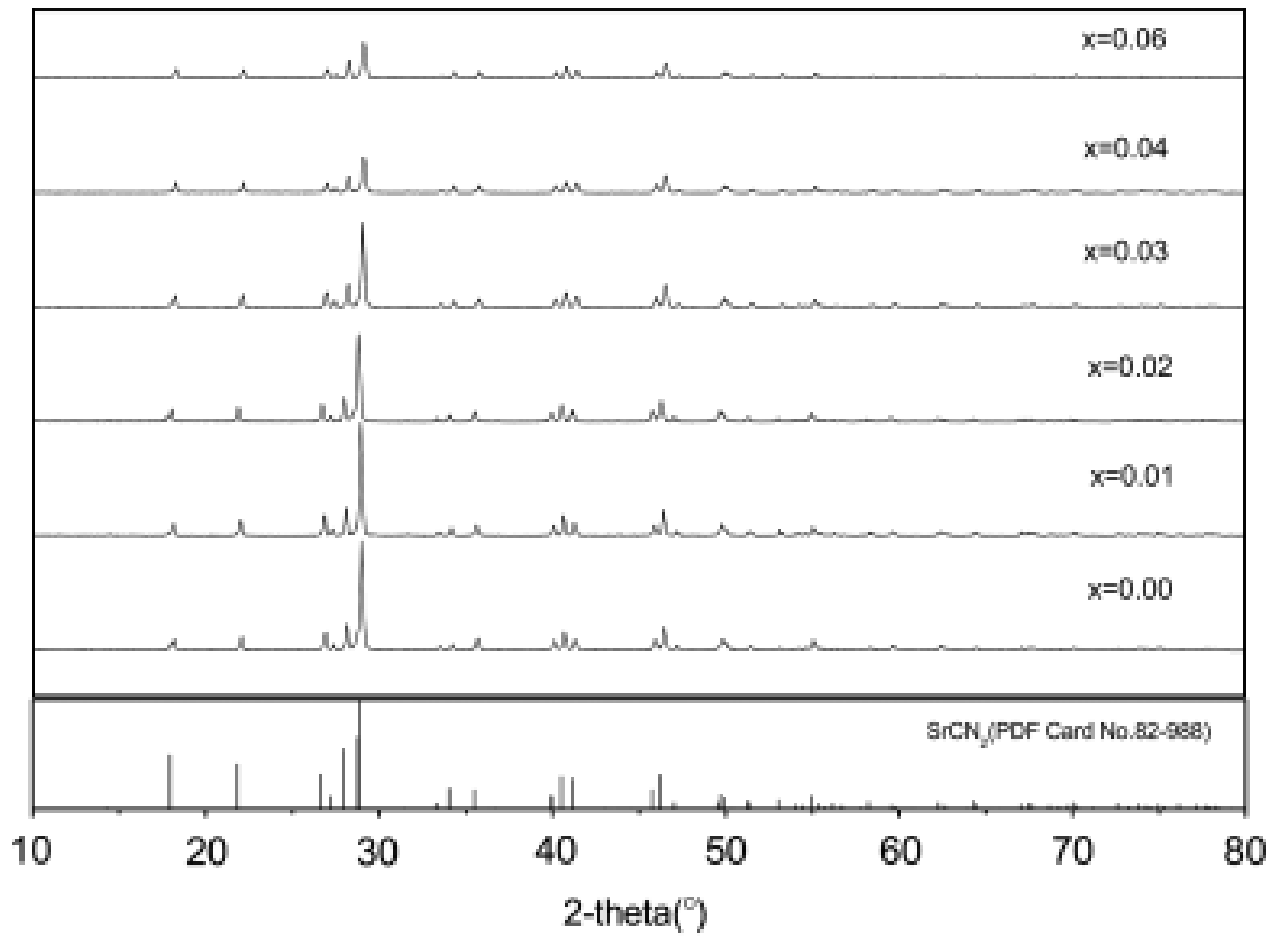


Figure 2

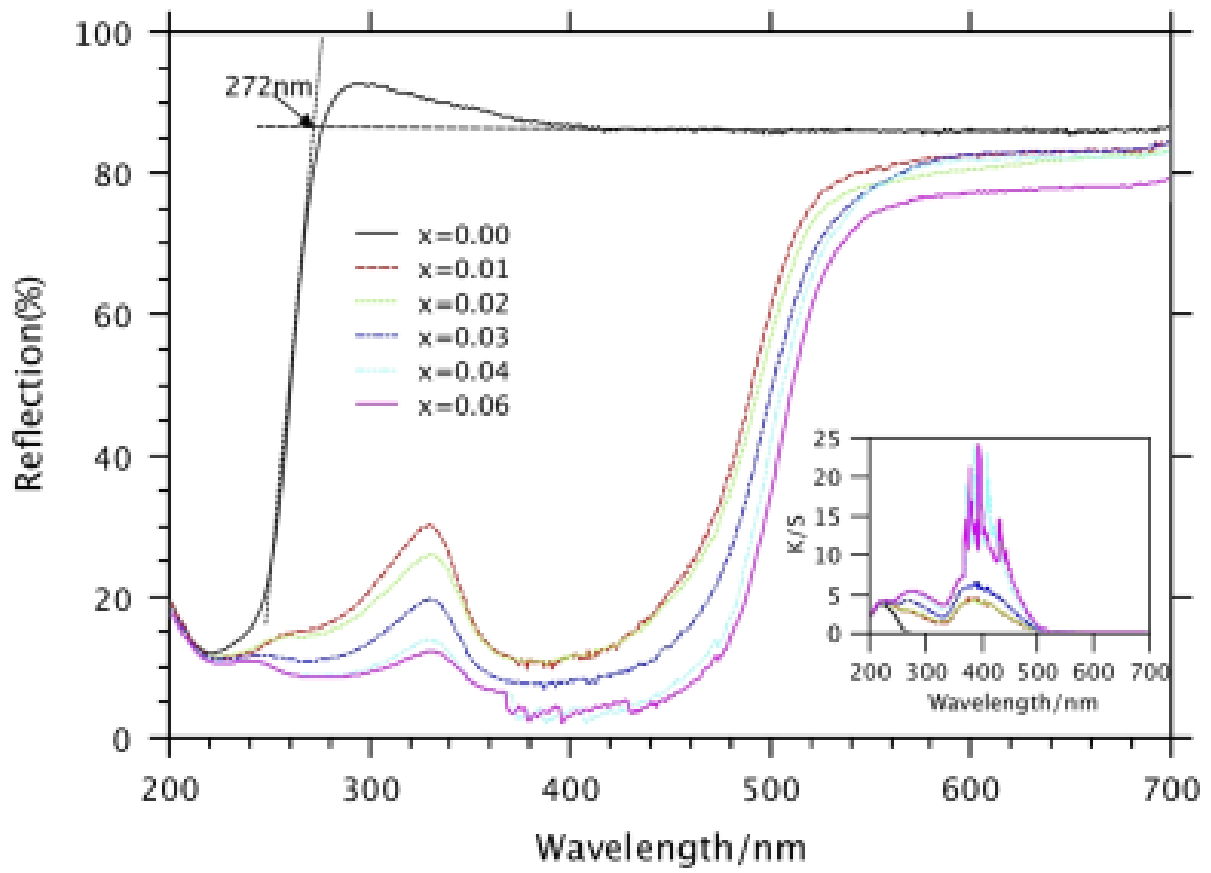


Figure 3

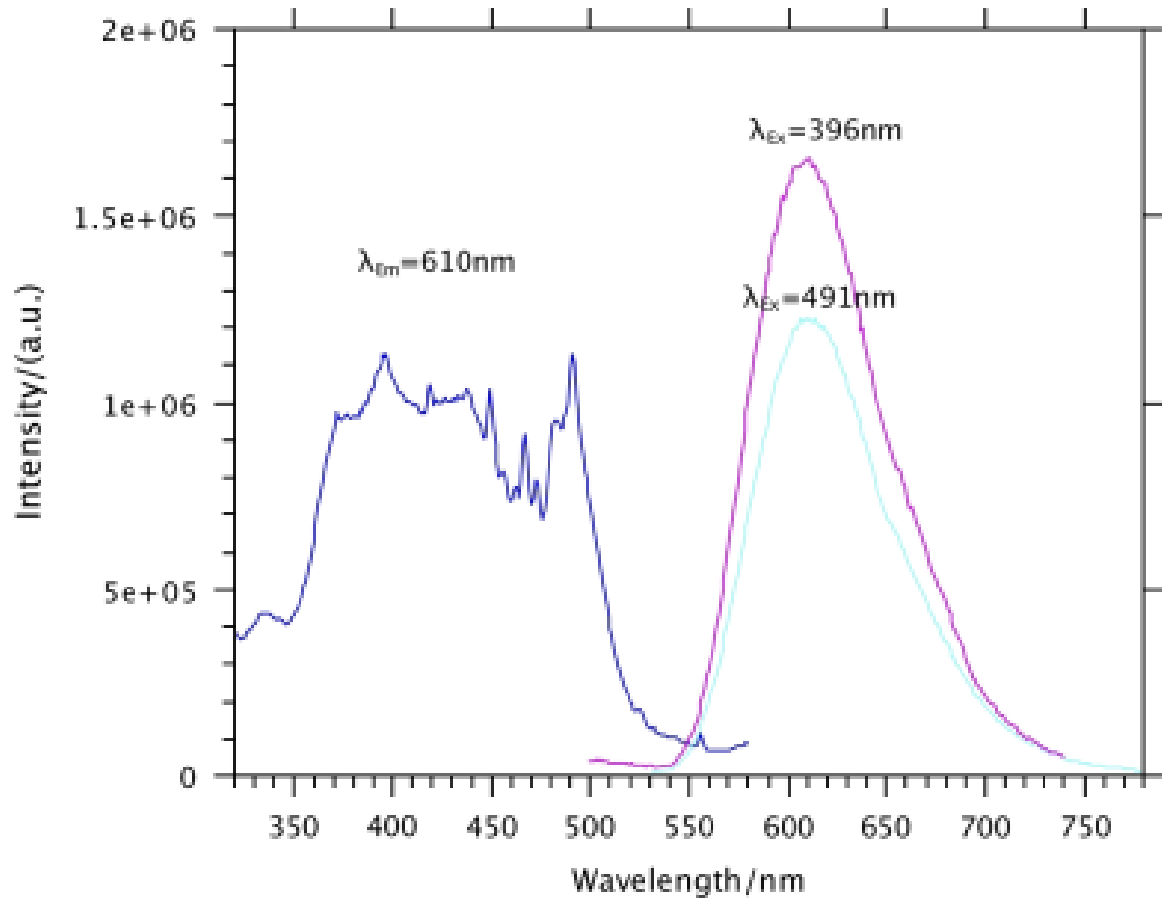


Figure 4

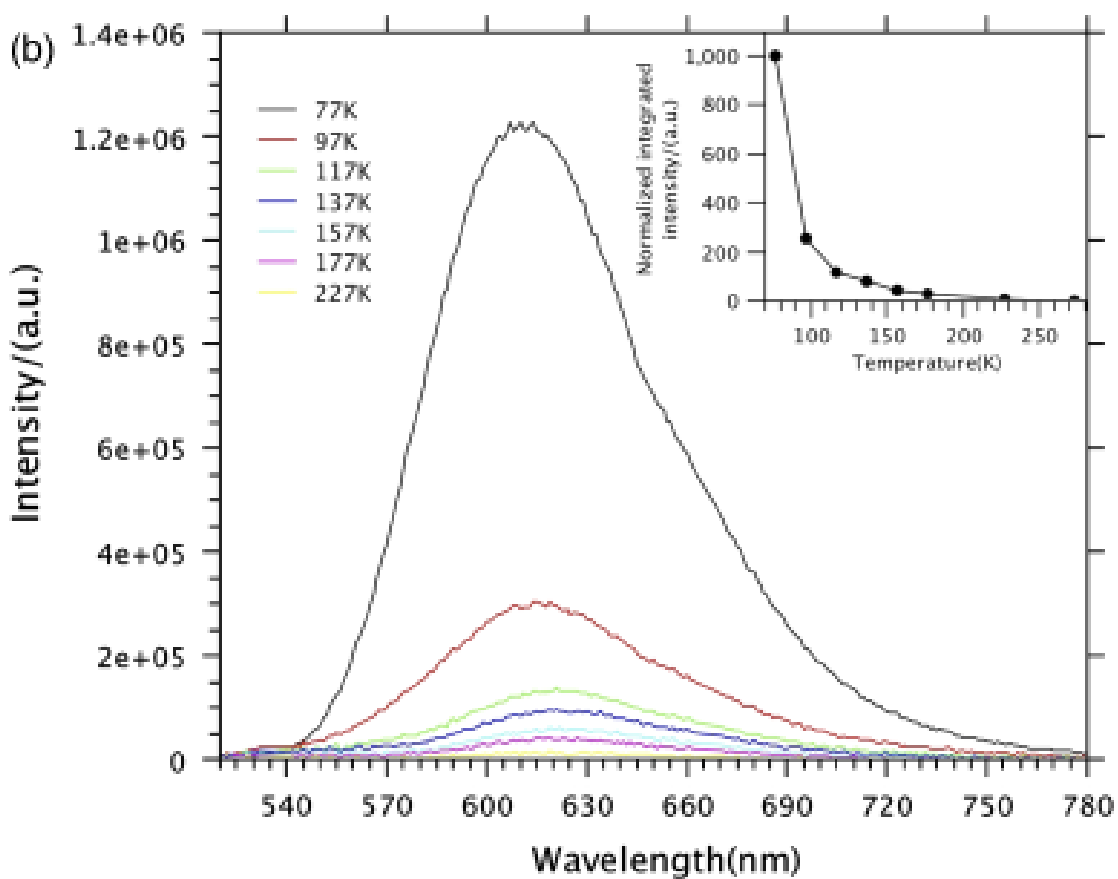
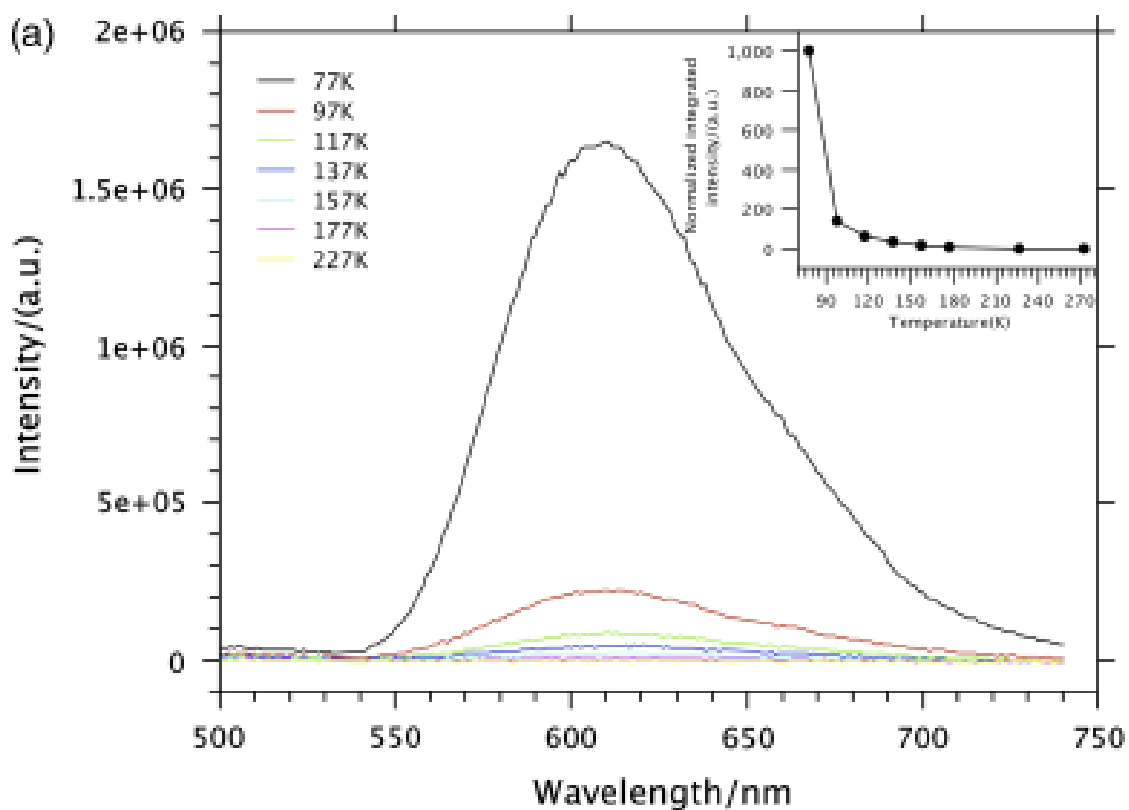


Figure 5

