

Photoluminescence properties of core/shell-type LnPO₄:Eu/LnPO₄ (Ln=La, Gd) nanophosphors

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Abstract

To overcome defect due to large surface of nanoparticle, a redispersible Eu doped LnPO₄:LnPO₄ core/shell nanoparticles were prepared in a high-boiling coordinating solvent. The particle size of the synthesized core/shell nanophosphors was estimated to be about 8 nm by TEM. In this core/shell nanoparticle, the concentration of Eu ion was optimized on the basis of the emission intensity under UV ray excitation. Also, the PL properties of the nanophosphors have been compared with those of the LnPO₄:Eu nanoparticles.

1. Introduction

The inorganic materials activated with rare-earth ions have the potential to be applied for various fields such as in lighting, information displays and telecommunication.[1,2] It is well known that the LnPO₄ host material has a monoclinic phase crystallographically and the Ln³⁺ ion site in the host can be easily substituted by any other rare-earth ions.[3,4] For example, the substitution of Eu³⁺ or Tb³⁺ for a portion of Ln³⁺ in the host gives to efficient phosphors and the incorporations of Nd³⁺, Pr³⁺ or Er³⁺ results in optical amplifying materials. On the other hand, several research groups have reported the syntheses of LnPO₄ particles via diverse methods such as solid-state reaction, spray pyrolysis and hydrothermal method.[4,5] In recent, Haase and Lehmann have successfully fabricated Eu-, Tb- and Er-doped LaPO₄ nanoparticles by a liquid phase synthesis using solvent mixture.[6,7] On the other hand, nano-sized luminescent materials doped with rare earth ions have been attracting much attention interest due to their potential of becoming a new class

of luminescent materials, which are used as phosphors in various applications by their optical properties due to transition of lanthanide ion. The luminescent nanoparticles like LnPO₄:Eu have large activity due to very small size and large surface area. As a result, non-active ions can be extant on the surface of the particles, resulting in the degradation of brightness and the deterioration of lifetime. To overcome the problems of the luminescent nanoparticles, it was carried out to synthesize the core/shell nanoparticles by forming LnPO₄ shell on LnPO₄:Eu core particle.

In the present work, we have prepared Eu³⁺-doped LnPO₄/LnPO₄ core/shell nanophosphor by liquid-phase reaction for application as display materials. The synthesized nanophosphors were characterized by using a XRD, TEM, FT-IR. In addition, the optimal composition was investigated on the basis of relative PL emission intensity.

2. Experimental

Synthesis of LnPO₄:Eu core nanoparticles: LnCl₃·H₂O together with EuCl₃·6H₂O in the appropriate molar ratio were dissolved in methanol. Then, tributyl phosphate was added into the solution. Using the rotary evaporator, removed methanol from the solution. Diphenyl ether was added and the coordinated water from ingredient was distilled off. Then trihexylamine and 2M solution of phosphoric acid in dihexyl ether were added. A prepared mixture was added into the metal solution and heated up to 200 °C under nitrogen ambience. After 16 h, the heating stopped and the solution was keep to room temperature. A portion of the reaction mixture was

injected to the 3-neck flask for the preparation for core/shell nanoparticles.

Synthesis of $\text{LnPO}_4:\text{Eu}/\text{LnPO}_4$ core/shell nanoparticles: For the formation of LnPO_4 shell, $\text{LnCl}_3 \cdot \text{H}_2\text{O}$ in the appropriate molar ratio were dissolved in methanol and added of tributyl phosphate. And the methanol removed with a rotary evaporator. Then diphenyl ether was added and coordinated waters from ingredient were distilled off and added trihexylamine. 2M solution of phosphoric acid in dihexyl ether was add to mixture of $\text{LnPO}_4:\text{Eu}$ and heated to 200°C under nitrogen. The solution using the quantitative pump was added drop by drop over a period of 2 h at 200°C . After 16 h, the heating stopped and the solution was keep to room temperature. The prepared reaction mixture was repeated washing process with methanol and collected core/shell nanoparticles using ultrafiltration cell with 5000 or 10000 NMWL membrane filter.

3. Results and discussion

The X-ray diffraction patterns in the range of $2\theta = 10\sim 70^\circ$ of the $\text{LnPO}_4:\text{Eu}/\text{LnPO}_4$ core/shell nanophosphors synthesized by liquid-phase reaction are shown in Fig. 1. Although the XRD pattern of the core/shell nanoparticle is not clear, the XRD patterns are well matched with that of the $\text{LnPO}_4:\text{Eu}$ nanoparticles reported by previous work, in which the XRD patterns of the nanocrystal powder were similar to that consistent with the monazite structure of JCPDS files.

Fig. 2 exhibits a photography of the $\text{GdPO}_4:\text{Eu}/\text{LnPO}_4$ core/shell nanoparticles observed by transmission electron microscopy. The photograph shows morphology and size of the prepared LnPO_4 core/shell nanoparticles. It is observed that the size of the particles is about 8 nm with narrow size distribution. Also, in the TEM photograph, the nanoparticles and core/shell nanoparticles have a good dispersivity without an agglomeration, which is due to the solvent molecules coordinated on the surfaces of nanoparticles as stated in the previous our report. In addition, the inset exhibits a higher magnification of a particle to illustrate the high crystallinity.

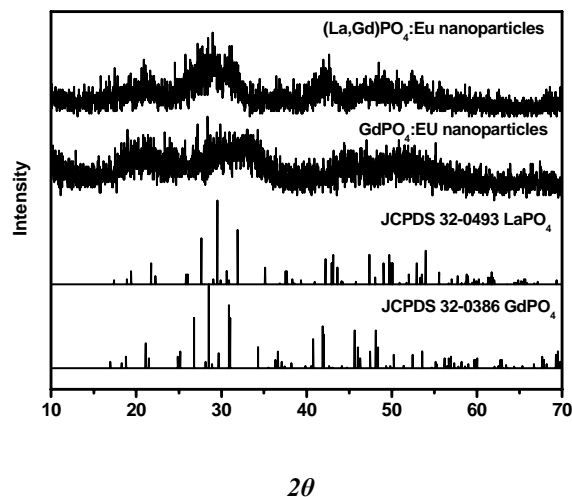


Fig. 1. XRD patterns of $\text{LnPO}_4:\text{Eu}$ and JCPDS files.

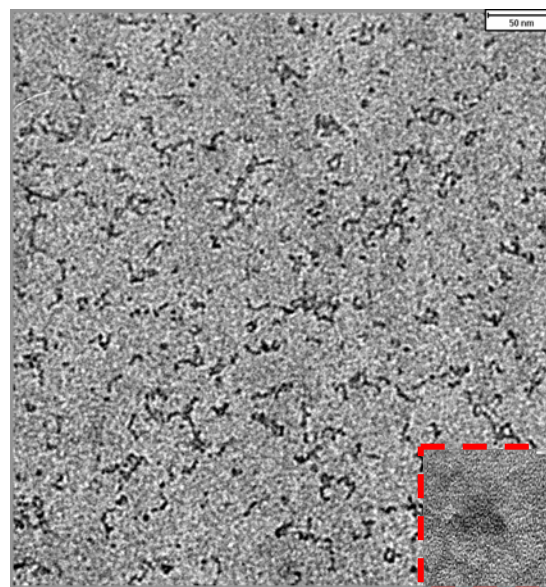


Fig. 2. TEM photographs of $\text{GdPO}_4:\text{Eu}$ nanoparticles and $\text{GdPO}_4:\text{Eu}/\text{LnPO}_4$ core/shell nanoparticles (inset).

To investigate the composition of the surface of the prepared $\text{LnPO}_4:\text{Eu}/\text{LnPO}_4$ core/shell nanoparticles was examined through FT-IR spectroscopy. As can be seen in Fig. 3, the broad absorption band at $3,400\text{ cm}^{-1}$ is assigned to O-H stretching vibration. Peaks at $2,950\text{--}2,850\text{ cm}^{-1}$ are due to C-H stretching vibration and at $1,460$ and $1,360\text{ cm}^{-1}$ are originated from bending vibrations of $-\text{CH}_2$ and $-\text{CH}_3$, respectively. In addition, some peaks between $1,360\text{ cm}^{-1}$ and 950 cm^{-1} are due to organic and inorganic PO_4^{3-} on the surface of the shell. This results indicate that the organic molecules used in the reaction as a solvent were adsorbed on the surface of the $\text{LnPO}_4:\text{Eu}/\text{LnPO}_4$ core/shell nanoparticles. Therefore, the surface of $\text{LnPO}_4:\text{Eu}/\text{LnPO}_4$ core/shell nanoparticles are capped by the used solvent molecules with high boiling point.

Fig. 4 shows the emission spectra of $\text{GdPO}_4:0.025\text{Eu}/\text{LaPO}_4$ core/shell nanoparticles and $\text{GdPO}_4:0.025\text{Eu}$ nanoparticles excited by the wavelength of 394 nm . The typical emission peaks due to the transition from $^5\text{D}_0$ to $^7\text{F}_J$ ($J=1,2,3,4$) of Eu^{3+} are observed. It have to be noticed that the emission intensity of the core/shell nanoposphor is more enhanced to that of the nanoposphor.

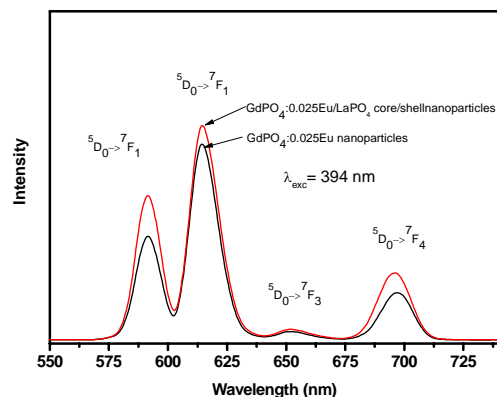


Fig. 4. Emission spectra of $\text{GdPO}_4:0.025\text{Eu}$ and $\text{GdPO}_4:0.025\text{Eu}/\text{LaPO}_4$ core/shell nanoparticles

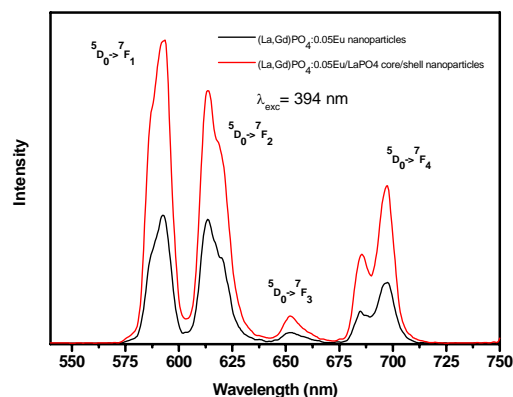


Fig. 5. Emission spectra of $(\text{La,Gd})\text{PO}_4:0.025\text{Eu}$ and $(\text{La,Gd})\text{PO}_4:0.025\text{Eu}/\text{LaPO}_4$ core/shell nanoparticles

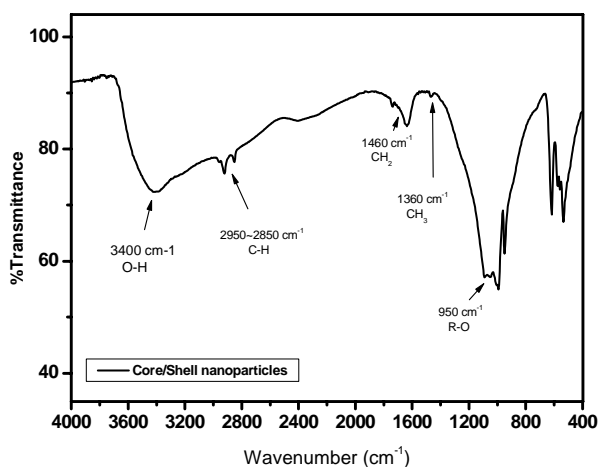


Fig. 3. FT-IR spectrum of $\text{LnPO}_4:\text{Eu}/\text{LnPO}_4$ core/shell nanoposphor

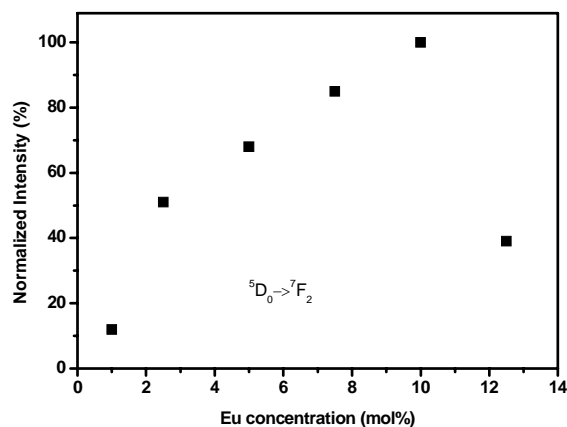


Fig. 6. Dependence of emission intensity on the contents of Eu contents in the $(\text{La,Gd})\text{PO}_4:\text{Eu}/\text{LaPO}_4$ nanoparticles

The emission spectra of $(\text{La}_{0.5}\text{Gd}_{0.5})\text{PO}_4:0.05\text{Eu}$ nanoparticles and $(\text{La}_{0.5}\text{Gd}_{0.5})\text{PO}_4:0.05\text{Eu}/\text{LaPO}_4$ core/shell nanophosphors are expressed in Fig. 5. The typical emission peaks due to the transition of Eu^{3+} are observed. It is an obvious fact that the relative brightness of the core/shell nanoparticles is stronger compared to the nanoparticles.

The dependence of relative intensity on Eu concentration in the $(\text{La}_{0.5}\text{Gd}_{0.5})\text{PO}_4:0.05\text{Eu}/\text{LaPO}_4$ core/shell nanophosphors is presented in Fig. 6. As can be seen, the emission intensity of the core/shell nanoparticles is enhanced with an increasing concentration of activator at the lower content region. At the composition of $(\text{La}/\text{Gd})\text{PO}_4:0.1\text{Eu}/\text{LaPO}_4$ core/shell nanoparticles, a maximum intensity is achieved and then is decreased with increasing Eu concentration. It indicates that the concentration quenching of the $(\text{La}_{0.5}\text{Gd}_{0.5})\text{PO}_4:0.05\text{Eu}/\text{LaPO}_4$ phosphor takes place at 10 mol% of Eu content.

4. Summary

The Eu-doped LnPO_4 core/shell nanoparticles with the composition changes were synthesized by a liquid-phase reaction. It were confirmed that the prepared core/shell nanoparticles have a single phase of monoclinic and exhibit about 8 nm of particles size with narrow size distribution. On the other hand, it was confirmed by FT-IR that the surface of core/shell nanoparticles are capped with the solvent molecules, which will possibly keep from the agglomerating between the core/shell nanoparticles. The optimum contents of $(\text{La},\text{Gd})\text{PO}_4:\text{Eu}/\text{LaPO}_4$ exhibiting the maximum emission intensity in the nanoparticles was about 10 mole%.

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6. References

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