Preparation and Luminescence Properties of $LaPO_4$:Eu/:$LaPO_4$ Core/Shell Nanoparticles

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Abstract

Due to an efficient red emission, Eu^{3+} ions have doped in various host materials. Eu-doped $LaPO_4$/$LaPO_4$ core/shell nanophosphor which emits red light in visible range, was synthesized by using a solution system. The mean size of the nanoparticle observed by TEM was about 7-8 nm. In this core/shell system, the thickness of $LaPO_4$ shell was optimized on the basis of relative PL emission intensity. In addition, the luminescent properties of $LaPO_4$:Eu/$LaPO_4$ core/shell particle have been compared with Eu-doped $LaPO_4$ bulk particle and nanoparticle.

1. Introduction

The $LaPO_4$ has been already employed to host of various luminescence materials such as laser materials and phosphors in lighting applications and in versatile information displays. It is known that the $LaPO_4$ has a monoclinic phase of monazite structure crystallographically, wherein La^{3+} ion is nine-coordinated to oxygen atoms and forming polyhedron described pentagonal interpenetrating in geometric[3]. The size of La^{3+} ion is similar to those of other lanthanide ions and La^{3+} ion site can be easily substituted by them. The substitutions of Eu^{3+} or Tb^{3+} for a portion of La^{3+} construct luminescent phosphors and the incorporations of Nd^{3+}, Pr^{3+} or Er^{3+} result in optical amplifying materials. Several researchers have reported the syntheses of $LaPO_4$ particles via diverse methods such as solid-state reaction, spray pyrolysis and hydrothermal method. In recent, Haase group have successfully fabricated Eu-, Tb- and Er-doped $LaPO_4$ nanocrystals by the liquid phase synthesis using high-boiling coordinating solvent[4-7].

On the other hand, rare earth ions doped nano-sized luminescent materials have been attracting much attention interest due to their high potential of becoming a new class of luminescent materials such as phosphors in information displays and fluorescence lamp, optical

amplifier by their optical properties. A crystalline mixed rare-earth phosphate of varying composition, have recently been proposed as primary hosts. For example, Eu^{3+}-doped $LaPO_4$ phosphor can be applied as a red component for display[1]. On the other hand, because one of major attributes of the nanoparticles is their size-dependent physicochemical properties. These nano-sized materials take advantage of size-induced changes in structural, optical and electronic properties to enhanced luminescent materials. On the other hand, in the Eu^{3+} doped $LaPO_4$ nanoparticle system, Eu^{3+} ions on the surface were predicted defect. Therefore, Eu^{3+} doped $LaPO_4$ nanoparticle surface needs constructing inorganic shell on there.

In the present work, we have prepared Eu^{3+}-doped $LaPO_4$/$LaPO_4$ core/shell nano-phosphor by liquid-phase reaction for application as display materials. The synthesized nano-powders 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

$LaCl_3$?$7H_2O$ (99.999%, Aldrich) together with $EuCl_3$ in the appropriate molar ratio were dissolved in methanol and tributyl phosphate, and the methanol was subsequently removed with a rotary evaporator. Then, diphenyl ether was added into the solution. Under vacuum condition of 80℃, the water ingredients contained in the solution were distilled off. A freshly prepared 2M solution of crystalline phosphoric acid was mixed with trihexylamine and the mixture was added into the metal solution and heated up to 200℃ under dry nitrogen. After 16 h the heating was stopped and the hot solution has been cooled to room temperature. The 3/4 of reaction mixture which contains $LaPO_4$:Eu nanoparticles was removed from the flask. The remaining 1/4 of the reaction mixture was used for preparation of core/shell naonoparticles. The pretreatment route of $LaPO_4$ shell has been applied a close resemblance $LaPO_4$:Eu nanoparticles. The prepared $LaPO_4$ shell solution was blended with reaction mixture. This solution was loaded into the metering pump and added drop by drop over 2 h to the reaction mixture of $LaPO_4$:Eu core and heated up to 200°C under dry nitrogen. After 16 h the heating was stopped and the hot solution has been cooled to room temperature. Reaction mixture was diluted with MeOH and was filled into a ultrafiltration cell equipped with membrane filter. The solution was moved through the membrane under a nitrogen pressure and the purification route was repeated 4 times. Finally, the core/shell nanoparticles were obtained from the reaction mixture by removing the methanol with rotary evaporator.

3. Results and Discussion

We are preparing various nanoparticles that can be applied as novel materials for information displays. Here we report the synthesis of $LaPO_4$:Eu/$LaPO_4$ core/shell nanoparticles from solution system and their luminescence properties. The X-ray diffraction patterns of $LaPO_4$:Eu/$LaPO_4$ core/shell nanoparticles synthesized by liquid-phase reaction and bulk $LaPO_4$:Eu particles calcined at 1100°C for 12 h by solid state method 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 $LaPO_4$:Eu nanoparticles reported by Riwotzki. The XRD patterns of the nanocrystal powder is similar to that of bulk $LaPO_4$:Eu and is consistent with the monazite-structure of bulk $LaPO_4$.

The TEM photograph of Fig. 2 shows morphology and size of the prepared $LaPO_4$ core/shell nanoparticle. It is confirmed that the size of the particles is about 7~8 nm with narrow size distribution. Also, the TEM image shows the $LaPO_4$:Eu core/shell nanoparticles have well-dispersed without aggregation. The inset exhibits a higher magnification of a particle to illustrate the high crystallinity.

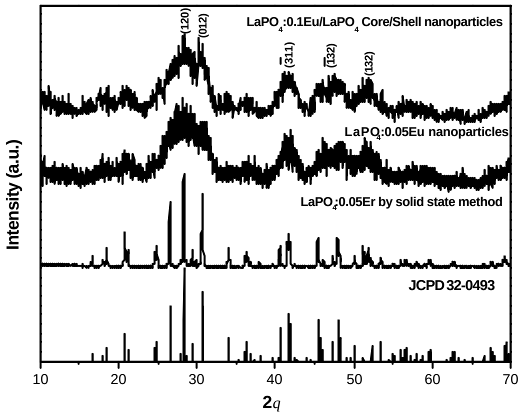

Fig. 1. XRD patterns of $LaPO_4$:0.1Eu/$LaPO_4$ Core/Shell nanoparticles, $LaPO_4$:0.05Eu nanoparticles, $LaPO_4$:0.05Eu by solid state method and JCPDS file.

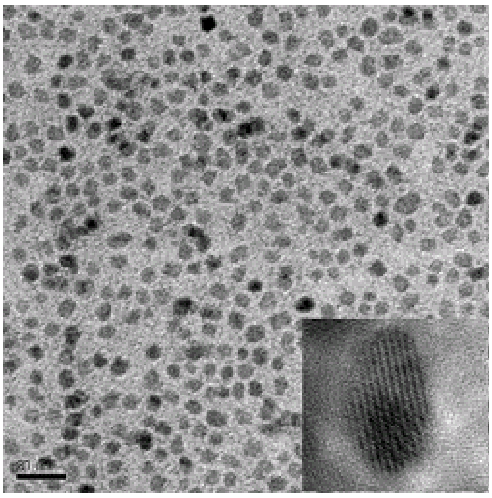

Fig. 2. TEM photograph of $LaPO_4$:Re/$LaPO_4$ core/shell nanoparticles.

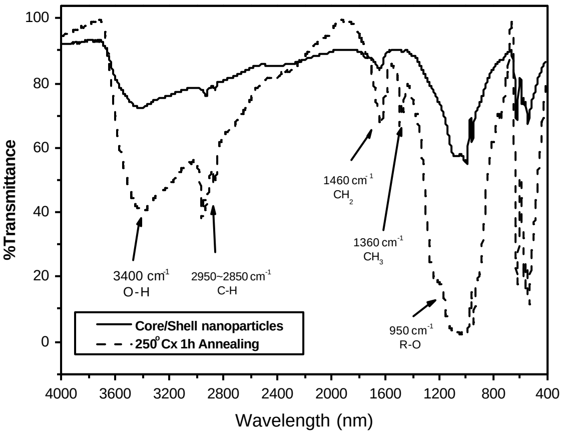

Fig. 3. FT-IR spectrum of $LaPO_4$:Re core/shell nanoparticles

The composition of the surface of the prepared $LaPO_4$:Eu/$LaPO_4$ core/shell nanoparticles has been examined through FT-IR spectroscopy. As shown is given in Fig. 3. The broad absorption band at 3,400 cm^{-1} is assigned to O-H stretching vibration. Peaks at 2,950 ~ 2,850 cm^{-1} are due to C-H stretching vibration and at 1,460 and 1,360 cm^{-1} are originated from bending vibrations of $-CH_2$ and $-CH_3$, respectively. In addition, some peaks between cm^{-1} and cm^{-1} are due to organic and inorganic PO_4^{3-} on the surface of the shell. This results could be considered that the organic molecules used in the reaction were adsorbed on the surface of the $LaPO_4$:Eu/$LaPO_4$ core/shell nanoparticles. Therefore, the surface of $LaPO_4$:Eu/$LaPO_4$ core/shell nanoparticles are capped by the used high b.p solvent molecules.

Fig. 4 shows the emission spectra in the ragnge of 560-720 nm for $LaPO_4$:Eu core/shell nanoparticles, $LaPO_4$:Eu nanoparticles and $LaPO_4$:0.1Eu bulk. The typical emission peaks due to the transition from $^5D_0$ to ^7F_J are observed. It was confirmed that the emission intensity of this core/shell nano-phosphor is almost similar to that of nano-phosphor. However, that is a little lower than the emission intensity of bulk phosphor.

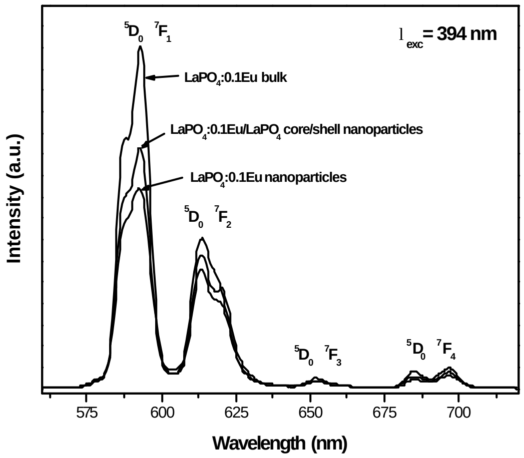

Fig. 4. Emission spectra of $LaPO_4$:0.1Eu nanoparticles, $LaPO_4$:0.1Eu/$LaPO_4$ core/shell and $LaPO_4$:0.1Eu bulk

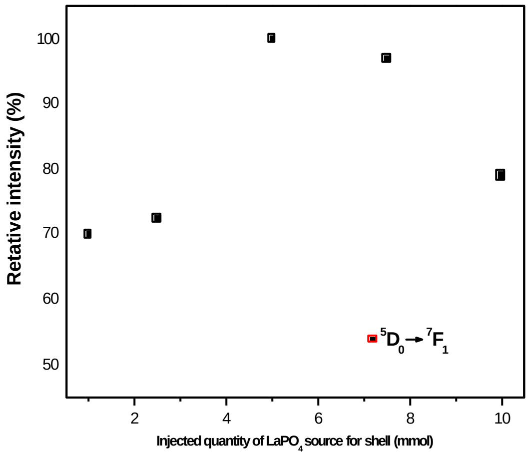

Fig. 5. Dependence of emission intensities on the contents of $LaPO_4$ shell in the $LaPO_4$:0.1Eu/$LaPO_4$ nanoparticles

The dependence of the relative emission intensities on the contents of $LaPO_4$ shell in Eu^{3+} doped $LaPO_4$/$LaPO_4$ core/shell nanoparticles is presented in Fig. 5. As can be seen, the emission intensity of the core/shell nanoparticles is increased with the increasing contents of $LaPO_4$ shell. At the composition of $LaPO_4$:0.1Eu/$LaPO_4$ (5 mmol), a maximum emission intensity is achieved and then is decreased with increasing $LaPO_4$ shell contents. This is explained by the facts that the decreasing defect between Eu^{3+} ions concentration in the $LaPO_4$:Eu/$LaPO_4$ system.

4. Conclusions

In the present work, Eu-doped $LaPO_4$ core/shell nanoparticles by the designed liquid-phase reaction. The prepared core/shell nanoparticles were confirmed to be a single phase of monazite structure and to have the 7-8 nm of particles size with narrow size distribution. On the other hand, it was confirmed by FT-IR that the surface of nanoparticles are capped with the solvent molecules, which will possibly keep from the agglomerating between the nanoparticles. The optimum contents of $LaPO_4$ shell exhibiting the maximum emission intensity in the nanopartciles was about 5 mmol.

5. References

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6. Acknowledgement

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