

Luminescent Properties of $\text{La}_3\text{PO}_7:\text{Eu}^{3+}$ Nanoparticles

Shaozhe Lü* and Jishen Zhang

Key Laboratory of Excited State Physics, Changchun Institute of Optics, Fine Mechanics, and Physics,
Chinese Academy of Sciences, 16 East Nanhu Road, Changchun 130033, P. R. China

$\text{La}_3\text{PO}_7:\text{Eu}^{3+}$ samples were prepared by combustion and annealing and characterized by X-ray diffraction and transmission electron microscopy. It was found that the average size of the particles is about 80 nm. The red emission from the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of the Eu^{3+} ions under ultraviolet light excitation is much stronger than the orange emission from the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition. The emission spectra, charge transfer band, laser selective excitation spectra, and time-resolved spectra indicate that symmetry of the local environment of Eu^{3+} lacks an inversion center and Eu^{3+} ions occupy at least two types of sites in the La_3PO_7 crystal. The superior color chromaticity compared to other phosphates and borates doped with Eu^{3+} means $\text{La}_3\text{PO}_7:\text{Eu}^{3+}$ may have potential as a luminescent material.

Keywords: Phosphate, Rare Earth, Luminescence, Nanostructures, Laser Selective Excitation.

1. INTRODUCTION

Luminescent materials doped with rare earth ions have been used extensively in many fields.^{1,2} For instance, $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ is an ideal red phosphor for lighting and projection TV. The luminescent characteristics of the bulk and nanometer materials doped with Eu^{3+} ions are continuously being investigated.^{3–5} In recent years, the luminescent properties of Eu^{3+} -doped phosphates and borates have been studied. Some, such as $\text{LaPO}_4:\text{Eu}^{3+}$, $\text{YBO}_3:\text{Eu}^{3+}$, $\text{GdBO}_3:\text{Eu}^{3+}$ exhibit high luminescence efficiency, but the ratio of the orange emission from the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition to the red emission from the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu^{3+} (O/R) is higher under ultraviolet (UV)-light excitation; therefore, they cannot meet commercial needs. Because plasma display panels (PDPs), field emission display (FED), and lighting require mostly 610–625 nm red light; work has been done to improve the color chromaticity in this range.^{6,7} In this paper, the $\text{La}_3\text{PO}_7:\text{Eu}^{3+}$ samples prepared by combustion and annealing are different from other phosphate and borate materials that exhibit mostly 593 nm emission under UV light and for which the major emission peak comes from the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu^{3+} at 615 nm. The excitation spectra and laser selective excitation spectra indicate that the Eu^{3+} ions occupy different sites in the La_3PO_7 host.

2. EXPERIMENTAL DETAILS

The samples were synthesized by the following method. An appropriate amount of high purity $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$

and $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in de-ionized water. Then, $(\text{C}_4\text{H}_9\text{O})_3\text{PO}$ and an appropriate amount of surfactant were added to the solution in an ultrasonic process for 3 h. The Eu^{3+} (8% and 16% molar ratio) products were obtained after the solution vaporized slowly by heating, self-combusted, and was annealed at 1,000 °C for 3 h. The crystal structure, morphology, and size of the particles were obtained using a Rigaku D/max-rA X-ray diffractometer (XRD) with a Cu target radiation source, transmission electron micrographs (TEM) using a JEM-2010 electron microscope, and field emission scanning electron microscope morphology (FE-SEM) using an X L-30 FEG ESEM SEM. The excitation and emission spectra in the UV range were obtained with a Hitachi F-4500 fluorescence spectrometer. The excitation spectra and site-selective excitation spectra were obtained at 10 K with an Nd:YAG laser and a R6G-dye laser; time-resolved spectra at 10 K were measured with a 266 nm laser from the fourth harmonic generator pumped by the same Nd:YAG laser; and all spectra were recorded by a TRIAX-550 spectrometer, an R928 photomultiplier, and a Boxcar integrator and were processed by a computer.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of the 16% sample prepared by annealing at 1,000 °C. It can be seen that the La_3PO_7 has a perfect monoclinic-phase crystal structure. All diffraction peaks originating from the La_3PO_7 are in accordance with JCPDS card 49-1023. Figure 2 shows a TEM image of the 8% sample prepared with the self-combustion method, with an average particle size

* Author to whom correspondence should be addressed.

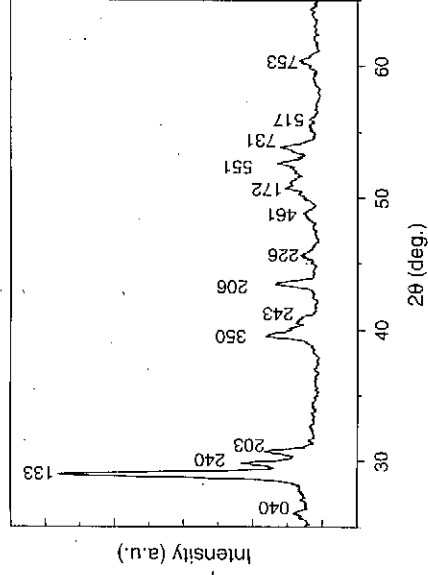


Fig. 1. The XRD pattern of the 16% $\text{La}_3\text{PO}_7:\text{Eu}^{3+}$ sample prepared by annealing at 1,000 °C.

smaller than 60 nm. The inset of Figure 2 shows an FE-SEM image of the 16% sample prepared by annealing at 1,000 °C for 3 h, with an average particle size of about 80 nm.

Figure 3 shows that the emission spectra are normalized to their maximum in which the samples prepared by annealing at 1,000 °C are marked 1 (16%) and 2 (8%), and the samples prepared by the combustion method are marked 3 (16%) and 4 (8%). The stronger peak at 615 nm originates from the emission from the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition of Eu^{3+} at 266 nm UV excitation. As known, Eu^{3+} ion is sensitive to local symmetry. Figure 3 shows that the intensity of the emission from the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition of Eu^{3+}

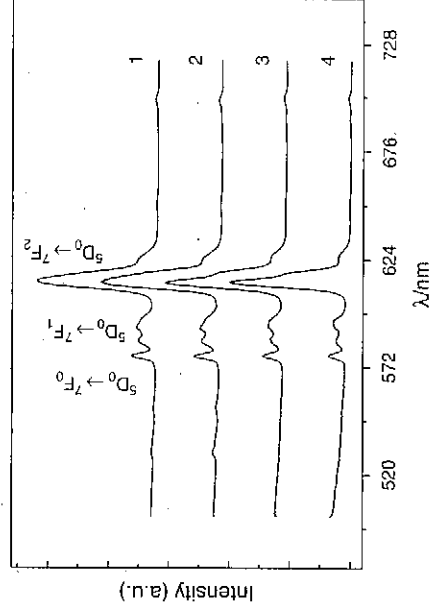


Fig. 3. The normalized emission spectra of sample 1 (16%) and sample 2 (8%) prepared by annealing at 1,000 °C and sample 3 (16%) and sample 4 (8%) prepared by combustion at 266 nm wavelength excitation.

at 615 nm is stronger than the intensity of the emission from the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition at 595 nm in these samples prepared with different methods, and the intensity ratio is ~ 6.5 , which is also observed for Eu^{3+} 2% and 4% molar ratio samples. The emission spectra indicate that the local symmetry of the Eu^{3+} ions lacks an inversion center since the magnetic-dipole transition peak is very weak. Figure 4 shows the time-resolved spectra of sample 1 in the range of 500–720 nm at 10 K. As delay time decreased, the relative emission intensity at 625 nm increased compared with that at 615 nm, and the fluorescent lifetime of emission at 625 nm was shorter than that at 615 nm. These results suggest that Eu^{3+} ions could occupy at least two types of sites in the La_3PO_7 .

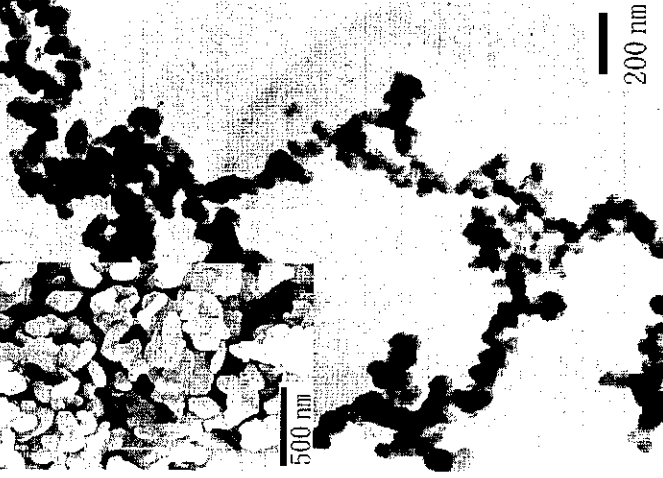


Fig. 2. TEM image of the 8% $\text{La}_3\text{PO}_7:\text{Eu}^{3+}$ sample prepared by self-combustion; the inset shows the FE-SEM image of the 16% $\text{La}_3\text{PO}_7:\text{Eu}^{3+}$ sample prepared by annealing at 1,000 °C.

RESEARCH ARTICLE

Figures 5(a) and (b) show the excitation spectra monitored at 591, 613, and 625 nm for samples 1 and 4, respectively. The broad band in the region of 200–350 nm is relative to the charge transfer band (CTB) of $\text{Eu}^{3+}-\text{O}^{2-}$, which originates from the interaction between Eu^{3+} and O^{2-} . It is clear that CTB produces a red shift in the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ emission at 625 nm compared with that at 613 nm. Some CTB studies have been reported.^{8–10} The

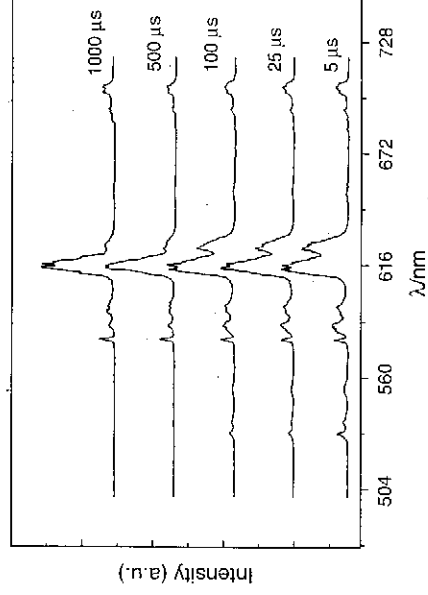


Fig. 4. Time-resolved spectra of sample 1 at 266 nm laser excitation.

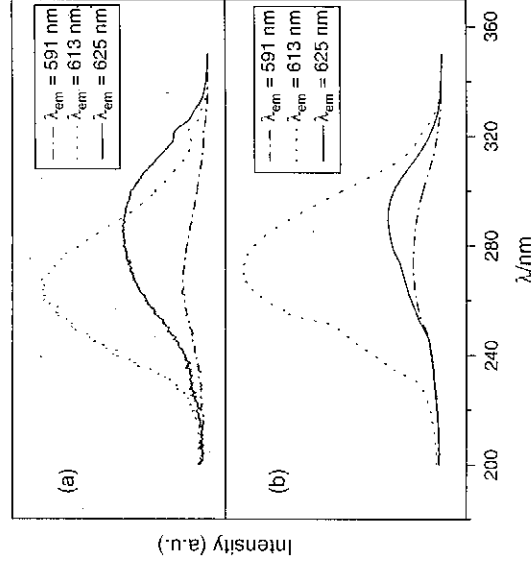


Fig. 5. The excitation spectra of the $\text{La}_3\text{PO}_7:\text{Eu}^{3+}$ obtained by monitoring the emissions of $^5\text{D}_0 \rightarrow ^7\text{F}_1$ at 591 nm, and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ at 613 and 625 nm: (a) for sample 1, (b) for sample 4.

shift of CTB may be related to the bond length of $\text{Eu}-\text{O}$ in the $\text{La}_3\text{PO}_7:\text{Eu}^{3+}$ crystal. Moreover, this result implies that different local environments surround the Eu^{3+} ions in the La_3PO_7 host. The Eu^{3+} ions can occupy at least two types of sites denoted as site A and site B. For monitoring the emission at the 613 nm of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition, the major excitation peak at 264 nm in the CTB was associated with site A, and for monitoring the emission at the 625 nm $^5\text{D}_0 \rightarrow ^7\text{F}_2$, the excitation peak at 290 nm in the CTB was associated with site B. We conclude that the bond average distance of $\text{Eu}-\text{O}$ of site A is shorter than that site B.

Figures 6(a) and (b) show that the emission spectra were normalized to their maximum for samples 1 and 4, respectively, at different UV wavelength excitations. It can be seen that as the exciting wavelengths become shorter, the emission intensity at 615 nm becomes stronger than that at 625 nm. The relationship between the CTB and emission spectra of Eu^{3+} ions at different UV wavelength excitations had been studied; for example, the some results proved that under different UV wavelengths excitation can change the composition of different sites spectrum components in the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanocrystal.¹¹ In our case, the changes in emission spectra were caused by changes in the compositions of the spectrum components at site A and site B. We conclude that the emission peak at 615 nm comes from site A and the peak at 625 nm comes from site B.

Figure 7 shows the excitation spectra of sample 1 obtained by monitoring 595, 615, 621, and 625 nm emissions at 10 K; the region of the excitation spectra from 578 to 582 nm is relative to the $^7\text{F}_0 \rightarrow ^5\text{D}_0$ transition. Excitation peaks were observed at 580.6 nm for the 625 nm emission and at 579.8 nm for the 615 nm emission. Generally, the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition of Eu^{3+} is forbidden, but

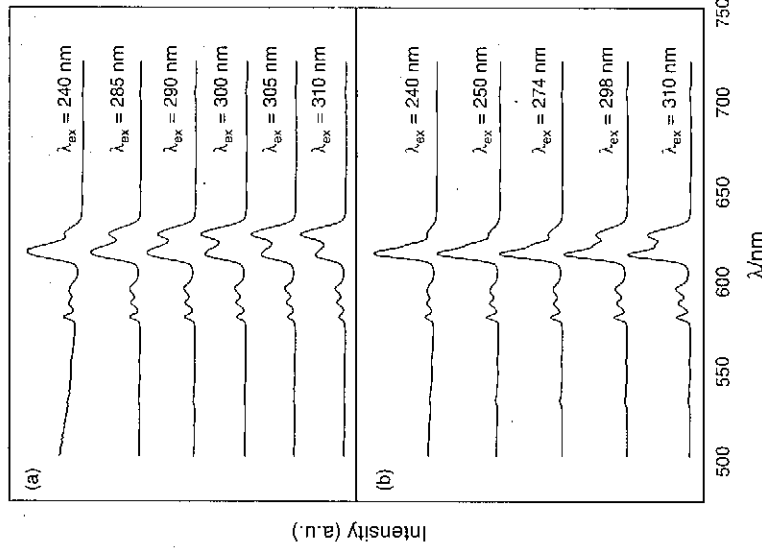


Fig. 6. The normalized emission spectra of samples 1 (a) and 4 (b) obtained under different UV excitation wavelengths.

emission spectra from the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition appear in the $\text{La}_3\text{PO}_7:\text{Eu}^{3+}$ samples seen in Figure 3. As reported by Nieuwpoort¹² and Reisfeld,¹³ when Eu^{3+} ions occupy one of the Cs, Cn, and Cnv symmetry sites, the emission from the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transitions of Eu^{3+} is allowed. Because crystal field does not split the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition of Eu^{3+} the number of the emission peaks can be used to estimate the number of Eu^{3+} ions occupying symmetry site types in a crystal. In our case, for 615 and 625 nm emissions, excitation peaks relating to site A and site B were observed,

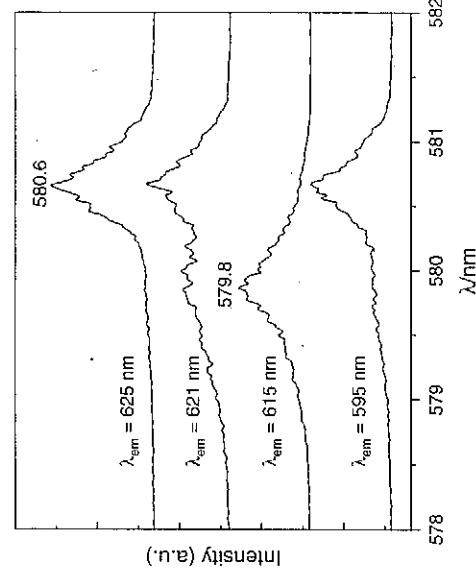


Fig. 7. The excitation spectra of sample 1 at 10 K obtained by monitoring emissions at 595, 615, 621, and 625 nm.

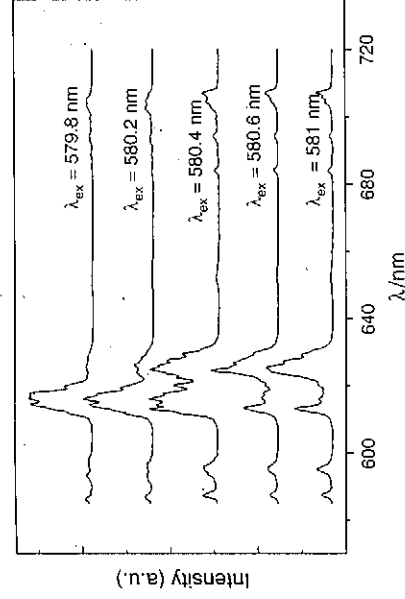


Fig. 8. The normalized emission spectra of sample 1 under different wavelength excitations.

respectively. In addition, from Figure 3 the higher intensity ratio of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ indicates that the local symmetry of the Eu^{3+} ions is without an inversion center. These results suggest that the crystal should have at least one type of site belonging to Cs, Cn, and Cnv. Because the site symmetry of Eu^{3+} ions in the La_3PO_7 host is not yet clear, more research is required. Figure 8 shows site selective excitation spectra from ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ ($j = 1, 2, 3, 4$) at 10 K. The emission peaks within the 610–630 nm range excited by 579.8 nm are relatively narrower, and the number of emission peaks is low, which is attributed to site A. The emission peaks in the same range excited by 580.6 nm are relatively broader, and some split peaks could be observed, which is attributed to site B. Obviously, the site selective excitation spectra indicate that there are at least two types of symmetry sites in the La_3PO_7 .

4. CONCLUSION

In summary, pure monoclinic-phase $\text{La}_3\text{PO}_7:\text{Eu}^{3+}$ samples were prepared by combustion and annealing methods, and their photoluminescence spectra were found to be different from the other phosphates and borates doped with

Eu^{3+} . In this host, the red emission from the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition of Eu^{3+} is much stronger than the orange emission from the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition under UV-light excitation, which indicates that symmetry of the local environment of Eu^{3+} lacks an inversion center. Moreover, in the crystal there should be at least one type of site belonging to Cs, Cn, and Cnv. The results of excitation, site-selective excitation, and time-resolved spectra indicate that Eu^{3+} ions can occupy at least two types of symmetry sites in the La_3PO_7 crystals for different concentrations of Eu^{3+} . The 625 nm emission is associated with one type of site and the 613 nm emission with another. As the site symmetry of the Eu^{3+} ions in the La_3PO_7 host is not yet clear more research is required. However, stronger red emission and superior chromaticity may make $\text{La}_3\text{PO}_7:\text{Eu}^{3+}$ a potential luminescent material.

References and Notes

1. U. Rambabu, D. P. Anjalmerkar, B. B. Kale, and S. Buddhu, *Mater. Chem. Phys.* **70**, 1 (2001).
2. J. Dexpert-gyhs, R. Mauricot, and M. D. Faucher, *J. Lumin.* **69**, 203 (1996).
3. G. Blasse and B. C. Grabmaier (eds.), *Luminescent Materials*, Springer, Berlin (1994).
4. W. Chen, J. Z. Zhang, and A. G. Joly, *J. Nanosci. Nanotechnol.* **4**, 919 (2004).
5. H. W. Song, B. J. Chen, H. S. Peng, and J. S. Zhang, *Appl. Phys. Lett.* **81**, 1776 (2002).
6. Z. G. Wei, L. D. Sun, C. S. Liao, J. L. Yin, X. C. Jiang, C. H. Yan, and S. Z. Li, *J. Phys. Chem. B* **106**, 10610 (2002).
7. R. Y. Wang, *J. Lumin.* **106**, 211 (2004).
8. Z. M. Qi, C. S. Shi, W. W. Zhang, W. P. Zhang, and T. D. Hu, *Appl. Phys. Lett.* **81**, 2857 (2002).
9. H. E. Hoefdraad, *J. Solid State Chem.* **15**, 175 (1975).
10. J. H. Lin, L. P. You, G. X. Lu, L. Q. Yang, and M. Z. Su, *J. Mater. Chem.* **8**, 1051 (1998).
11. M. L. Jia, J. H. Zhang, S. Z. Lu, J. T. Sun, Y. S. Luo, X. G. Ren, H. W. Song, and X. J. Wang, *Chem. Phys. Lett.* **384**, 193 (2004).
12. W. C. Nieuwpoort and G. Blasse, *Solid State Commun.* **4**, 227 (1966).
13. R. Reisfeld and C. K. Jørgensen, *Lasers and Excited States of Rare Earths*, Springer-Verlag, Berlin (1977).

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